Interaction of oil components and clay minerals in reservoir sandstones

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Abstract

The free oil (first Soxhlet extract) and adsorbed oil (Soxhlet extract after the removal of minerals) obtained from the clay minerals in the <2 μm size fraction as separated from eight hydrocarbon reservoir sandstone samples, and oil inclusions obtained from the grains of seven of these eight samples were studied via GC, GC–MS and elemental analyses. The free oil is dominated by saturated hydrocarbons (61.4–87.5%) with a low content of resins and asphaltenes (6.0–22.0% in total) while the adsorbed oil is dominated by resins and asphaltenes (84.8–98.5% in total) with a low content of saturated hydrocarbons (0.6–9.5%). The inclusion oil is similar to the adsorbed oil in gross composition, but contains relatively more saturated hydrocarbons (16.87–31.88%) and less resins and asphaltenes (62.30–78.01% in total) as compared to the latter.

Although the amounts of both free and adsorbed oils per gram of clay minerals varies substantially, the residual organic carbon content in the clay minerals of the eight samples, after the free oil extraction, is in a narrow range between 0.537% and 1.614%. From the decrease of the percentage of the extractable to the total of this residual organic matter of the clay minerals with burial depth it can be inferred that polymerization of the adsorbed polar components occurs with the increase of the reservoir temperature.

The terpane and sterane compositions indicate that the oil adsorbed onto the clay surfaces appears to be more representative of the initial oil charging the reservoir than do the oil inclusions. This phenomenon could possibly demonstrate that the first oil charge preferentially interacts with the clay minerals occurring in the pores and as coatings around the grains. Although the variation of biomarker parameters between the free and adsorbed oils could be ascribed to the compositional changes of oil charges during the filling process and/or the differential maturation behaviors of these two types of oils after oil filling, the fractionation of the ratios of $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ regular steranes and C_{27} diasteranes/C_{27} regular steranes between these two types of oils can be unambiguously ascribed to the selective adsorption effects by the polar components and the active clay surfaces during the interaction of oil phase and clay surfaces.

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1. Introduction

Several studies have examined the interaction between oil components and mineral surfaces in reservoir rocks (e.g., Larter and Aplin, 1995; Wilhelms et al., 1996; Schwark et al., 1997; Pan and Yang, 2000; van Duin and Larter, 2001). Wilhelms et al. (1996) assumed that the first petroleum entering the pore system of a sandstone reservoir interacts most strongly with the mineral surfaces, while the subsequent petroleum interacts only with the initial one. They performed a three-step sequential extraction of crushed reservoir rocks using a suite of solvents with increasing polarity and observed that, although there are great differences in gross compositions, there are only very minor variations in molecular biomarker distributions among the three extracted fractions (Wilhelms et al., 1996). Schwark et al. (1997) developed a flow-through extraction system capable of efficiently extracting core plugs while preserving the pore system of the samples by using two solvent systems. The purpose of their study was to obtain two different types of oils in reservoir rocks: free oil that is comparable to produced oil or drill stem test (DST) oil, and adsorbed oil that resembles an asphaltic residue (Schwark et al., 1997).

Although many interesting results were obtained in the above studies, some fundamental aspects about the interaction of the oil phase and mineral surfaces remain unresolved. In particular, the geochemical features of the organic matter adsorbed on mineral surfaces, such as the amount and its controlling factors, the elemental composition (e.g., C/N atomic ratio) and maturation behavior (condensation to form pyrobitumen) with the increase of the reservoir temperature, are not well understood. Furthermore, as the selective adsorption/desorption among oil components by mineral surfaces plays the dominant role for the migration-related compositional fractionation in reservoir rocks, some biomarker parameters, e.g., the ratios of $\alpha\beta\beta/(\alpha\alpha\alpha + \alpha\beta\beta)$ regular steranes and diasteranes/regular steranes have been recognized as sensitive indicators for oil migration based on field observation for many years (e.g., Seifert and Moldowan, 1978, 1981, 1986). However, these ratios do not show similar variation trends between the free and adsorbed oil as revealed in the studies by Wilhelms et al. (1996) and Schwark et al. (1997).

The main purpose of the present study is to separate the adsorbed oil which can reflect the geochemical features of the initial oil charging the reservoir and the adsorptive effect of mineral surface. Our work is focused on the oil components adsorbed onto the surfaces of clay minerals (fraction <2 μm) of reservoir sandstones. In reservoir sandstones, clay minerals occur in the pore system or as a coating around grains (e.g., Hamilton et al., 1992). Once oil fills the reservoirs, it preferentially interacts with the clay minerals. Therefore, "adsorbed

oil" on clay minerals may represent the first oil charge that fills the reservoir rocks (Pan and Yang, 2000). In sandstones, there may also be some indigenous organic matter or kerogen (e.g., Larter and Aplin, 1995) which is likely closely associated with the detrital minerals. The clay minerals in sandstones can be both detrital and diagenetic. Generally, clay minerals >2 μm may be detrital while those in the fraction <2 μm may mainly form as a result of diagenesis (e.g., Hamilton et al., 1992). Therefore, the oil adsorbed onto the surfaces of clay minerals <2 μm size fraction will not be significantly affected by the indigenous organic matter. Although the clay mineral <2 μm size fraction comprises only several weight percent or less of the sandstone rocks, they contribute a major part in terms of the mineral surface areas.

It is a critical point in this type of study whether the molecular fractionation between the free and adsorbed oils is induced by the sequential extraction experimental process or is a pre-existing phenomenon. This issue is discussed in detail in the present study based on an extensive review on the results of previous studies in sequential extraction both on source rocks and reservoir rocks, and the comparison of the results in the present study to those of the previous ones (e.g., Sajgo et al., 1983; Spiro, 1984; Price and Clayton, 1992; Wilhelms et al., 1996; Schwark et al., 1997; Pan and Yang, 2000).

2. Samples and experimental

2.1. Samples

Eight samples were collected from the hydrocarbon reservoirs of the Dongpu Depression, which is located in the southwestern part of the Bohai Bay Basin in Northern China (Fig. 1). Out of the eight samples, each weighing 300–800 g, seven were collected from the oil zones, and one (PS4-3) was collected from the gas zone of Shahejie Formation of Eocene age (Es_2–Es_3 sections) (Fig. 2) with a current burial depth ranging from 2497.2 to 4044.5 m (Table 1). These samples are well-sorted, medium-grained sandstone rocks. The mineralogical composition of the grains of these samples is characterized by 80–90% quartz and 10–20% feldspar. The clay minerals of these samples, as determined via X-ray analysis, are mainly kaolinite, illite and mixed-layered illite/smectite (Table 1). As demonstrated by many electron microscope images of reservoir sandstones in the study area, kaolinite and illite mainly occur as coatings around the grain surfaces.

2.2. Clay separation

The sandstone samples were first crushed gently to obtain specific size clasts. These disintegrated grains
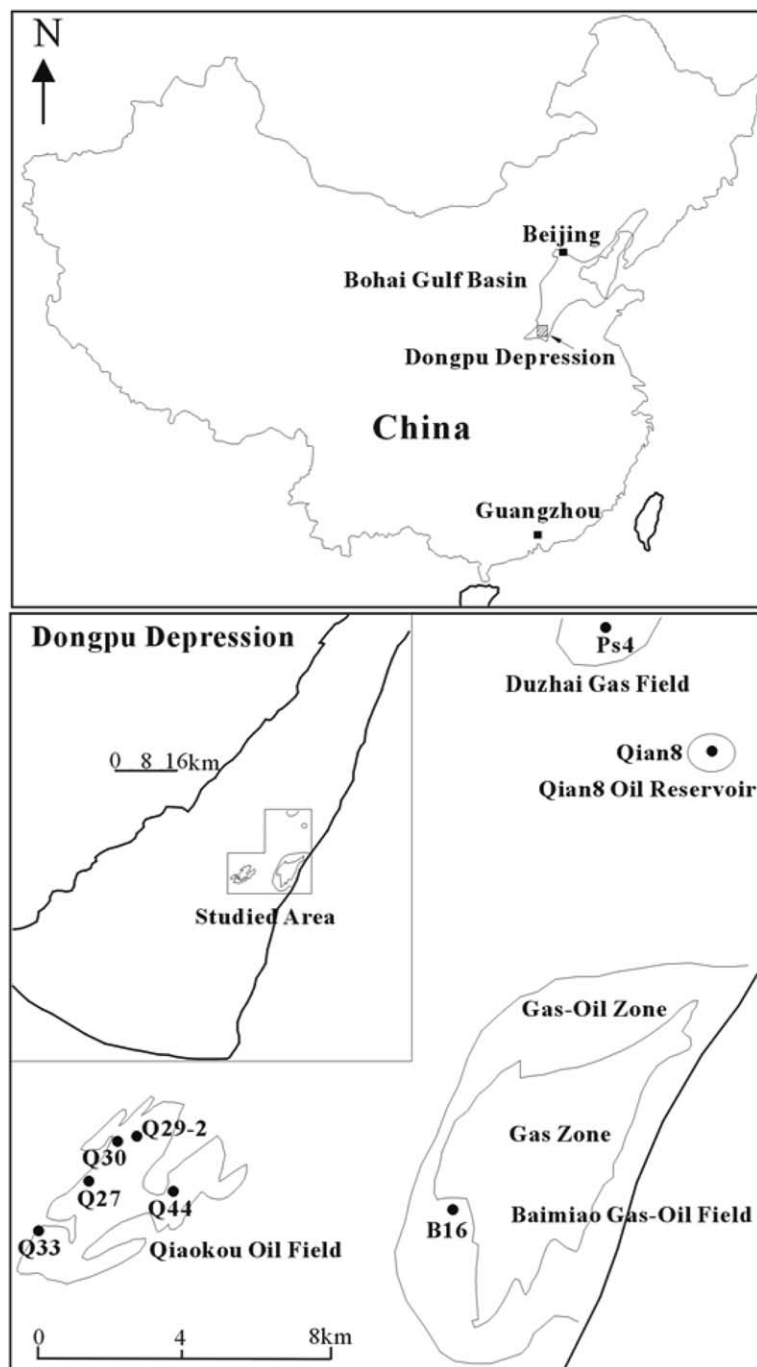
Fig. 1. Location map of Dongpu Depression and sampling.

were submerged in deionized water and frozen for about 8 h. During the thaw cycle at room temperature (20–30 °C), the clay minerals coating the grain surfaces were separated. This freeze–thaw cycle was repeated five times for each sample. The defrosted samples were then stirred

and washed in deionized water. Finally, the clay- and silt-bearing "dirty" water was decanted into a large glass (2 L).

The clay minerals in the fraction <2 μm were obtained by the conventional settling method based on
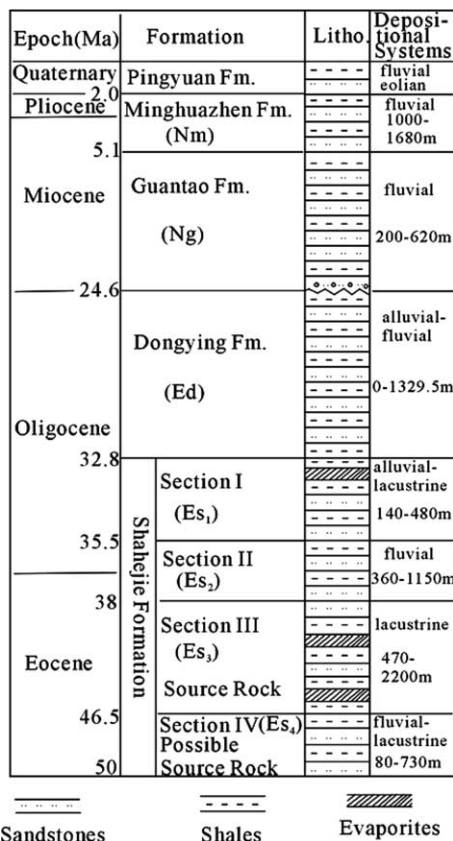
Fig. 2. Schematic stratigraphic chart for Dongpu Depression, Bohai Gulf Basin.

Stokes' formula. The "dirty" water as held in the glass was allowed to settle for 12 h, and then, the top 10 cm clay-bearing water column in the glass was collected. The glass was filled with deionized water and stirred again. After settling for 12 h, the top 10 cm clay-bearing water column was again collected. This process was repeated usually seven times until most clay minerals in

this size fraction were collected from the glass. The clay-bearing water was held in a bowl and frozen, then, allowed to thaw at room temperature. During the thaw cycle, the clay minerals settled to the bottom of the bowl and the water became clear.

2.3. Extraction of the free and adsorbed oils

The clay minerals as separated from the core samples were first Soxhlet extracted with dichloromethane:methanol (DCM:MeOH, 93:7 v/v) for 72 h. The first extract is considered as the free oil. After the Soxhlet extraction, a small part of each clay sample (about 0.5 g) was taken for clay compositional analysis as well as organic carbon and nitrogen analyses. The remaining solvent extracted clay sample was further treated with HCl and HCl:HF to remove clay minerals. The residual (kerogen-like) matter was Soxhlet extracted again with DCM:MeOH (93:7 v/v) for 72 h. The second extract is considered as the adsorbed oil.

2.4. Solvent extraction of oil-bearing fluid inclusion

Analysis of oil-bearing fluid inclusions was performed on seven of the eight samples (except PS4-3). After clay separation, the clasts from these samples were sieved to obtain the 0.3–0.1 mm size fractions. About 100 grams of clasts in this size range were taken from each sample for analysis of oil inclusions. The experimental procedure is described in detail in previous studies (Pan et al., 2003). Our experimental procedure is similar to that introduced by Karlsen et al. (1993), but with some modifications.

2.5. Oil fractionation

The free and adsorbed oils from the clay fractions obtained from the eight core samples and the oil inclusions obtained from the seven core samples were deasphaltened using 40× excess of hexane. The free oils were frac-

Table 1
Mineral composition of clay minerals in the <2 μm fraction as separated from reservoir sandstone samples from the Dongpu Depression, Bohai Gulf Basin

Sample	Well	Depth (m)	Kaolinite	Illite	Illite/smectite[a]	Smectite	Chlorite
Q27-3	Q27	2497.2	29.9	29.1	22.2	18.8	–[b]
Q29-5-2	Q29-5	2509.6	67.1	19.3	13.6	–	–
Q30-1	Q30	2554.2	43.4	34.3	22.3	–	–
Q44-1	Q44	2960.3	54.3	29.4	16.3	–	–
Q33-4	Q33	3695.4	49.3	28.4	22.3	–	–
PS4-3	PS4	3704.7	53.1	10.0	24.7	12.2	–
B16-1	B16	3908.9	34.9	–	41.7	6.9	16.5
Qian8-3	Qian8	4044.5	21.9	64.0	14.1	–	–

[a] Mixed-layer clay mineral.
[b] Trace amount.

tionated on a silica:alumina column using hexane, benzene and methanol as eluants to yield the aliphatic, aromatic, and resin fractions, respectively. The adsorbed and inclusion oils were fractionated via similar method using hexane and benzene as eluents to yield the aliphatic and aromatic fractions. However, the amounts of resins for the adsorbed and inclusion oils were calculated by difference.

2.6. GC and GC–MS analyses

Gas chromatographic (GC) analysis of the saturated fractions from all free, adsorbed and oil inclusions was performed in 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 a carrier gas of nitrogen. 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) analyses of these saturated fractions were carried out using a Micromass Platform II interfaced to an HP5890 GC fitted with the column aforementioned and a carrier gas of helium. 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.

For the free oils, n-alkanes were removed from the saturated fractions by urea adduction to concentrate the terpanes and steranes before GC–MS analyses. However, for the adsorbed oil and oil inclusions, the GC–MS analyses were carried out directly on the saturate fractions without urea adduction.

2.7. Residual organic carbon and nitrogen analyses

After Soxhlet extraction for free oil, the clay fractions from the eight sandstone samples were further analyzed for organic carbon and nitrogen contents by using a Heraeus Elemental Analyzer (CHN-O-RAPID), after the removal of carbonate minerals by HCl treatment. The measured data are defined as the contents of residual organic carbon and nitrogen.

3. Results

3.1. Amounts and gross compositions of the free and adsorbed oils and oil inclusions

The amounts and gross compositions of the free and adsorbed oils as extracted from the clay minerals of the eight sandstone samples are shown in Table 2. Those of the oil inclusions obtained from the grains of seven selected samples are shown in Table 3.

The amount of free oil from the clay minerals in the fraction <2 μm of these eight samples varies sub-

Table 2
Amounts and gross compositions of the free and adsorbed oils obtained from the clay minerals in reservoir sandstone samples from the Dongpu Depression, Bohai Gulf Basin

Sample	Well	Depth (m)	Core weight (g)	Clay weight (g)	Oil I (mg)[a]	Oil I (mg/g clay)[b]	Oil I gross composition (%)				Oil II (mg)[c]	Oil II (mg/g clay)[d]	Oil II gross composition (%)		
							Sat.	Aro.	Res.	Asp.			Sat.	Aro.	Polar
Q27-3	Q27	2497.2	425	10.66	910.88	85.45	74.3	12.2	13.1	0.4	63.07	6.24	0.7	0.8	98.5
Q29-5-2	Q29-5	2509.6	471	2.17	206.09	94.97	77.5	13.3	7.1	2.1	12.68	7.84	1.2	1.5	97.3
Q30-1	Q30	2554.2	620	20.02	1590.28	79.44	79.9	9.7	8.7	1.7	110.76	5.69	0.6	1.1	98.3
Q44-1	Q44	2960.3	416	8.39	572.31	68.21	61.4	16.6	18.6	3.4	37.07	4.72	0.6	0.9	98.5
Q33-4	Q33	3695.4	444	10.21	90.19	8.83	87.5	6.5	3.1	2.9	6.30	0.65	6.2	3.3	90.5
PS4-3	PS4	3704.7	246	9.31	11.34	1.22	75.5	5.3	16.9	2.3	1.58	0.18	9.5	5.7	84.8
B16-1	B16	3908.9	386	11.16	225.07	20.17	82.4	7.2	7.8	2.6	17.28	1.62	4.0	2.4	93.6
Qian8-3	Qian8	4044.5	476	16.37	723.79	44.21	84.8	6.0	7.9	1.3	10.94	0.69	7.4	4.2	88.4

[a] Oil I: free oil.
[b] Oil I (mg/g clay) = oil I (mg)/clay weight (g).
[c] Oil II: adsorbed oil.
[d] Oil II (mg/g clay) = oil II (mg) × F/clay weight (g); F (correction factor) = (clay weight (g) × 1000 − oil I (mg))/(clay weight (g) × 1000 − oil I (mg) − 500), before treatment with HCl and HF, 500 mg clay sample was taken away for the analyses of clay mineral composition and organic carbon and nitrogen contents.

Table 3
Total amounts and gross compositions of oil inclusions obtained from the grains (about 100 g for each sample) of seven reservoir sandstone samples from the Dongpu Depression, Bohai Gulf Basin

Sample	Total (mg)	Sat. (%)	Aro. (%)	Polar (%)
Q27-3	2.82	17.02	4.96	78.01
Q29-5-2	3.71	30.13	4.58	65.28
Q30-1	2.49	16.87	5.22	77.91
Q44-1	6.43	22.55	5.60	71.85
Q33-4	2.18	19.17	4.59	76.24
B16-1	4.69	19.19	4.69	76.12
Qian8-3	8.94	31.88	5.82	62.30

stantially and generally ranges from 1.22 to 94.97 mg/g clay. It is greater than 20 mg/g clay for six samples, but is only 1.22 and 8.83 mg/g clay, respectively, for samples PS4-3 and Q33-4. The free oils for all samples are dominated by saturated fractions, which range from 61.4% to 87.5%. The total content of resins and asphaltenes together only ranges from 6.0% to 22.0%.

The amount of the free oil could be influenced by a number of factors, such as total pore volume of sandstone reservoir rock, the degree of oil saturation, and the chemical and physical features of the oil itself, i.e., gas/oil ratio (GOR) and relative proportion of light to heavy hydrocarbons which influence the amount of mass lost during evaporation. It is demonstrated from Table 2 that the amount of free oil is the lowest in PS4-3 because this sample was collected from the gas zone. The amount of free oil is also lower in samples Q33-4 and B16-1 relative to the other five samples because they are located at gas-oil transition zones and contain relatively high amounts of light hydrocarbons.

The amount of the adsorbed oil in these eight samples ranges from 0.18 to 7.84 mg/g clay. It is higher than 1.6 mg/g clay in five of them but is only 0.18, 0.65 and 0.69 mg/g clay, respectively, in the samples PS4-3, Q33-4 and Qian8-3. All eight adsorbed oils are dominated by polar components (resins and asphaltenes), whose content ranges from 84.8% to 98.5%. In contrast, the content of the saturated fraction only ranges from 0.6% to 9.5%.

As demonstrated in Fig. 3, the content of adsorbed oil is well correlated with the content of free oil, except sample Qian8-3. The content of free oil for sample Qian8-3 is relatively higher due to the lower extent of free oil evaporation.

The gross compositions of oil inclusions as obtained from seven analyzed samples are similar to those of adsorbed oils. However, the oil inclusions contain relatively higher amounts of saturated hydrocarbons and relatively lower amounts of polar components than do the adsorbed oils (Table 3 and Fig. 4).
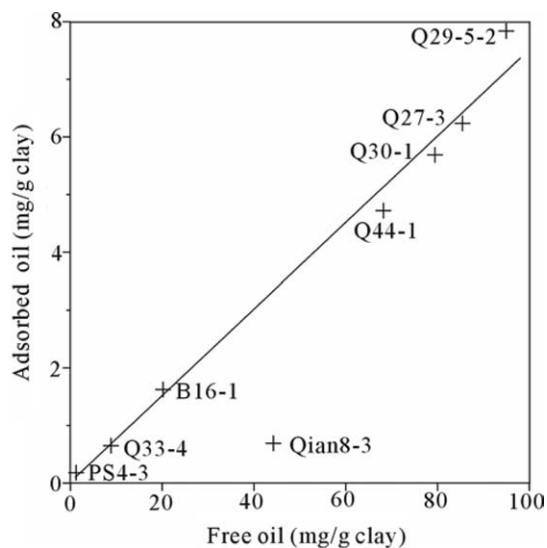

Fig. 3. Relationship between the amounts of free oil versus adsorbed oil obtained from the clay fractions (<2 μm) of reservoir sandstones.

3.2. Amounts of residual organic carbon and nitrogen on the clay surfaces

The residual organic carbon and nitrogen contents of the clay fractions obtained from the eight reservoir rocks were analyzed after removal of free oil by Soxhlet extraction. The results are shown in Table 4. Every sample was analyzed in duplicate. The reproducibility of results is good for all samples (OC: ±0.072%, ON: ±0.024%) except for sample PS4-3 (Table 4).

For the eight clay fractions, the content of residual organic carbon is generally in the range between 0.537% and 1.614%, and varies from 0.805% to 1.292% for six of them. The ratio of adsorbed oil/ residual organic matter is substantially higher in the four shallow samples Q27-3, Q29-5-2, Q30-1 and Q44-1 than in the four deep samples Q33-4, PS4-3, B16-1 and Qian8-3 (Table 4 and Fig. 5). The content
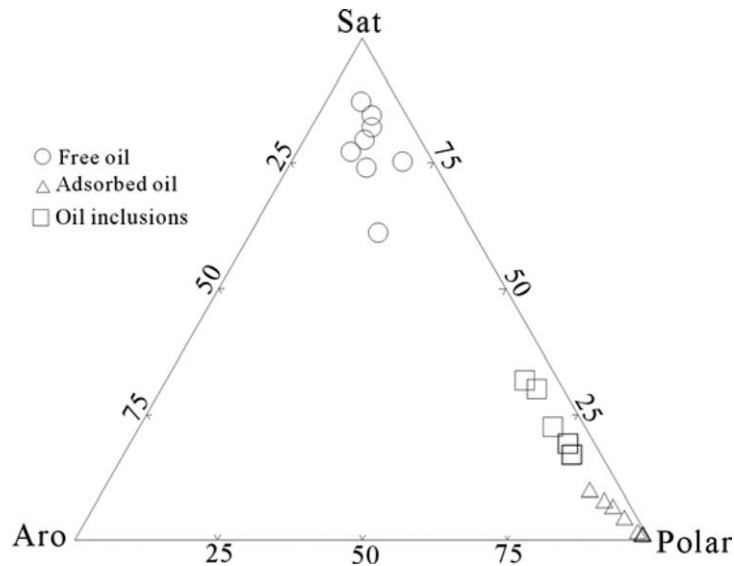
Fig. 4. Ternary diagram of saturated, aromatic and polar composition for the free, adsorbed and inclusion oils.

Table 4
The contents of residual organic carbon (OC) and nitrogen (ON) of the clay minerals (after the free oil extraction) in the <2 μm fraction

Sample	Well	Depth (m) formation	OC (wt.%)	ON (wt.%)	N/C (atomic)	Free oil/Res. OM[a]	Adsorbed oil/Res. OM (%)[b]
Q27-3	Q27	2497.2	0.948	0.071	0.064	8.18	59.7
Q27-3d[c]	Q27	Es_3^1	0.956	0.077	0.069		
Q29-5-2	Q29-5	2509.6	1.607	0.080	0.043	5.42	44.7
Q29-5-2d	Q29-5	Es_3^1	1.621	0.088	0.047		
Q30-1	Q30	2554.2	0.809	0.069	0.073	8.91	63.8
Q30-1d	Q30	Es_2	0.805	0.074	0.079		
Q44-1	Q44	2960.3	1.220	0.101	0.071	4.86	33.6
Q44-1d	Q44	Es_3^1	1.292	0.125	0.083		
Q33-4	Q33	3695.4	1.150	0.158	0.118	0.64	4.7
Q33-4d	Q33	Es_3^1	1.182	0.174	0.126		
PS4-3	PS4	3704.7	0.587	0.164	0.240	0.19	2.8
PS4-3d	PS4	Es_3^1	0.488	0.130	0.228		
B16-1	B16	3908.9	0.945	0.139	0.126	1.79	14.8
B16-1d	B16	Es_3^2	0.974	0.150	0.132		
Qian8-3	Qian8	4044.5	1.231	0.099	0.069	3.13	4.9
Qian8-3d	Qian8	Es_3^2	1.235	0.098	0.068		

[a] Amount of free oil/amount of residual organic matter, here amount of residual organic matter = OC (%) × 1.2 × [amount of clay minerals (mg) − amount of free oil (mg)].

[b] Amount of adsorbed oil/amount of residual organic matter, here amount of residual organic matter = OC (%) × 1.2 × [amount of clay minerals (mg) − amount of free oil (mg) − 500 mg]. After removal of free oil by Soxhlet extraction, 500 mg clay was taken from each sample for X-ray and organic carbon and nitrogen analyses.

[c] Duplicate.

of residual organic nitrogen of the eight samples is in the range of 0.069–0.174%, and the atomic ratio of N/C varies between 0.045 and 0.234. The relatively high nitrogen contents and high N/C ratios for these eight samples, especially PS4-3, may indicate that these clays contain inorganic nitrogen, i.e., NH_4^+. As
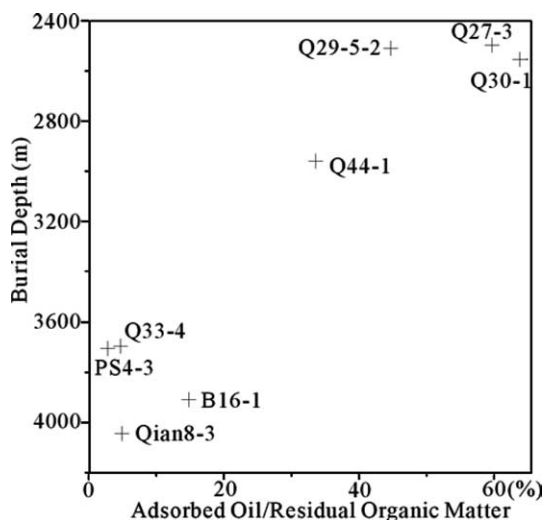
Fig. 5. Relationship between the ratio of adsorbed oil/residual organic matter and the burial depth.

the samples were treated with HCl acid prior to organic carbon and nitrogen analyses, the influence of inorganic nitrogen is limited.

3.3. n-Alkanes and isoprenoids

The gas chromatograms of the free and adsorbed oils and oil inclusions obtained from each analyzed sample are shown in Figs. 6–13. As demonstrated in the gas chromatograms, the free oils contain low amounts of short chain n-alkanes relative to long chain n-alkanes, indicating a strong evaporation effect due to core storage for many years (Figs. 6–13a). However, the adsorbed oils contain a high abundance of short chain n-alkanes, suggesting less eva'poration (Figs. 6–13d). Pr/Ph ratio decreases while Pr/nC_{17} and Ph/nC_{18} ratios increase with evaporation. Therefore, Pr/Ph ratio is relatively lower while Pr/nC_{17} and Ph/nC_{18} ratios are relatively higher in the current free oils than in the original free oils when the core samples were just brought out from the boreholes. However, the Pr/nC_{17} and Ph/nC_{18} ratios are substantially lower in the current free oils than in the adsorbed oils [Table 5, Figs. 6–13(a) and (d), and 14(a)]. It can be estimated that these two ratios could be lower in the original free oils, in comparison with their corresponding adsorbed oils.

The ratios of Pr/nC_{17} and Ph/nC_{18} are relatively lower in the oil inclusions than in the current free oil for most
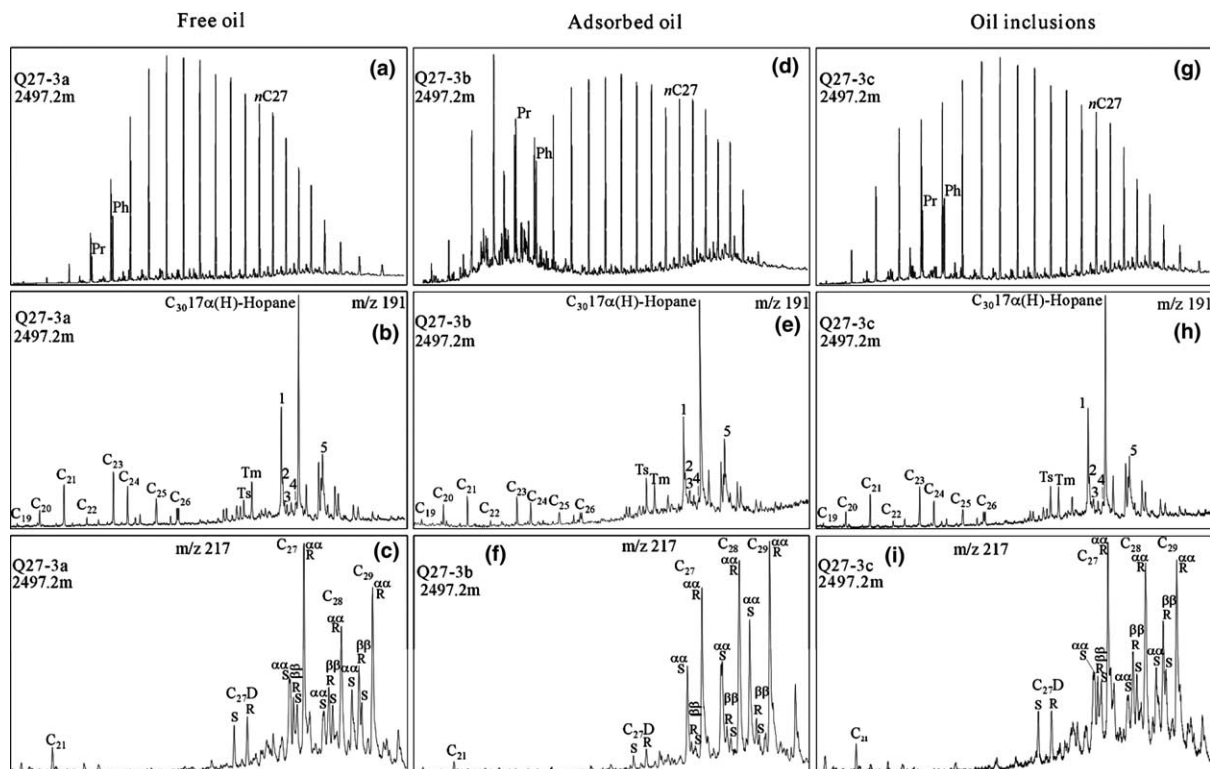

Fig. 6. Gas chromatograms and m/z 191 and m/z 217 mass chromatograms of sample Q27-3. (a)–(c) Free oil; (d)–(f) adsorbed oil; (g)–(i) oil inclusions; in (b), (e) and (h), C_{19}–C_{25}: tricyclic terpanes; 1: C_{29}-17α(H)-hopane; 2: C_{29}Ts; 3: C_{30}-17α(H)-diahopane; 4: Oleanane; 5: Gammacerane.
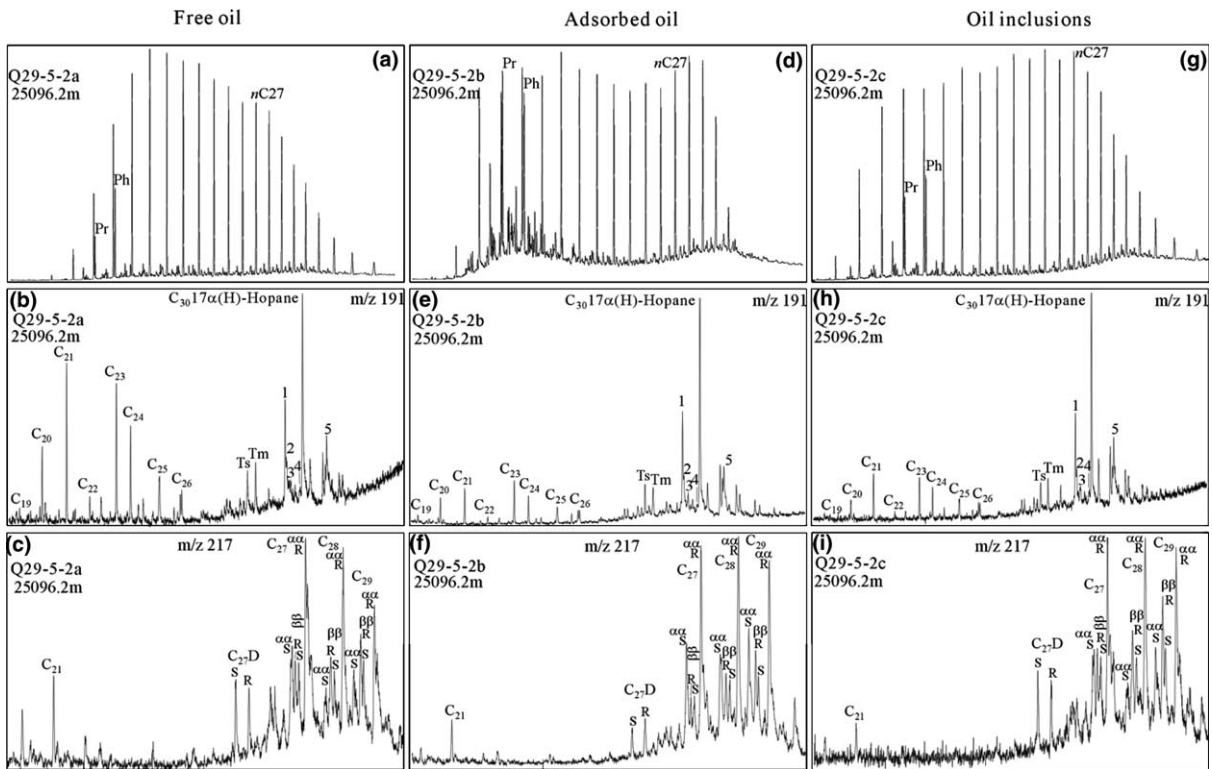
Fig. 7. Gas chromatograms and *m/z* 191 and *m/z* 217 mass chromatograms of sample Q29-5-2. (a)–(c) Free oil; (d)–(f) adsorbed oil; (g)–(i) oil inclusions; in (b), (e) and (h), C_{19}–C_{25}: tricyclic terpanes; 1: C_{29}-17α(H)-hopane; 2: C_{29}Ts; 3: C_{30}-17α(H)-diahopane; 4: Oleanane; 5: Gammacerane.

samples [Table 5 and Fig. 14(a)]. This result can be mainly accredited to the evaporative effect. The inclusion oils apparently evaporated substantially less than did the free oils in the present study [Figs. 6–12(d)], although the oil inclusions can easily lose their light molecular weight hydrocarbons during solvent evaporation due to their small amounts (e.g., Karlsen et al., 1993; George et al., 1997; Pan et al., 2003).

3.4. Terpanes and steranes

The *m/z* 191 and *m/z* 217 mass chromatograms for the free and adsorbed oils and oil inclusions obtained from the analyzed samples are demonstrated in Figs. 6–13. Some selected parameters are listed in Table 5 and demonstrated in Fig. 14(b)–(d) and 15. There are several common variation trends in regard to the terpane and sterane distributions between the free oils and the corresponding adsorbed oils for the eight samples analyzed: (1) the abundance of tricyclic terpanes relative to pentacyclic terpanes is higher in the free oils than in the corresponding adsorbed oils; (2) the abundance of C_{21} steranes relative to C_{27}–C_{29} steranes is higher in the free oils than in the adsorbed oils; (3) the

abundance of C_{27} regular steranes relative to C_{28} and C_{29} steranes is higher in the free oils than in the adsorbed oils; (4) the ratio of C_{29} $\alpha\beta\beta/(\alpha\alpha\alpha + \alpha\beta\beta)$ steranes is higher in the free oils than in the adsorbed oils for seven of the eight samples analyzed except for sample PS4-3 where this ratio is slightly lower in the former than in the latter; and (5) the abundance of C_{27} diasteranes relative to C_{27} regular steranes is higher in the free oils than in the adsorbed oils for seven of the eight analyzed samples except for sample PS4-3, where the relative abundance is similar in both the free oils and adsorbed oils. In addition, for samples B16-1 and Qian8-3, the adsorbed oil contains notably lower amounts of C_{29}Ts, C_{30}-diahopane and oleanane relative to C_{29}-17α(H)-hopane and C_{30}-17α(H)-hopane than does the free oil [Figs. 11(b) and (e) and 12(b) and (e)]. Other terpane and sterane parameters, as listed in Table 5, vary differently among the eight samples, but no clear variation trends between these two types of oils can be observed.

The oil inclusions of the seven analyzed samples generally exhibit intermediate characteristics in terpane and sterane distributions between the corresponding free oils and adsorbed oils (Table 5 and Figs. 6–12, 14(b), (d) and 15).
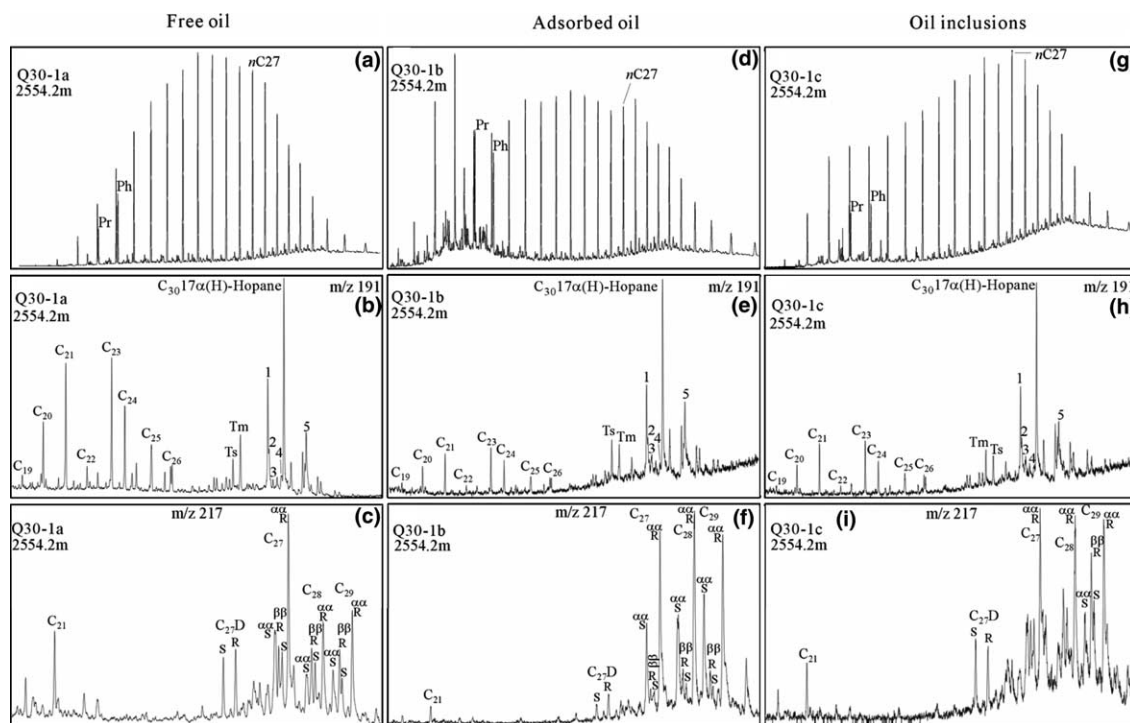
Fig. 8. Gas chromatograms and m/z 191 and m/z 217 mass chromatograms of sample Q30-1. (a)–(c) Free oil; (d)–(f) adsorbed oil; (g)–(i) oil inclusions; in (b), (e) and (h), C_{19}–C_{25}: tricyclic terpanes; 1: C_{29}-17α(H)-hopane; 2: C_{29}Ts; 3: C_{30}-17α(H)-diahopane; 4: Oleanane; 5: Gammacerane.

3.5. Homogenization temperatures of oil-bearing fluid inclusions

Oil-bearing fluid inclusions have been observed in all the seven oil sandstones. Homogenization temperature data measured for these inclusions are shown in Table 6. These inclusions were not found in PS4-3, which was collected in the gas zone. However, they were observed on an oil sandstone PS4-4 which was collected in the same well 300 m deeper than PS4-3 (Table 6). The homogenization temperatures range from 72.3–106.1 °C for the eight analyzed samples.

4. Discussion

4.1. Abundance and condensation of adsorbed organic matter

Although the surface areas of the clay minerals were not measured, we expect that in the present study they would be in a relatively narrow range "per gram" clay minerals due to their similar particulate size (<2 μm) for the eight samples. The narrow range of the residual organic carbon contents in these samples may suggest that a fixed relationship exists between the residual or-

ganic carbon contents and the mineral surface areas, which has already been documented in many studies on recent marine sediments (e.g., Keil et al., 1994a,b; Mayer, 1994a,b, 1999; Bergamaschi et al., 1997; Ganeshram et al., 1999). Nevertheless, the exact relationship between the contents of the residual organic carbon and the clay surface areas is not known at present. Therefore, more research work is necessary to improve our knowledge about this issue.

After entering the reservoir, oils could be further affected by thermal alteration (Tissot and Welte, 1984). With burial depth and temperature increasing, crude oils in reservoirs become lighter and contain an increasing amount of low molecular weight hydrocarbons. This process is accompanied by the formation of insoluble pyrobitumen (Tissot and Welte, 1984). In the studied area, the current geothermal gradient is relatively high, about 33 °C/km, and the surface temperature is about 14 °C. For samples Q27-3, Q29-5-2, Q30-1 and Q44-1, the current reservoir temperatures are similar to the measured homogenization temperatures of oil-bearing fluid inclusions (Table 6). However, as to the other four samples, i.e., B16-1, PS4-3, Q33-4 and Qian8-3, the former are substantially higher than the latter (Table 6). If the oil-bearing fluid inclusions were saturated with respect to gas during entrapment,
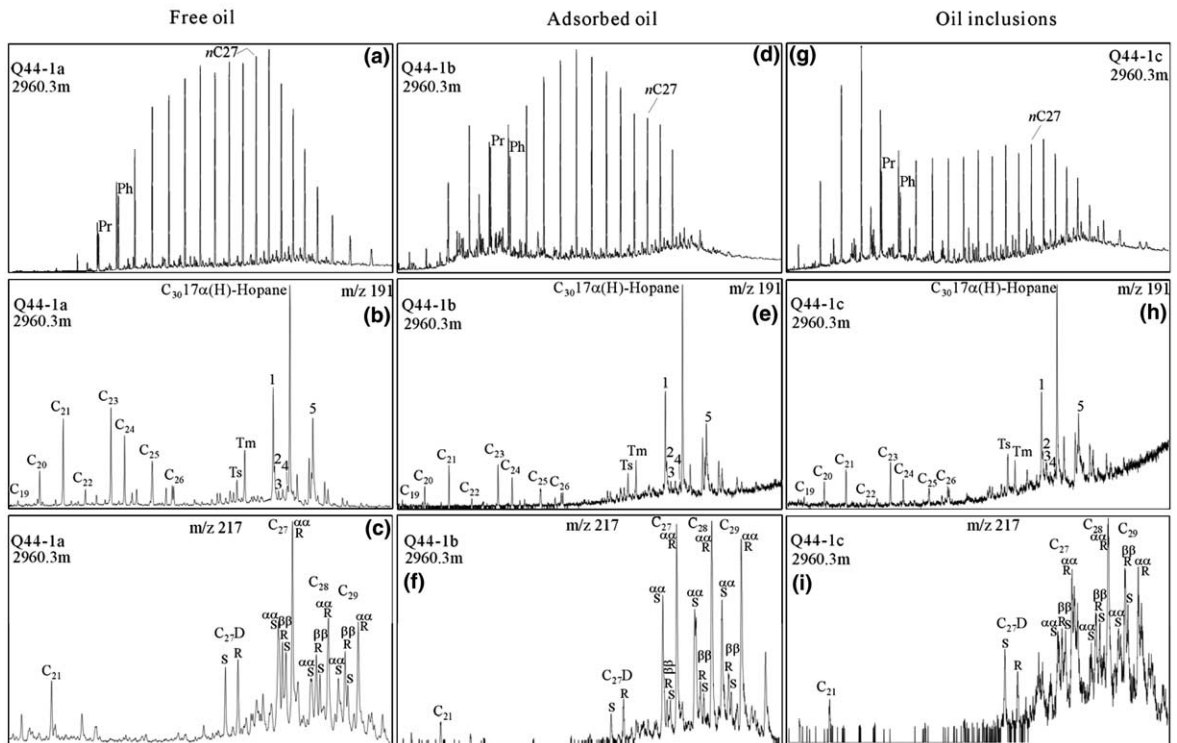
Fig. 9. Gas chromatograms and *m/z* 191 and *m/z* 217 mass chromatograms of sample Q44-1. (a)–(c) Free oil; (d)–(f) adsorbed oil; (g)–(i) oil inclusions; in (b), (e) and (h), C_{19}–C_{25}: tricyclic terpanes; 1: C_{29}-17α(H)-hopane; 2: C_{29}Ts; 3: C_{30}-17α(H)-diahopane; 4: Oleanane; 5: Gammacerane.

their homogenization temperatures are equal to their entrapment temperatures, representing the paleotemperatures of the reservoirs during oil filling. This result suggests that the reservoir temperatures remain unchanged for the four shallow samples but have substantially increased for the four deep samples after oil charging.

In the present study, as discussed later, we believe that indigenous organic matter is too minimal to account in the diagenetic clay minerals and that the residual organic matter is overwhelmingly from the migrating oil. The original residual organic matter could be almost totally soluble and dominated by polar components. With temperature increasing, it gradually transforms to insoluble organic matter (pyrobitumen) due to thermal alteration. As a result, the residual organic matter includes the adsorbed oil and pyrobitumen. Here, we use the ratio of the amount of adsorbed oil to the amount of residual organic matter to indicate the rank of thermal alteration. The higher this ratio, the lower the thermal alteration rank. The ratio of adsorbed oil to residual organic matter of the eight clay fractions is in the range between 2.8% and 63.8% (Table 4 and Fig. 5). For the four shallow samples, i.e., Q27-3, Q29-5-2, Q30-1 and Q44-1, this ratio is high, ranging from

33.6% to 63.8%, demonstrating a low rank of thermal alteration. In contrast, for the four deep samples, i.e., B16-1, PS4-3, Q33-4 and Qian8-3, it is low, ranging from 2.8% to 14.4%, demonstrating a high rank of thermal alteration. Furthermore, the total content of saturated and aromatic hydrocarbons in the extracted adsorbed oils are significantly higher for the four deep-buried samples (6.4–15.2%) than for the four shallow-buried samples (1.5–2.7%) (Table 2). This result could explain the extensive incorporation of polar components in the residual organic matter to pyrobitumen that leads to the concentration of the saturated and aromatic fractions in the adsorbed oils of the four deep-buried samples.

For the four shallow samples, although reservoir temperatures appear not to have increased significantly, a considerable amount of insoluble pyrobitumen has formed (36.2–66.4%). This result may indicate that once polar components are adsorbed onto the clay surfaces they are easily polymerized. Collins et al. (1995) suggested that organic matter adsorption onto mineral surfaces in recent sediments could favor subsequent condensation reactions (polymerization) by concentrating the reactants, which leads to the formation of kerogen.
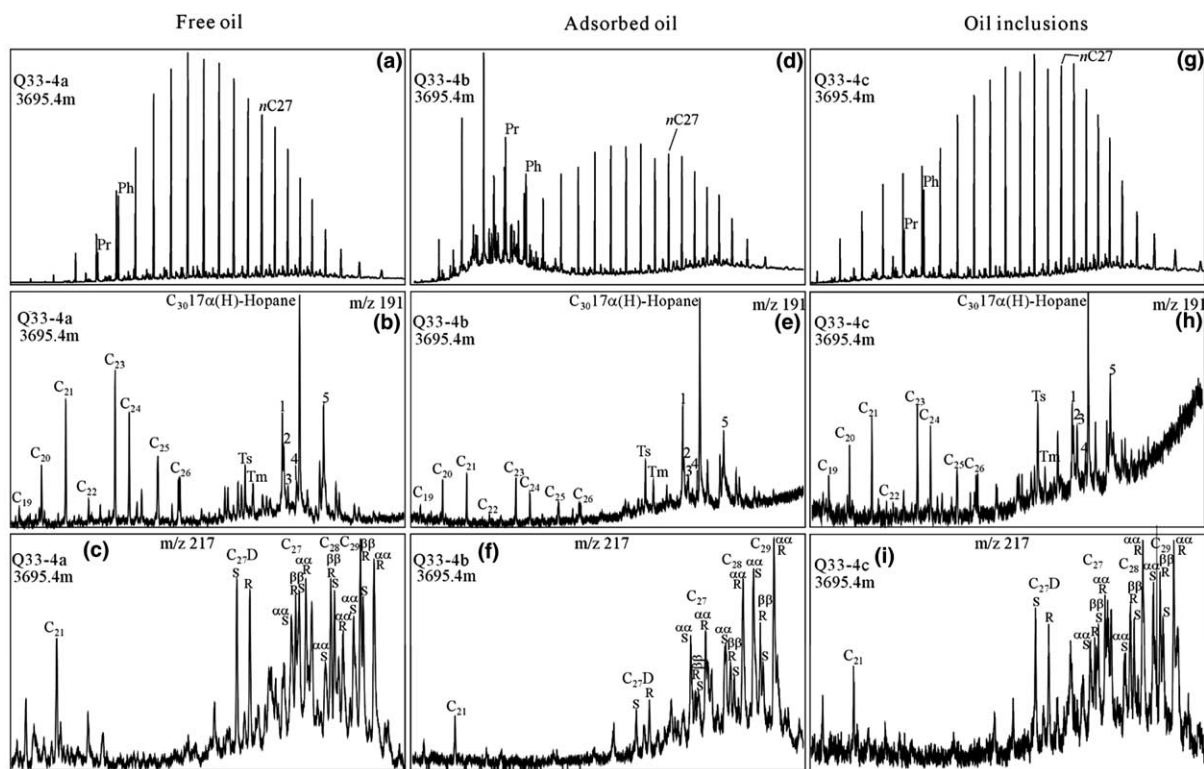
Fig. 10. Gas chromatograms and *m/z* 191 and *m/z* 217 mass chromatograms of sample Q33-4. (a)–(c) Free oil; (d)–(f) adsorbed oil; (g)–(i) oil inclusions; in (b), (e) and (h), C_{19}–C_{25}: tricyclic terpanes; 1: C_{29}-17α(H)-hopane; 2: C_{29}Ts; 3: C_{30}-17α(H)-diahopane; 4: Oleanane; 5: Gammacerane.

Sandstone reservoir rocks in the studied area were deposited in alluvial–fluvial fan or fan delta facies. The extremely oxidizing sedimentary conditions, active percolation of meteoric water and bacterial breakdown greatly reduce the amount and the hydrocarbon potential of indigenous organic matter in these sandstone reservoir rocks (Bjørlykke, 1989; Wilhelms et al., 1996). In our opinion, the only significant indigenous organic matter in sandstone deposited in fluvial facies, such as fluvial fan and fan delta, is from the large tree fragments that obviously cannot be present in the clay fraction.

Sample PS4-3 is located at the gas zone and has the lowest content of residual organic carbon (about 0.5%). The abundance of the free oil to residual organic carbon is higher than 20% for this sample. According to our unpublished data, the ratio of Soxhlet extracted bitumen to total organic carbon in 20 dark shales from Shahejie Formation in this region, is between 0.6% and 7.9%. Furthermore, the content of the saturated fraction in the free oil of sample PS4-3 (75.5%) is also substantially higher than that in the bitumen of these 20 dark shales (21.4–31.5%). Therefore, the evidence obtained in this study is that the free oil and the residual organic matter in PS4-3 are mainly from migrating oil, rather

than syngenetic kerogen. This will be discussed further later.

4.2. Correlation of free oil versus adsorbed oil

4.2.1. Definition and immobility of adsorbed oil

It has been documented that the adsorption of polar components on mineral surface of oil in a reservoir is irreversible: once these compounds are adsorbed they do not equilibrate further by diffusive mixing (Larter and Aplin, 1995; Stoddart et al., 1995; Schwark et al., 1997). During the formation of an adsorbed oil zone, non-polar hydrocarbons are trapped/occluded in the polar compounds. These hydrocarbons could retain, to some extent, the original geochemical features due to their hindered mobility (Wilhelms et al., 1996; Schwark et al., 1997).

We hypothesize that oil adsorbed onto the mineral surfaces in the reservoir rocks actually consists of two components: an inner zone where polar compounds are directly bonded (e.g., via hydrogen bonding) onto the mineral surfaces and an outer zone where oil is not in contact with or chemically bonded to mineral surfaces. Outer zone oil can be extracted with solvent while,
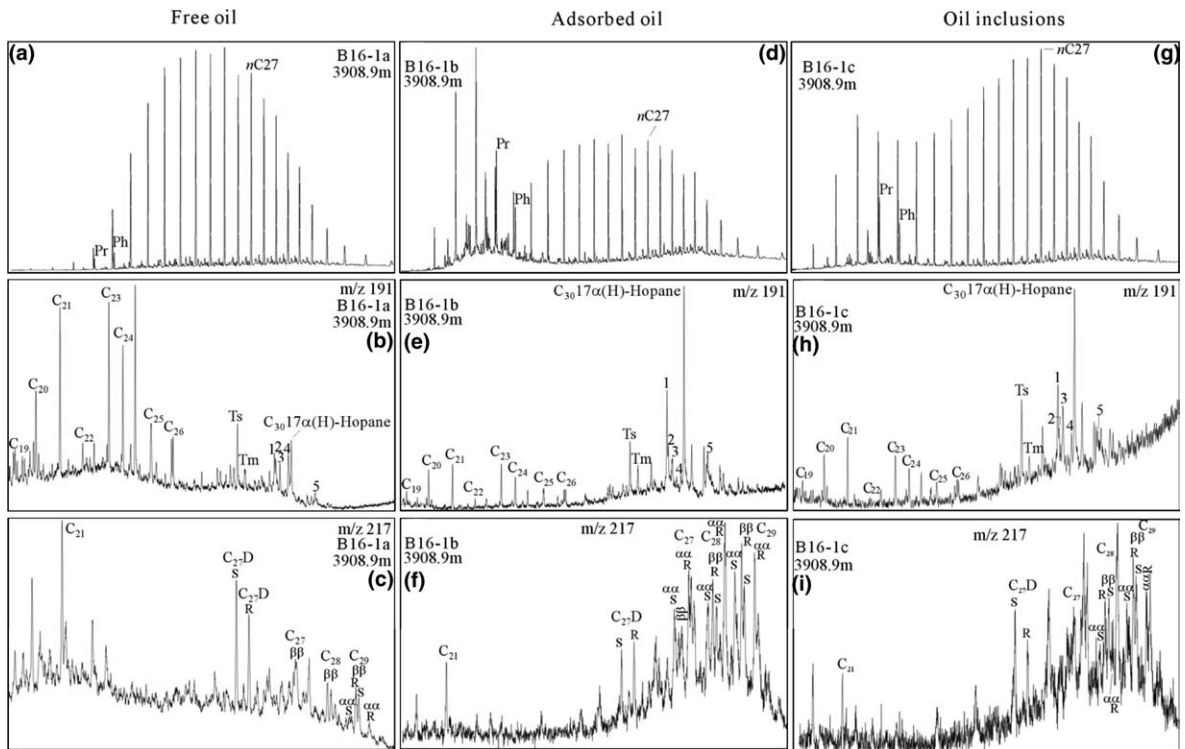
Fig. 11. Gas chromatograms and m/z 191 and m/z 217 mass chromatograms of sample B16-1. (a)–(c) Free oil; (d)–(f) adsorbed oil; (g)–(i) oil inclusions; in (b), (e) and (h), C_{19}–C_{25}: tricyclic terpanes; 1: C_{29}-17α(H)-hopane; 2: C_{29}Ts; 3: C_{30}-17α(H)-diahopane; 4: Oleanane; 5: Gammacerane.

in contrast, inner zone oil cannot be extracted by solvent without the application of HCl and HF for the removal of the minerals. Following this definition, the adsorbed oil as referred to by Schwark et al. (1997) and the later extracts as referred to by Wilhelms et al. (1996) are from the outer part of the adsorbed oil zone while the adsorbed oil referred in the present study and our previous one (Pan and Yang, 2000) is from the inner part of the adsorbed oil zone.

The variations of saturated hydrocarbon compositions, such as the acyclic isoprenoid, terpane and sterane distributions, between the free oil and the corresponding adsorbed oil revealed in the present study and our previous one (Pan and Yang, 2000) are substantial in comparison to those observed in the studies by Wilhelms et al. (1996) and Schwark et al. (1997). These observations indicate that hydrocarbons trapped in the outer part of the adsorbed oil zone are significantly more mobile than are those in the inner part of the adsorbed oil zone. These results suggest that the former are only trapped in the networks of polar components and can be mixed with the free oil by diffusion while the latter are trapped between the polar components and clay surfaces and are almost immobile. As the polar compounds are firmly bound to the clay surface the hydrocarbon

trapped between the bonded polar compound and the clay surface is also fixed.

4.2.2. Experimentally induced or pre-existing compositional heterogeneity?

Sequential extraction studies of source rocks have been reported previously (e.g., Sajgo et al., 1983; Spiro, 1984; Price and Clayton, 1992). In the study by Sajgo et al. (1983), the "coarse extract" was obtained by Soxhlet extraction (chloroform, 40 h) from the crushed grains in 1–2 cm size range while the "fine extract" was obtained by Soxhlet extraction of the previously extracted grains after grinding. Similarly, in the study by Price and Clayton (1992), six extracts were obtained from the same source rock sample (unground friable rocks or cutting chips) by sequential extraction with removal and replacement of dichloromethane in the extractor after 2, 3.5, 12, 24, 72 and 240 h, respectively. In the study by Spiro (1984), the "free bitumen" and "bound bitumens" (associated with carbonates and silicates) were obtained by stepwise extraction before and after selective mineral dissolution. Although the experimental procedures are more or less different from each other in the above-mentioned three studies, the results are very similar: the gross and molecular compositions are
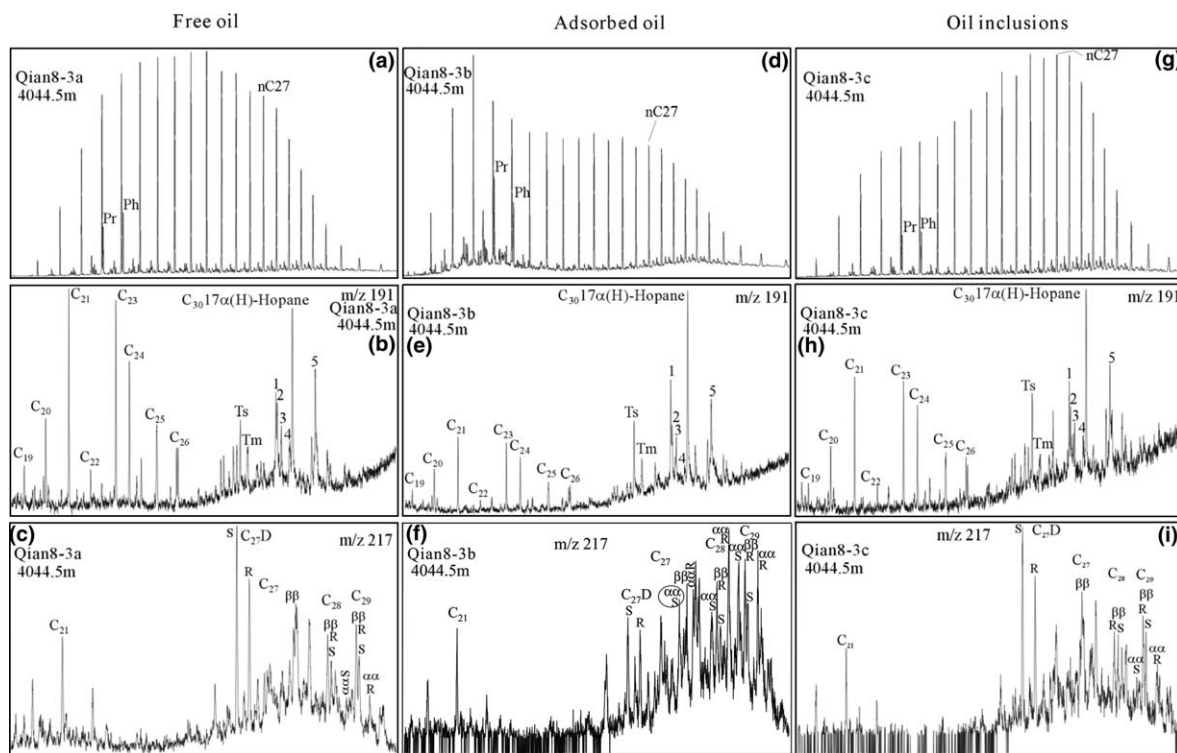
Fig. 12. Gas chromatograms and m/z 191 and m/z 217 mass chromatograms of sample Qian8-3. (a)–(c) Free oil; (d)–(f) adsorbed oil; (g)–(i) oil inclusions; in (b), (e) and (h), C_{19}–C_{25}: tricyclic terpanes; 1: C_{29}-$17\alpha(H)$-hopane; 2: C_{29}Ts; 3: C_{30}-$17\alpha(H)$-diahopane; 4: Oleanane; 5: Gammacerane.

significantly different between the "coarse extract" and "fine extract", among the six extracts, and among the free and bound bitumens from the same source rock sample (Sajgo et al., 1983; Spiro, 1984; Price and Clayton, 1992). The variation trends of gross composition and some molecular parameters, from the first extract to the later extracts, are as follows: (1) the content of aliphatic hydrocarbons in the bitumens decreases; (2) the ratio of short chain n-alkanes to long ones decreases; (3) the ratio of triaromatic to monoaromatic plus triaromatic steroids increases; (4) the ratios of lower molecular weight steroids to the corresponding higher molecular weight ones, i.e., $C_{21}/(C_{21} + C_{29})$ steranes, $C_{21}/(C_{21} + C_{27} + C_{28} + C_{29})$ monoaromatic steroids and $C_{20}/(C_{20} + C_{28})$ triaromatic steroids, decrease; and (5) the ratio of small tricyclic terpanes to pentacyclic terpanes decreases (Sajgo et al., 1983; Spiro, 1984). Price and Clayton (1992) believed that the compositional differences between the progressive extracts from the same source rock sample indicated heterogeneity of bitumen in this sample. However, as documented by Pepper (1992) and Sandvik et al. (1992), the residual oils, or extracted bitumens in source rocks, are mainly absorbed by kerogens, and oil expulsion cannot occur until the

kerogen is saturated by the generated oil in the source rocks. This implies that hydrocarbons in the source rock are homogeneous once the source rock gets into the oil generation window. When sequential extraction is performed, every step of partial extraction of oil from source rocks naturally induces compositional fractionation between extracted and residual oil, and the compositional fractionation is controlled by the partition of oil components between the kerogen and solvent phases. The results of the above-mentioned three studies can be interpreted by selective extraction and absorption of oil components in source rocks. Price and Clayton (1992) also suggested that bonding and trapping of organic compounds to and in kerogens may be partly responsible for their observation.

As demonstrated by Schwark et al. (1997), at the early stage of sequential extraction (step 1) of an oil-bearing sandstone core, the extracts are nearly identical in gross and molecular compositions. During this stage, about 80% of the total oil was extracted and no compositional fractionation effects were observed (Schwark et al., 1997). This phenomenon can be explained by all compounds in the free oil phase being highly soluble in the solvent (DCM:MeOH). In the subsequent extraction
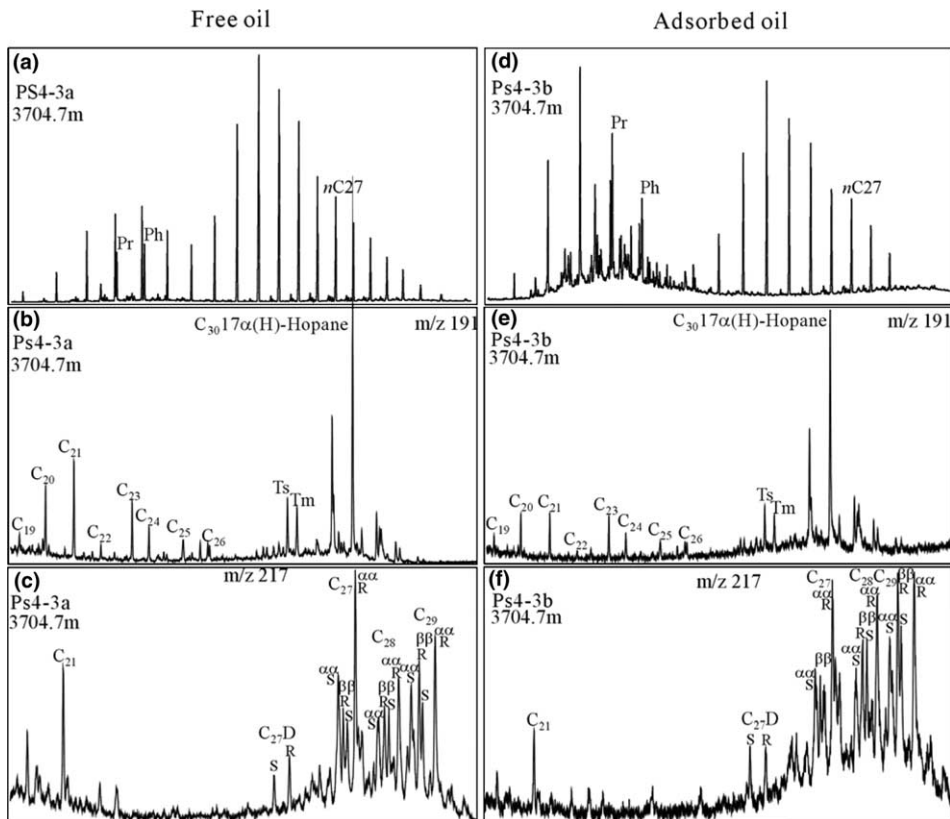
Fig. 13. Gas chromatograms and m/z 191 and m/z 217 mass chromatograms of sample PS4-3. (a)–(c) Free oil; (d)–(f) adsorbed oil; in (b) and (e), C_{19}–C_{25}: tricyclic terpanes; 1: C_{29}-17α(H)-hopane; 2: C_{29}Ts; 3: C_{30}-17α(H)-diahopane; 5: Gammacerane.

(steps 2–5), the abundances of resins and asphaltenes in the extracts sharply increase while the abundances of saturated hydrocarbons decrease correspondingly. Although the gross compositions are greatly different the compositions of saturated biomarkers, i.e., acyclic isoprenoids, steranes and terpanes, are very similar between the free oil and absorbed oil in both the studies by Wilhelms et al. (1996) and Schwark et al. (1997). The results of these two studies demonstrate that solvent sequential extraction itself does not create the fractionation of saturated biomarker compounds in reservoir rocks, unlike in source rocks. This difference is consistent with the kerogen in source rocks being insoluble while polar components (resins and asphaltenes) in reservoir rocks are soluble in solvent except those bonded directly onto mineral surfaces.

In the present study, the adsorbed oil contains more short chain n-alkanes than does the corresponding free oil, which is in contrast to the result of the sequential extraction studies on source rocks (Sajgo et al., 1983; Spiro, 1984; Price and Clayton, 1992). This result indicates that although the free oil has been severely evaporated the adsorbed oil remains unchanged during storage.

4.2.3. Implications for oil reservoir filling history and migration-related compositional fractionation

During the filling process of the reservoir, the molecular compositions of the charging oil, including facies and maturity parameters, usually vary significantly (e.g., England et al., 1987; Leythaeuser and Rückheim, 1989; England, 1990; Larter and Aplin, 1995). The inclusion oil, obtained from oil sandstone, is generally considered to be the representative of paleo oil or initial oil charging the reservoir (e.g., Karlsen et al., 1993; George et al., 1997, 1998; Bhullar et al., 1999; Jones and Macleod, 2000; Pan and Yang, 2000; Pan et al., 2003). Prior to the release and extraction of oil-bearing fluid inclusions, the adsorbed oil zone on the grain surfaces was completely removed by repeated Soxhlet extractions and chromic acid digestion in the present study and Pan et al. (2003). Therefore, we believe that the similar variation trends of the ratios of C_{23} tricyclic terpanes/(C_{23} tricyclic terpane + C_{30}-hopane), C_{21}/(C_{21} + ΣC_{29}) steranes and the composition of C_{27}, C_{28} and C_{29} regular steranes between the free oil and adsorbed oil and between the free oil and oil inclusions reflect the compositional variation of charging oil during the filling process of the reservoirs (Table 5 and Figs.

Table 5
Molecular parameters of the free, adsorbed and inclusion oils in the sandstone reservoir rocks from the Dongpu Depression, Bohai Gulf Basin

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Q27-3a	0.62	0.74	0.16	0.51	0.32	0.05	0.07	0.44	0.04	0.17	0.32	0.34	38	29	33
Q27-3b	1.41	1.17	0.08	1.04	0.36	0.05	0.03	0.30	0.02	0.07	0.42	0.14	29	36	35
Q27-3c	0.48	0.55	0.12	0.98	0.35	0.10	0.07	0.42	0.03	0.22	0.33	0.44	30	37	33
Q29-5-2a	0.59	0.70	0.27	0.99	0.51	0.09	0.07	0.38	0.10	0.41	0.47	0.47	28	47	25
Q29-5-2b	1.39	1.34	0.13	0.93	0.45	0.10	0.02	0.27	0.05	0.13	0.41	0.34	31	38	31
Q29-5-2c	0.47	0.64	0.12	0.96	0.45	0.13	0.08	0.43	0.04	0.25	0.32	0.41	31	38	31
Q30-1a	0.68	0.89	0.35	0.52	0.40	0.02	0.10	0.40	0.20	0.42	0.35	0.35	47	27	26
Q30-1b	1.25	1.11	0.11	1.00	0.41	0.20	0.10	0.40	0.03	0.10	0.42	0.16	31	38	31
Q30-1c	0.46	0.58	0.14	0.93	0.42	0.15	0.09	0.44	0.06	0.28	0.29	0.46	30	38	32
Q44-1a	0.89	1.03	0.29	0.42	0.29	0.03	0.10	0.58	0.13	0.31	0.33	0.42	44	30	26
Q44-1b	1.17	1.02	0.14	0.88	0.34	0.05	0.05	0.46	0.03	0.14	0.39	0.24	33	36	31
Q44-1c	0.68	0.81	0.11	1.23	0.39	0.08	0.09	0.35	0.05	0.43	0.34	0.51	25	46	29
Q33-4a	0.72	1.12	0.34	1.19	0.75	0.13	0.19	0.68	0.12	0.77	0.42	0.47	31	29	40
Q33-4b	1.60	1.77	0.11	1.42	0.46	0.12	0.08	0.46	0.04	0.37	0.49	0.30	20	35	45
Q33-4c	0.53	0.95	0.25	1.50	0.73	0.18	0.13	0.62	0.06	0.52	0.40	0.48	19	41	40
PS4-3a	0.61	0.71	0.17	1.05	0.42	0.08	0.04	0.21	0.16	0.18	0.44	0.43	39	30	31
PS4-3b	1.88	2.12	0.10	1.07	0.44	0.10	0.07	0.27	0.06	0.19	0.41	0.45	26	37	37
B16-1a	0.61	0.36	0.67	2.26	0.92	0.42	0.71	0.22	0.57	3.05	0.46	0.70	48	22	30
B16-1b	1.45	1.18	0.13	1.69	0.41	0.21	0.09	0.27	0.08	0.42	0.42	0.46	25	38	37
B16-1c	0.58	0.43	0.12	2.05	0.46	0.36	0.16	0.23	0.08	0.45	0.46	0.50	35	38	27
Qian8-3a	0.30	0.36	0.44	1.23	1.13	0.26	0.37	0.85	0.24	1.90	0.42	0.68	41	33	26
Qian8-3b	0.63	0.56	0.17	1.65	0.79	0.28	0.14	0.47	0.08	0.70	0.53	0.47	23	47	30
Qian8-3c	0.33	0.39	0.32	2.47	0.94	0.23	0.33	0.72	0.13	1.36	0.45	0.61	34	41	25

"a": free oil; "b": adsorbed oil; "c": inclusion oil; 1: Pr/nC_{17}; 2: Ph/nC_{18}; 3: C_{23}-tricyclic terpane/(C_{23}-tricyclic terpane + C_{30}-17α(H)-hopane); 4: Ts/Tm; 5: C_{29}Ts/C_{29}-17α(H)-hopane; 6: C_{30}-17α(H)-diahopane/C_{30}-17α(H)-hopane; 7: Oleanane/C_{30}-17α(H)-hopane; 8: Gammacerane/C_{30}-17α(H)-hopane; 9: C_{21}-sterane/(C_{21} + ΣC_{29}) steranes; 10: C_{27}-diasteranes/C_{27}-regular steranes; 11: C_{29}-20S/(S + R) steranes; 12: C_{29}-$\alpha\beta\beta$/($\alpha\alpha\alpha$ + $\alpha\beta\beta$) steranes; 13: %$C_{27}\alpha\alpha\alpha$20R sterane; 14: %$C_{28}\alpha\alpha\alpha$20R sterane; 15: %$C_{29}\alpha\alpha\alpha$20R sterane; 3–8 measured on m/z 191 mass chromatograms, 9–15 measured on m/z 217 mass chromatograms.

6–15). The molecular composition of oil inclusions is actually intermediate between the free oil and adsorbed oil in the above parameters (Table 5 and Figs. 6–15). This phenomenon can be interpreted by the two reasons: (1) the first oil charge preferentially interacts with the clay minerals in the reservoir pores and as grain coatings (Pan and Yang, 2000), and (2) the maturation of these biomarkers in the inner adsorbed oil zone, which are firmly trapped between the polar components and clay surfaces, is substantially retarded due to the reduced chances to get into contact with catalysts (e.g., Rubinstein et al., 1979; Samman et al., 1981; Peng et al., 1997; Pan and Yang, 2000). Based on these parameters, the adsorbed oil appears to be more representative of the initial oil filling the reservoir than do the oil inclusions. For the samples B16-1 and Qian8-3, the notable differences in the abundances of C_{29}Ts, C_{30}-diahopane and oleanane relative to C_{29}-17α(H)-norhopane and C_{30}-17α(H)-hopane among the free and adsorbed oils and oil inclusions can be either ascribed to the compositional

variation of charging oil, or differential maturation rates or both [Table 5, Figs. 11 and 12(b), (e) and (h)].

The striking differences in the ratios of 20S/(20S + 20R) and $\alpha\beta\beta$/($\alpha\alpha\alpha$ + $\alpha\beta\beta$) C_{27}–C_{29} steranes among the free, adsorbed and inclusion oils for seven of the eight samples (except PS4-3) cannot be ascribed to a maturity difference among these three oil types, but rather to selective adsorption by clay surfaces [Table 5, Figs. 6–12(c), (f) and (i), and 14(c)] (Seifert and Moldowan, 1981, 1986). Because 20S/(20S + 20R) ratio is relatively higher while $\alpha\beta\beta$/($\alpha\alpha\alpha$ + $\alpha\beta\beta$) ratio is substantially lower in the adsorbed oil than both in the free oil and oil inclusions, the maturity variation trends suggested by these two ratios are inconsistent. The four adsorbed oils, i.e., Q27-3b, Q30-1b, Q44-1b and Q33-4b, are so rich in 5α,14α,17α(H) isomers relative to 5α,14β,17β(H) isomers that they are substantially different from any natural oil and bitumen extracted from sediments in terms of sterane distribution [Figs. 6(f) and 8–10(f)]. These results demonstrate that adsorptive

selectivity of clay surfaces between $5\alpha,14\alpha,17\alpha(H)$ and $5\alpha,14\beta,17\beta(H)$ isomers in the reservoir rocks is very strong. In contrast, the free oils B16-1a and Qian8-3a are extremely rich in $5\alpha,14\beta,17\beta(H)$ isomers relative to $5\alpha,14\alpha,17\alpha(H)$ isomers [Figs. 11 and 12(c)]. This phenomenon can be obviously accounted for by the preferential removal of $5\alpha,14\alpha,17\alpha(H)$ isomers by clay surface adsorption that leads to the relative enrichment of the $5\alpha,14\beta,17\beta(H)$ isomers during oil migration (Seifert and Moldowan, 1981). Our results are consistent with those of the studies by Seifert and Moldowan (1981, 1986). As this phenomenon was not observed in the sequential extraction studies on source rocks by Price and Clayton (1992), Sajgo et al. (1983) and Spiro (1984), and on reservoir rocks by Schwark et al. (1997) and Wilhelms et al. (1996), it is unlikely to be created by the experimental procedure of sequential extraction.

The exactly similar variation trend of the ratio of C_{27} diasteranes/C_{27} regular steranes to the ratio of $\alpha\beta\beta/(\alpha\alpha\alpha + \alpha\beta\beta)$ C_{29}-steranes between the free and adsorbed oils demonstrates that both are influenced by the adsorption/desorption selectivity of clay surfaces [Table 5, Figs. 6–13(c), (f) and 14(d)]. This is consistent with the result of the study by Seifert and Moldowan (1978).

The high ratios of Pr/nC_{17} and Ph/nC_{18} in the adsorbed oil relative to the corresponding free oil for all samples may also be ascribed to selective adsorption of the clay surfaces under the consideration that this variation trend is not observed between the oil inclusions and the corresponding free oil [Fig. 14(a)]. Selective adsorption by clay surfaces may also induce the variations of the ratios of C_{23}-tricyclic terpane/(C_{23}-tricyclic terpane + C_{30}-17$\alpha(H)$-hopane) and $C_{21}/(C_{21} + \Sigma C_{29})$ steranes and the composition of C_{27}, C_{28} and C_{29} regular steranes, between the free and adsorbed oils. However, the fractionations of these compounds were more likely created by the compositional variations of oil charges during filling process and differential maturation rates between the free and adsorbed oils as discussed earlier.

In the present study, experiments on duplicate samples were not performed to test the reproducibility of the molecular analyses. However, all the seven oil sandstones show similar variation trends in acyclic isoprenoids, terpanes and steranes among the free and adsorbed oils and oil inclusions (Figs. 6–12). Especially, the compositions of C_{27}–C_{29} regular steranes in both the free and adsorbed oils are very similar among samples Q27-3, Q30-1 and Q44-1 [Figs. 6(c) and (f), 8 and 9(c) and (f)]. The peculiar distribution pattern of C_{27}–C_{29} regular steranes ($\alpha\alpha\alpha$ and $\alpha\beta\beta$ isomers) in the adsorbed oil of these three samples excludes any possibility of contamination. Similar molecular variation trends were also observed among the free and adsorbed oils and oil inclusions of two oil sandstones from the Junggar Basin (Pan and Yang, 2000). However, in that study, the effect of

selective adsorption by the clay surfaces was not discussed and the molecular fractionations were only ascribed to the compositional variations of oil charges during filling process and differential maturation rates between the free and adsorbed oils.

Although the migration effect on saturated molecular parameters has been discussed in the early studies by Seifert and Moldowan (1978, 1981, 1986), so far, the molecular variations caused by oil migration effect have not been recognized as clearly as those of source, maturation and biodegradation effects (Peters and Moldowan, 1993), and "Geochromatography" has been, and still remains, a controversial topic (Krooss et al., 1992). In recent years, progress has been made in studies of organic nitrogen compounds as migration parameters (Yamamoto, 1992; Li et al., 1995; Larter et al., 1996). However, as the saturated biomarkers are routinely used as facies and maturity parameters (e.g., Mackenzie et al., 1980; Mackenzie, 1984; Seifert and Moldowan, 1986; Peters and Moldowan, 1993), an extensive understanding of how, and to what extent, the mineral selective adsorption of the saturated biomarkers occurs can greatly help us to properly use these parameters. We consider that the nature of the stationary phase and mobile phase is the critical point to this issue. In typical source rocks with 1–5% TOC, where the mineral surfaces are mainly covered by kerogen, the stationary phase is actually the kerogen polymer while the mobile phase is the expelled liquid oil or gaseous hydrocarbons. The compositional fractionation during primary oil migration is determined by the partition of oil components between the kerogen and expelled oil (or gaseous hydrocarbon) phases (Pepper, 1992; Sandvik et al., 1992; Leythaeuser and Poelchau, 1992). In fresh reservoir rocks, where mineral surfaces have not yet reacted with the migrating oil, the stationary phase is mineral surface while the mobile phase is oil or gaseous hydrocarbons. In reservoir rocks with high oil saturation value, the mineral surface is coated by adsorbed oil components (mainly resins and asphaltenes). The oil fractionation phenomenon resulted from geochromatography with different stationary phases, e.g., mineral surface and solid organic phase (kerogen, resin, asphaltene, pyrobitumen, etc.), seems to be characterized by the similarity in gross composition (aliphatic, aromatic and polar) and the difference in molecular compositions (e.g., Fan and Philp, 1987; Jiang et al., 1988; Sandvik et al., 1992; Pan et al., 2002). Laboratory study by Carlson and Chamberlain (1986) using a water-free montmorillonite stationary phase, indicated that the $5\alpha,14\beta,17\beta(H)$ isomers move more rapidly than do the $5\alpha,14\alpha,17\alpha(H)$ isomers of steranes. In addition, the abundance of tricyclic terpanes relative to pentacyclic terpanes and the distribution pattern of pentacyclic terpanes also greatly changed during the laboratory chromatography experiments as carried out by Fan and
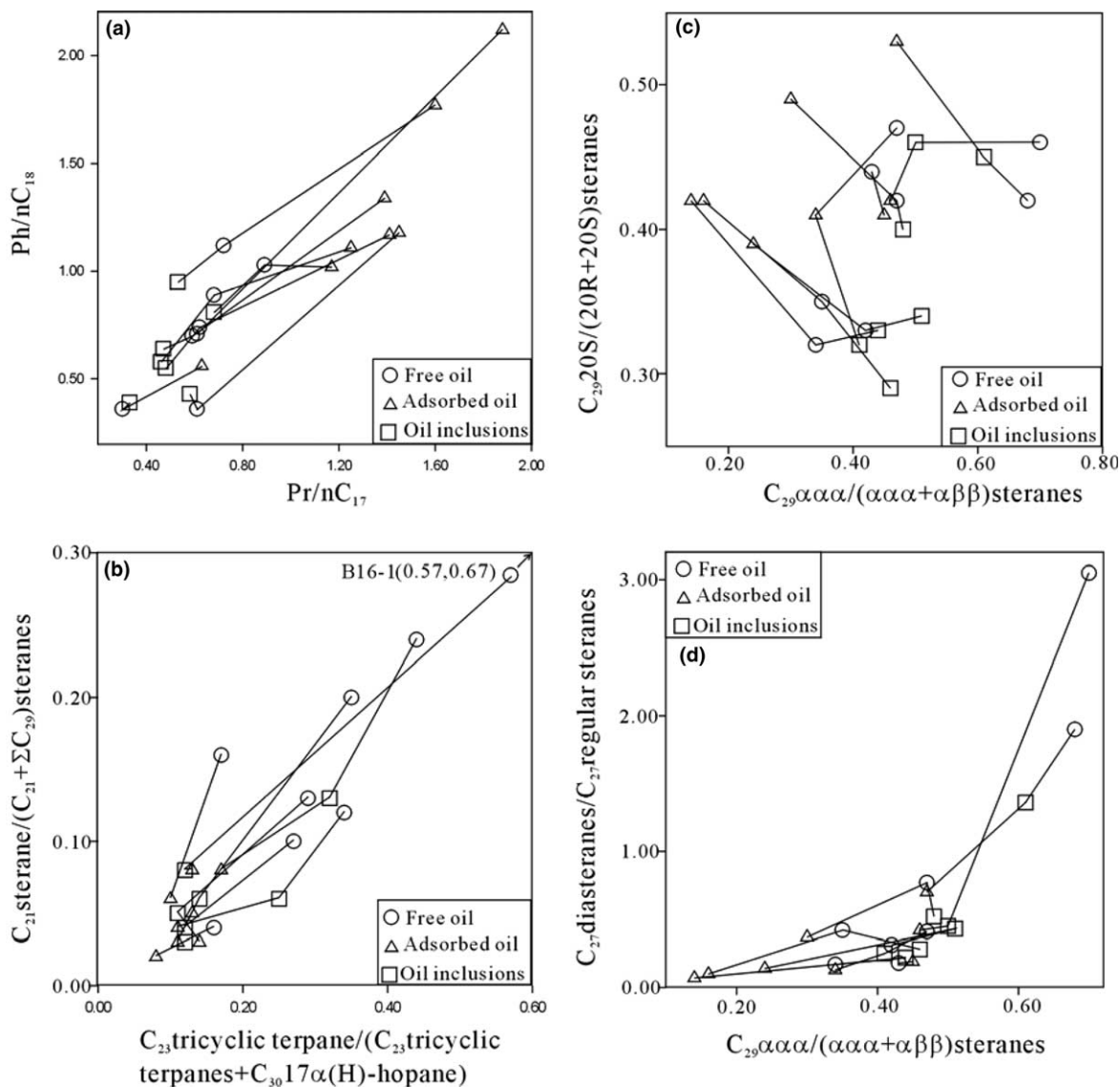
Fig. 14. Crossplots of molecular parameters for the free and adsorbed oils and oil inclusions. (a) Crossplot of the ratios of Pr/nC_{17} versus Ph/nC_{18}; (b) crossplot of the ratios of C_{23}-tricyclic terpane/(C_{23}-tricyclic terpane + C_{30}-17α(H)-hopane) versus C_{21}-sterane/(C_{21} + ΣC_{29}) steranes; (c) crossplot of the ratios of αββ/(αΣα + αββ) versus 20S/(S + R) C_{29} steranes; (d) crossplot of the ratios of αββ/(ααα + αββ)C_{29} steranes versus C_{27} diasteranes/C_{27} regular steranes.

Philp (1987) and by Jiang et al. (1988). However, the fractionation of pentacyclic terpanes was neither observed in the present study, nor in the studies by Seifert and Moldowan (1978, 1981, 1986). In natural reservoir rocks, the stationary phase is actually the mineral surface with water film while the mobile phase is the oil. In the laboratory experiments performed by Fan and Philp (1987) and by Jiang et al. (1988), the stationary phase was water-free alumina while the mobile phase was non-polar pentane. The different fractionation phe-

nomenon between these laboratory experiments and in the natural reservoirs observed by Seifert and Moldowan (1981), and revealed in the present study, could be ascribed to the nature of both the stationary and mobile phases.

The laboratory experimental study by Carlson and Chamberlain (1986) indicated that the presence of only small quantities of water practically eliminates any molecular fractionation effects of saturated hydrocarbons. Krooss et al. (1992) believed that chromato-
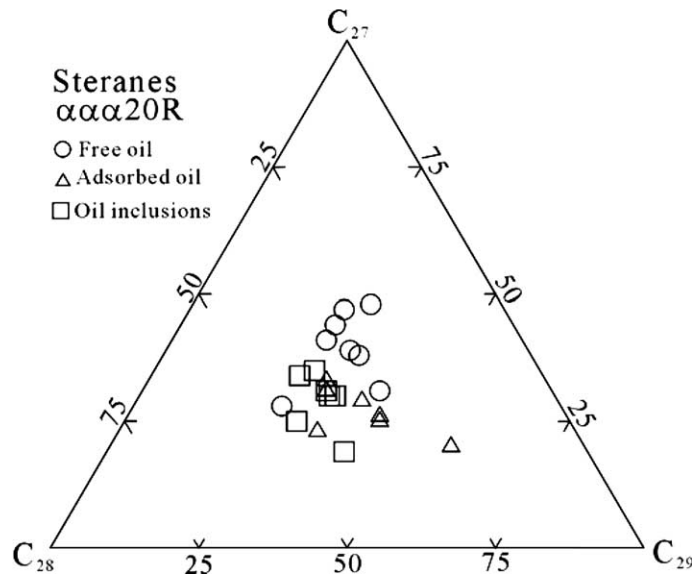
Fig. 15. Ternary diagram of C_{27}, C_{28} and C_{29} sterane composition for the free and adsorbed oils and oil inclusions.

Table 6
Current reservoir temperatures and homogenization temperatures of oil-bearing fluid inclusions in the oil sandstones

Sample	Depth (m)	Current temperature (°C)	Range of Th (°C)	Measured Th (°C)
Q27-3	2497.2	96.4	94.5–105.0	94.5, 96.5, 97.0, 97.5, 105.0
Q29-5-2	2509.6	96.8	82.8–89.8	82.8, 83.1, 84.5, 87.6, 89.1, 87.0, 89.8
Q30-1	2554.2	98.3	86.0–106.1	86.0, 88.0, 102.5, 106.1, 105.8, 88.3, 90.3, 88.4, 89.1, 95.0, 103.4
Q44-1	2960.3	111.7	85.0	85.0
Q33-4	3695.4	135.9	88.0–96.6	88.0, 92.0, 96.6
B16-1	3908.9	143.0	78.6–95.0	78.6, 80.7, 82, 82.9, 79.6, 86.8, 87.2, 88.0, 92.0, 90.5, 95.0
PS4-4[a]	4078.5	148.6	92.0–94.0	92.0, 94.0
Qian8-3	4044.5	147.5	72.3–74.7	72.3, 74.7, 74.5

[a] An oil sandstone collected from the same well as PS4-3.

graphic processes in nature (water wet) systems involving liquid mobile hydrocarbon phase can result only in compound class fractionation (saturates, aromatics and polars) whereas molecular fractionation may be expected to occur with a gaseous mobile phase, involving gas/solid or gas/liquid partitioning. This point of view is obviously inconsistent with the result of the present study. As indicated by the ratio of C_{29} $\alpha\beta\beta/(\alpha\alpha\alpha + \alpha\beta\beta)$ steranes, strong molecular fractionation effects of saturated hydrocarbon can be observed between the free oil and adsorbed oil for the seven oil reservoir sandstones but not observed for a gas reservoir sandstone in our study.

In a natural reservoir, the saturated compounds themselves would rarely have the chance to encounter the mineral surfaces with the presence of water due to their affinities. However, the polar compounds (resins and asphaltenes) in oil phase could replace the water film and react with mineral surfaces (Larter and Aplin, 1995). Saturated hydrocarbons could be sorbed by the large resins and asphaltenes, and then, attached onto the mineral surfaces along with these polar components. However, the partition of saturated biomarker compounds between the large polar compound phase and oil phase is unable to account for the fractionation of these biomarkers between the free oil and adsorbed oil obtained from the clay surfaces. As indicated in our recent study on sequential extraction of precipitated asphaltenes, no significant variation in the ratio of $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ regular steranes between the free and asphaltene-sorbed hydrocarbons was observed (Pan et al., 2002). The sequential studies on source rocks by

Sajgo et al. (1983) and by Price and Clayton (1992) and on reservoir rocks by Wilhelms et al. (1996) also show little change in this ratio between the "coarse extract" and "fine extract", or among the first extract and the latter extracts. The preferential sorption of $5\alpha,14\alpha,17\alpha(H)$ isomers over $5\alpha,14\beta,17\beta(H)$ isomers of regular steranes and of C_{27} regular steranes over C_{27} diasteranes onto the clay surfaces as revealed in the present study could be ascribed to the joint effect of the polar components and the active clay surfaces during the interaction of oil phase and clay surfaces.

The exception of sample PS4-3 to the other analyzed samples in the fractionation behavior of the ratios of $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ C_{29}-steranes and C_{27}-diasteranes/C_{27} regular steranes between the free and adsorbed oils can be due to the fact that this sample was collected from a gas reservoir while the other seven were from oil reservoirs. For PS4-3, the adsorbed organic layer coating the clay surfaces actually formed from the interaction of water phase and clay surfaces. Those organic components had been mainly partitioned in the water phase, rather than in the gaseous phase before they were adsorbed onto the clay surfaces. This sample apparently has never been charged with a liquid oil phase because both the amounts of the free and adsorbed oils are too low and no oil-bearing fluid inclusions were observed in this sample. However, the aforementioned sandstone PS4-4 (Table 6), 300 m below PS4-3, contains a high amount of free oil (about 800 mg extracted from 100 g grains), and abundant oil-bearing fluid inclusions, indicating oil charging. In an oil reservoir, the reservoir water contains abundant oil components, especially polar compounds, which are dissolved or occur as colloids in water (cf. Larter and Aplin, 1995). For the other seven oil sandstones, the adsorbed organic layer obviously formed mainly from the interaction between oil phase and clay surface. Furthermore, both the amounts of the free and adsorbed oils in PS4-3 are so small in comparison to the other samples that the indigenous organic matter may have a significant effect on the sterane distributions in both the free and adsorbed oils.

5. Conclusions

The free and adsorbed oils obtained from the clay fraction (<2 μm) separated from eight hydrocarbon reservoir sandstones and oil-bearing fluid inclusions obtained from the isolated grains of seven of these eight samples collected from Dongpu Depression, Bohai Gulf Basin, China, exhibit substantial differences both in gross and molecular compositions.

Among the eight samples, the amount of the adsorbed oil (0.18–7.84 mg/g clay) is correlated closely with that of the free oil (1.22–94.97 mg/g clay). The free oil contains mainly saturated hydrocarbons (61.4–87.5%) with a low content of resins and asphaltenes (6.0–22.0% in total). However, the adsorbed oil is dominated by resins and asphaltenes (84.8–98.5% in total) with a low content of saturated hydrocarbons (0.6–9.5%). The oil inclusions in the seven samples are similar to the adsorbed oils in gross composition, but contain relatively more saturated hydrocarbons (16.87–31.88%) and less resins and asphaltenes (62.30–78.01% in total).

Although both the amounts of the free and adsorbed oils vary substantially, the organic carbon content of the clay minerals in this size range after the free oil extraction varies in a narrow range between 0.537% and 1.614% for the eight samples in this study, and is in the range between 0.805% and 1.292% for six of them. The percentage of the extractable to the total of this residual organic matter of the clay minerals is significantly higher for four shallow-buried samples (i.e., Q27-3, Q29-5-2, Q30-1 and Q44-1 with the burial depth varying from 2497.2 to 2960 m, ranging 33.6–63.8%), than four deep-buried ones (i.e., B16-1, PS4-3, Q33-4 and Qian8-3 with burial depth varying from 3695.4 to 4044.5 m, ranging 2.8–14.4%). These results suggest that extensive transformation (condensation) of the adsorbed polar components into insoluble macro pyrobitumens occurred for the four deep-buried samples due to temperature increase after oil filling.

The variation trends of terpane and sterane parameters among the free oil, adsorbed oil and oil inclusions from the same sample suggest that the adsorbed oil on the clay surfaces appears to be more representative of the initial oil charging the reservoir than do the oil inclusions. This phenomenon may result from the first oil charge preferentially interacting with the clay minerals occurring in the pores and as coatings around the grains, and/or to the severe retardation of the maturation of these biomarkers in the adsorbed oil during burial of the reservoir after oil filling.

The ratio of $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ regular steranes is substantially lower in the adsorbed oil than the corresponding free oil and oil inclusions for the seven oil sandstones analyzed. Especially for the adsorbed oils Q27-3b, Q30-1b, Q33-4b and Q44-1b, the regular steranes are overwhelmingly the $5\alpha,14\alpha,17\alpha(H)$ isomers. This result is strong evidence favoring the selective adsorption by clay surfaces (Seifert and Moldowan, 1981, 1986). The preferential sorption of $5\alpha,14\alpha,17\alpha(H)$ isomers by clay surfaces leads to the particular enrichment of $5\alpha,14\beta,17\beta(H)$ isomers in the free oils B16-1a and Qian8-3a. The ratio of C_{27} diasteranes/C_{27} regular steranes also exhibits similar fractionation effects. The fractionation of these two ratios between the free oil and the adsorbed oil could be ascribed to the joint effect of the polar components and the active clay surfaces during the interaction of oil phase and clay surfaces.

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