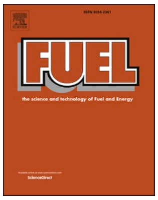
Fuel 381 (2025) 133732

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

Molecular characterization of condensates altered by thermochemical sulfate reduction and evaporative fractionation using high-resolution mass spectrometry

Dongyong Wang [a,b,c], Jianfa Chen [a,d], Meijun Li [a,b,d,*], Jianxun Wu [e,*], Quan Shi [e], Wenqiang Wang [f], Shuofan Li [e], Zichao Ran [a,d], Zi'ao Geng [a,d], Xin Wang [a,d], Huiqiang Qin [a,d], Xianli Zou [b], Sajjad Ali [a,d]

[a] *State Key Laboratory of Petroleum Resources and Engineering, China University of Petroleum (Beijing), Beijing 102249, China*
[b] *Faculty of Petroleum, China University of Petroleum-Beijing at Karamay, Xinjiang 834000, China*
[c] *University of Alberta, Edmonton, Alberta T6G 2R3, Canada*
[d] *College of Geosciences, China University of Petroleum (Beijing), Beijing 102249, China*
[e] *State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering and Environment, China University of Petroleum (Beijing), Beijing 102249, China*
[f] *School of Earth and Engineering, Xi'an Shiyou University, Shanxi 710065, China*

ARTICLE INFO

Keywords:
Condensate
High resolution mass spectrometry
Organosulfur compounds
Thermochemical sulfate reduction
Evaporative fractionation
Secondary alteration

ABSTRACT

Conventional biomarkers are least available for the origin and formation mechanism investigation in condensates due to their extremely low concentrations. Heteroatomic compounds in condensates can provide unique insights for their origin and formation, but these compounds are with the low separation ability by conventional mass spectrometry tools. They can be characterized with the advance of the high-resolution mass spectrometry, but few study focuses on the altered condensate oil and their molecular-level compositions. In this study, a total of 19 condensates are analyzed to study the effects of thermochemical sulfate reduction and evaporative fractionation on the changes of molecular compositions characterized by Orbitrap mass spectrometry. The results show that thermochemical sulfate reduction (TSR) make the oils considerably enriched in S_1 species (sulfur-containing compounds with one sulfur atom) (>90 %) and depleted in CH_2s species (hydrocarbons compounds) (<3%) relative to the non-TSR altered oils due to the consumption of hydrocarbon and yield of sulfur-containing compounds. Relatively abundant S_1 species with low DBE (Double Bond Equivalent) values (0–3) likely corresponding to thiols and thioethers in TSR-altered oils. However, the relative abundance of CH_2s species in the oils undergoing evaporative fraction are much higher than that in non-evaporative fraction altered oils leading by the strong solubility of hydrocarbon in gas. Therefore, the relative contents of heteroatomic compounds are significant for the TSR alteration and evaporative fraction definition of condensates and their origin investigation.

1. Introduction

Condensate oils are defined as hydrocarbon present as gas state in subsurface and would be transitioned into liquid state in the surface due to the decrease of temperature and pressure [1]. These hydrocarbons are mainly composed of low molecular weight (C_5–C_{11}) compounds [2] and therefore, considered as a kind of high-quality petroleum resource. Two types of condensate oil reservoirs, i.e., primary and secondary reservoirs, occur in sediment basin, where condensate oil in primary reservoir are directly generated from kerogen in the high mature stage [3,4] and that in secondary reservoir generally undergo the secondary alterations [5], e.g., thermochemical sulfate reduction (TSR) [6], evaporative fractionation [7,8] and thermal cracking [9,10].

TSR involves a complex set of redox reactions between sulfates and petroleum, which generally occur in deep carbonate or evaporite reservoirs with high temperature (>120 °C) [11]. The reaction is firstly triggered by the formation of contact ion-pair destabilizing the sulfate tetrahedron and is further promoted by H_2S [6,12,13]. This process is considered to be autocatalytic due to the yield of H_2S with ongoing TSR reaction, which can promote the formation of bisulfate and/or contact

---

* Corresponding authors at: 18 Fuxue Road, Changping District, Beijing 102249, China.
E-mail addresses: meijunli@cup.edu.cn (M. Li), wjx@cup.edu.cn (J. Wu).

https://doi.org/10.1016/j.fuel.2024.133732
Received 29 July 2024; Received in revised form 25 October 2024; Accepted 10 November 2024

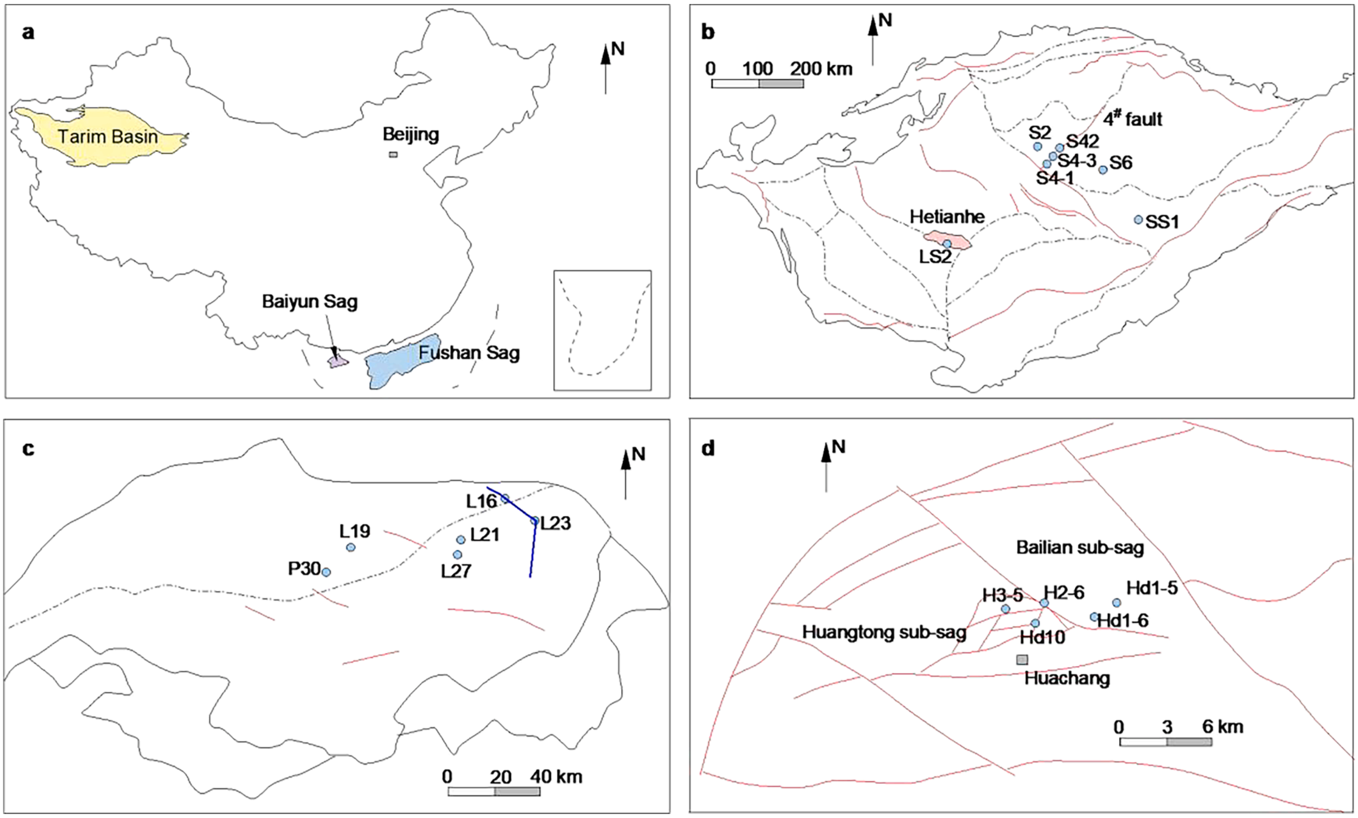


Fig. 1. (a) The locations of studied basin and tectonic sketch maps of (b) the Tarim Basin, (c) the Baiyun Sag in the Pearl River Mouth Basin, and (d) the Fushan Sag in the Beibuwan Basin.

ion pairs accelerating the reaction [6,11,14,15]. H_2S can also be produced from the thermal cracking of labile sulfur-containing compounds [16] and, therefore, the rate of TSR reaction is attributed to the hydrocarbon composition [12,15]. TSR alteration can be understood as a disproportionation reaction briefly in this process, whereby petroleum could be oxidized to two parts [17], i.e., condensates composed of light hydrocarbons and TSR-altered solid bitumens composed of heavy compositions, respectively. On the one hand, TSR alteration make oils enriched in lighter more volatile hydrocarbons [18–20] with high API gravity due to the high reservoir temperatures, which forms secondary condensate oil reservoirs [20]. On the other hand, with the ongoing thermal and TSR-induced process, other residual materials constitute solid bitumens [14,21,22], which are characterized by high concentrations of insoluble compositions, high reflectivity (>1.5 %Ro), high content of thiophenic sulfur with highly aromatic [23,24].

Another category of secondary condensate oil reservoirs is related to the evaporative fractionation alteration [7,25,26], which have been found in several areas and sediment basins around the globe, such as the Gulf of Suez [27], Eastern Carpathians of Poland [28], North Java Basin of Indonesia [29], Barrandian Basin of Czech Republic [30], Sinai Basin of Egypt [31], Lungu area in the Tarim Baisn [32], Baiyun Sag in the Pearl River Mouth Basin [33,34] and Xihu Sag in the East China Sea Basin of China [35]. Natural gas can invade into the early primary oil pools and carry light hydrocarbons easily dissolved into gas [7,8]. Fractionation would occur if the stratal erosion- or fault-initiated pressure releases within reservoirs, in which oils will be separated from the carrier and accumulate to form a secondary condensate oil reservoir [5]. In that process, the aromaticity and normality of oil increase while the paraffinicity decrease [8].

The study of sulfur-containing compounds in condensates is limited to volatile compositions using the gas chromatographic in previous reports due to the low separation ability [24]. The characterizations of organic sulfur compounds of heavy fractions in a molecular level are advanced with the introduction of high-resolution mass spectrometry, e.g., Fourier transform–ion cyclotron resonance mass spectrometry and Orbitrap mass spectrometry, to petroleum geology and geochemistry [36–39]. Li et al. (2011) showed that oils from Lower Ordovician reservoirs of Tazhong Uplift in Tarim Basin with high concentrations of dibenzothiophene may be led by the TSR alteration [40]. Purcell et al. (2006) indicated that APPI (atmospheric pressure photoionization ionization) ion source is helpful for the ionization of organosulfur species in oil, although the method is unavailable for the non-aromatic compounds [41]. Using this approach, in TSR-altered oils, Walters et al. (2001, 2015) Walters et al. (2001, 2015) observed a series of highly condensed polynuclear aromatic and naphthenoaromatic compounds containing 0–3 sulfur atoms, which was defined as TSR-altered proto-solid bitumen species [23,24]. Relatively abundant and unstable sulfur-containing compounds such as thiols and thiadiamondoids have been identified in condensate oils from Tazhong area, Tarim Basin, which indicates those oils are altered by TSR in various degrees [42–44].

In this study, using high resolution mass spectrometry, the heteroatomic compounds distributions in 19 condensate oils, including 7 samples from the Shunbei area of the Tarim Basin, 6 samples from Baiyun Sag of the Pearl River Mouth Basin and 6 samples from Fushan Sag of the Beibuwan Basin, were investigated, and further their origin are discussed.

2. Geological setting

The Tarim Basin is a significant petroliferous basin in the northwestern China (Fig. 1a) and its petroleum geological characterization has been reported in previous study [45–47]. Recently, a large of petroleum resources has been discovered in the deep-buried Ordovician reservoir with a depth over 8000 m [48–50]. The source rocks of those oils are mainly Cambrian-Lower Ordovician mudstone [49,51]. The oils discovered in the southern part of No.4 fault zone, e.g., wells S42, S4-1

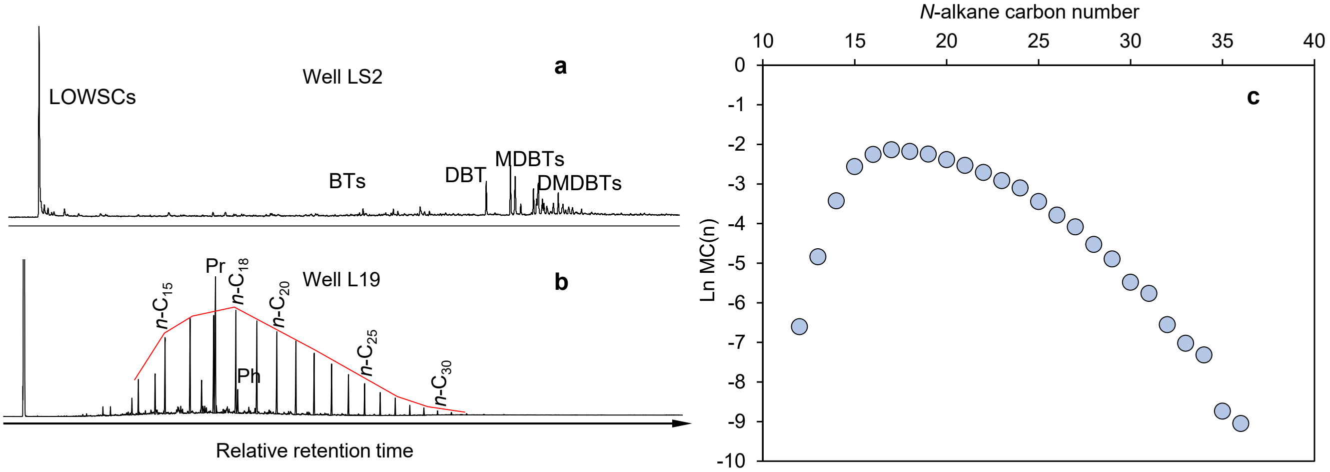


Fig. 2. (a) GC-SCD chromatogram of LS2 oil from the Tarim Basin showing the distribution of organosulfur compounds; (b) GC-FID chromatogram of L19 oil from the Baiyun Sag (Pearl River Mouth Basin, PRMB) showing the distributions of *n*-alkanes; and (c) *n*-alkane mass molar concentration depletion of condensate from Well L19 in the Baiyun Sag. LOWSCs: low molecule weight organosulfur compounds; BTs: benzothiophenes; DBT: dibenzothiophene; MDBTs: methyldibenzothiophenes; DMDBTs: dimethyldibenzothiophenes; Pr: pristane; Ph: phytane; MC(*n*): the molar contents of *n*-alkanes.

and S4-3, have been shown that they undergone a TSR reaction [52], which is likely responsible for high abundances of dibenzothiophene and thiadiamondoids in those oils [53–55]. However, other oils, like S2 oil from No.2, S6 oil from No.6 fault zones and SN1 oil from the Shunnan area are primary condensates without TSR or other secondary alterations. The origin of LS2 oil from the Hetianhe area has been fully investigated based on the compositional, molecular biomarker and isotope data in previous study [56,57]. TSR alteration has been considered to be an accepted reason for the high content of H_2S, high abundance of dibenzothiophene, high content of thiadiamondoid series compounds in the LS2 oil [42,58]. Moreover, those oil is characterized by a high content of organosulfur compounds with low molecule weight (Fig. 2a), which may correspond to thiol, thioether, thiophene series.

The Baiyun Sag, one of the most important petroliferous area in the South China Sea, is located in the northern part of the Pearl River Mouth Basin (Fig. 1a). In recent years, a major exploration breakthrough of condensate and natural gas has been made in this area [59]. The Wenchang, Enping, and Zhuhai formations are considered to be the source rocks for the discovered oil, especially Enping Formation [60–62]. The Zhuhai and Zhujiang formations are the favorite zones for the petroleum accumulation. Late Miocene mudstones, overlaying the main reservoir, play a key role in preventing the leak of petroleum. Several previous reports have been shown that the most oils discovered in the Baiyun Sag undergone varying degrees of gas invasion and evaporation fraction [34,63,64]. For example, the distribution of *n*-alkanes the L19 oil in the northern part of the Baiyun Sag (Fig. 1c), has a maximum at *n*-C_{18} (Fig. 2b). The contents of *n*-alkanes under *n*-C_{18} have a loss and the depletion of *n*-alkanes is over 70 % based on the relationship between the logarithm of molar abundance and carbon numbers of *n*-alkanes (Fig. 2c).

The Fushan Sag is one of the numerous Mesozoic–Cenozoic rifting half-grabens developed in the northern continental shelf of the South China Sea [65]. Major oil pools mainly were discovered in the first and third members of the Eocene Liushagang Formation [66,67]. Those oils are predominant by light oils or condensates with a mean of gravity of 47° (API) [68,69]. They are sourced from the second member of the Eocene Liushagang Formation characterized by type II and III kerogens with an input of terrestrial organic matter in the high-mature stage [70]. They are not changed by any secondary alteration and are considered to be primary lacustrine condensate.

Table 1
Relative contents (%) of major compounds in the selected oil samples.

Area	Alteration	Well	TAs/Q	CH_2s	S_1	N_1	S_1	O_1S_1	S_2	O_1S_2	N_1O_1	N_1S_1
Tarim	TSR	LS2	192[a]	0.06	93.58	0.07	93.58	0.65	5.62	0.03	0.00	0.00
	TSR	S4-1	/	1.43	97.75	0.27	97.75	0.35	0.05	0.00	0.15	0.00
	TSR	S42	37.2[b]	1.32	98.30	0.07	98.30	0.14	0.04	0.00	0.12	0.00
	TSR	S4-3	/	0.00	99.77	0.02	99.77	0.13	0.08	0.00	0.00	0.00
	Primary marine	S6	/	48.81	45.64	1.17	45.64	0.72	0.00	0.00	3.66	0.00
	Primary marine	SS1	/	29.96	57.72	6.69	57.72	2.27	0.11	0.00	3.22	0.02
	Primary marine	S21	/	70.24	24.19	1.00	24.19	2.33	0.00	0.00	2.24	0.00
Baiyun	Evaporative fractionation	L19	92.12	0.60	45.78	33.81	45.78	9.68	0.09	0.00	9.92	0.12
	Evaporative fractionation	P30	85.63	24.92	41.89	22.45	41.89	5.59	0.32	0.00	0.00	0.05
	Evaporative fractionation	L23	33.63	22.44	44.66	22.27	44.66	5.10	0.09	0.00	5.23	0.21
	Evaporative fractionation	L21	26.35	1.36	41.88	40.81	41.88	10.46	0.00	0.00	5.13	0.36
	Evaporative fractionation	L16	35.64	12.92	46.61	35.51	46.61	4.46	0.00	0.00	0.36	0.13
	Evaporative fractionation	L27	14.23	39.09	32.93	19.43	32.93	4.78	0.27	0.00	3.33	0.05
Fushan	Primary lacustrine	H10	/	8.60	63.59	24.52	63.59	2.33	0.00	0.00	0.83	0.13
	Primary lacustrine	H2-16	/	6.67	67.65	23.12	67.65	1.90	0.00	0.00	0.50	0.17
	Primary lacustrine	H3-5	/	3.25	68.15	24.71	68.15	1.48	0.00	0.00	1.80	0.60
	Primary lacustrine	HD1-6	/	7.83	75.66	12.33	75.66	2.68	0.00	0.00	1.17	0.34
	Primary lacustrine	H2-6	/	7.93	66.77	22.67	66.77	1.35	0.00	0.00	1.28	0.00
	Primary lacustrine	HD1-5	/	3.67	70.86	20.11	70.86	3.04	0.00	0.00	1.57	0.75

Note: /: No data; [a] from reference [52]; [b] from reference [56]; TAs: total thiaadamantanes for TSR-altered oil; Q: the depletion of *n*-alkanes for oils with evaporative fractionation.

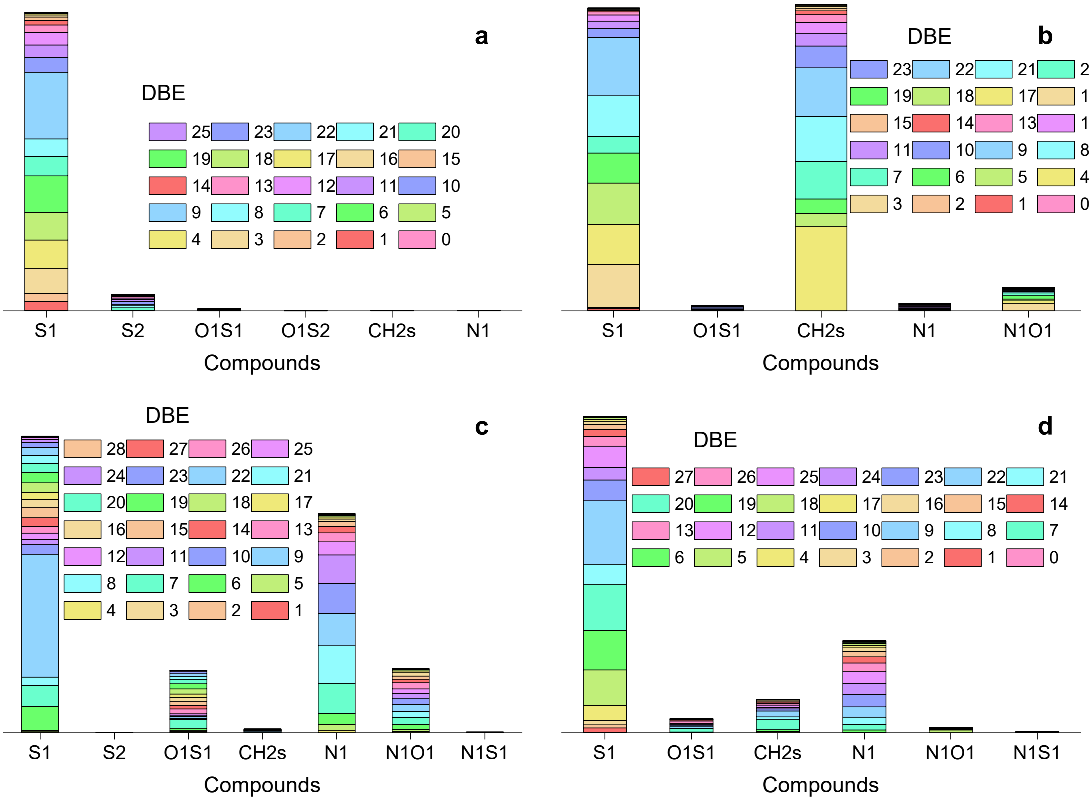


Fig. 3. Histograms showing the relative abundances of major compounds in wells (a) LS2 from the Tarim Basin; (b) S6 from the Tarim Basin; (c) L19 from the Baiyun Sag (PRMB); and (d) H10 from the Fushan Sag (Beibuwan Basin). DBE: Double Bond Equivalent.

3. Samples and experiments

3.1. Samples

A total of 19 condensate samples were collected in this work (Fig. 1). Among those, seven condensates were from the Tarim Basin, including the LS2 oil from the Hetianhe area, S2, S4-1, S42, S4-3 and S6 oils from the Shunbei area, and SS1 oil from Shunnan area (Fig. 1b). Among those oils, the contents of total thiaadamantanes in LS2 and S42 oils are much higher than the threshold in TSR-altered oils (>20 μg/g), and they have been considered to undergo TSR alterations [52]. The locations of S4-1 and S4-3 oils are just close to that of the S42 oil (Fig. 1b) and with similar molecular and isotopic compositions, which thought to have been also altered TSR. Six condensates were sampled from Panyu and Liuhua area in the Baiyun Sag (Fig. 1c). Based on the computations by Thompson et al. (1988) [7], the depletion of *n*-alkanes in those oils was listed in Table 1, indicating that those oil has experienced strong gas invasion and evaporative fractionation. Other six samples were from the Huchang oilfield in the Fushan Sag (Fig. 1d).

3.2. Methylation

Approximately 100 mg oil sample was dissolved in 1 mL dichloromethane. About 0.5 g $AgBF_4$ and 1.0 g MeI were added into the above dichloromethane solution, which was stirred in dark space for 24 h to convert the sulfur-containing compounds to sulfonium salts.

3.3. Orbitrap MS analysis

The oil samples methylated to sulfonium salts were carried out positive-ion ESI Orbitrap Fusion MS (made by Thermo Scientific, America) analysis. The cumulative number of ions was about 500,000 within a cumulative time of 100 ms. The scan mass range was between 100–800 Da. The methylated samples were dissolved in toluene/MeOH (1:3, v/v) to about 0.2 mg/mL, which were then injected into ESI by an automatic peristaltic pump with a rate of 3 μL/min. The positive ion spray voltage was 3600 kV. The flow rates of sheath gas, auxiliary and sweep gas were 5, 2 and 0.1 arbitrary units, respectively.

4. Results and discussion

4.1. Major compounds

Major compound species in the selected condensates are similar but their contents are distinctly various (Fig. 3). In the TSR-altered oils, sulfur-containing compounds with one sulfur atom are dominated (Fig. 3a), whose relative abundances are over 90 % with an average of 93.75 %. The relative abundances of S_2 (sulfur-containing compounds with two sulfur atoms) and O_1S_1 (heteroatomic compounds with one sulfur atom and one oxygen atom) species have a mean of 4.15 % and 0.32 % respectively. The total contents of other compounds classes including O_1S_2 (heteroatomic compounds with two sulfur atoms and one oxygen atom), CH_2s (hydrocarbon compounds) and N_1 (nitrogen-containing compounds with one nitrogen atom) species contents are less than 2 %. In non-TSR altered oil in the same area, S_1 and CH_2s species are predominant (Fig. 3b) and their relative contents are in a range of 24.19–57.72 % (an average of 42.51 %) and 29.96–70.24 % (an average of 49.67 %), respectively. In well L19, as an oil example experienced evaporative fractionation alteration, the relative abundance of S_1 species is highest (Fig. 3c) and in a range between 32.93–46.61 % with an average of 42.29 %, followed by those of N_1 species ranging from 19.43–40.81 % with an average of 29.05 %. Those oils have O_1S_1 and N_1O_1 (heteroatomic compounds with one nitrogen atoms and one oxygen atom) species between 4.46–10.46 % and 0.00–9.92 % respectively, but have little S_2, CH_2s and N_1S_1 species (<1.0 %). The Fushan oil samples, representing as the primary condensate from kerogen in the

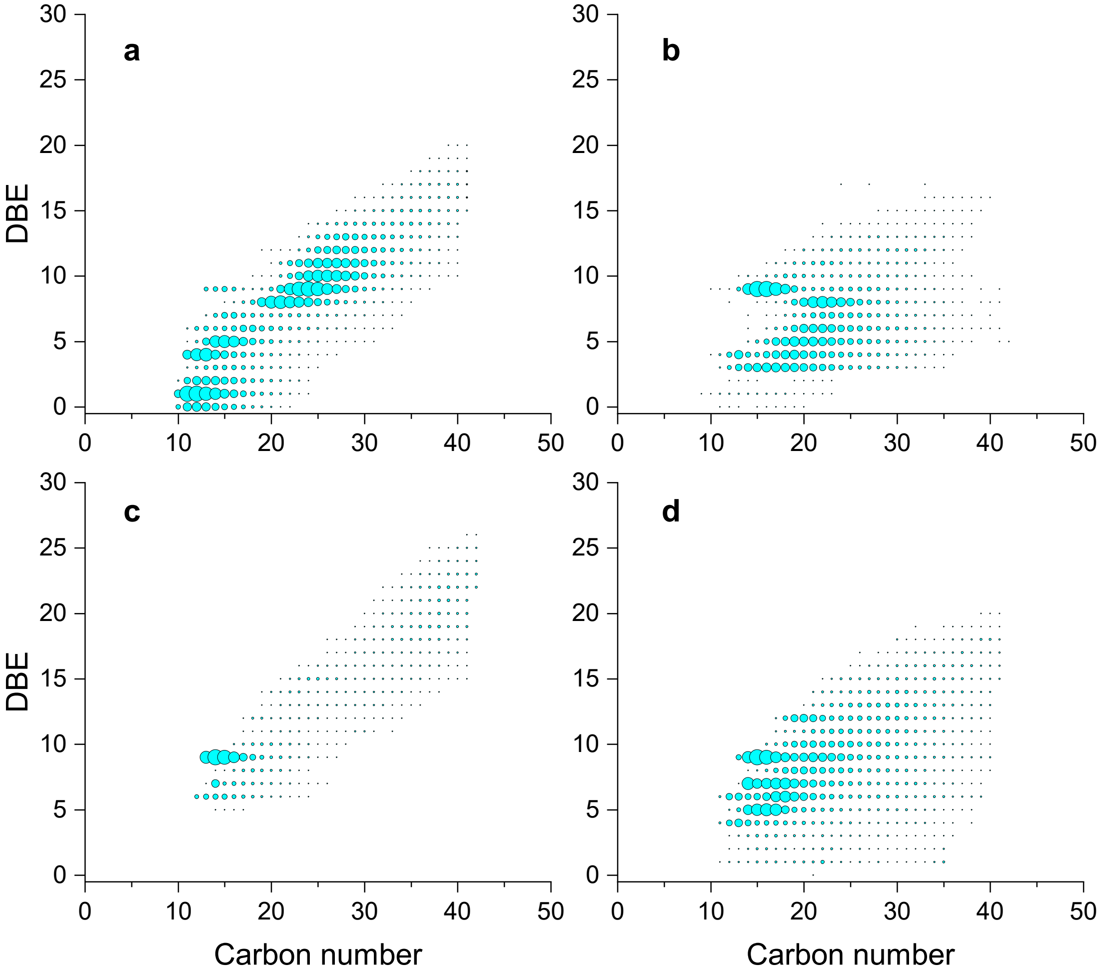


Fig. 4. Cross plots of DBE and carbon number showing the relative abundance of S_1 species in wells (a) LS2 from the Tarim Basin; (b) S6 from the Tarim Basin; (c) L19 from the Baiyun Sag (PRMB); and (d) H10 from the Fushan Sag (Beibuwan Basin).

high mature stage, are characterized by high contents of S_1 and N_1 species (Fig. 3d), falling into a range of 63.59–75.66 % and 12.33–24.71 % respectively, and contain a mean of 6.32 % CH_2s species, 2.13 % O_1S_1 species and 1.19 % N_1O_1 species.

By combination with the primary marine S6 oil (Fig. 3b), the TSR-altered LS2 oil has very low CH_2s species contents and absolute predominance of S_1 species (Fig. 3a), which is attributed to the generation of sulfur-containing compounds. Moreover, the DBE and carbon number distributions of each class in TSR and non-TSR altered oils are also various which would be detailedly discussed in the following contents. The relative abundances of S_1 species in L19 oil with evaporative fractionation is lower than that in primary lacustrine H10 oil, while the CH_2s and N_1 species contents shows the opposite trend (Fig. 3). The relative contents of nitrogen-containing compounds in LS2 and S6 oils are much lower than that in L19 and H10 oils likely ascribed to the different organic matter source, where the former is marine [49,51] and the latter is lacustrine [60,66]. The heteroatomic compounds compositions of LS2 and H10 oils appear to be similar, especially with high contents of S_1 species. Based on the previous reports [65–67], it seems to commonly acknowledge that the oils in the Fushan Sag is primary and without any secondary alterations. Given the geological considerations, an insufficient sulfur was present in the Fushan Sag, where the clastic rocks were well developed and the anhydrite or H_2S is very little [67]. This condition limited the TSR reaction. The high contents of S_1 species present in the Fushan oils is mainly due to a high maturity.

4.2. *S_1 species*

Fig. 4 illustrates the cross-plots of DBE and carbon number showing the relative contents of S_1 species in condensates with different secondary alteration. The highly abundant S_1 species with low DBE = 0 and 3, corresponding to thiol and thiaadamantane respectively [42], occur in the TSR-altered oil, which also contains high abundant S_1 species with DBE = 8–13 referring to thiophenes compounds (Fig. 3a). In the non-TSR altered condensate from well S6, the most abundant S_1 species are dibenzothiophene (DBE = 9) followed by DBE values of 5–8 corresponding to the dicyclic sulfides [37]. The S_1 species with low DBE values of 0–3 is minor in those samples (Fig. 4b). The crude oil from well L19 experienced by evaporative fraction is characterized by the highest abundance of dibenzothiophene that is S_1 species with DBE = 9 and hardly contains other lower members of the series compounds. However, a set of highly concentrated S_1 species with high DBE values (21–28) and carbon numbers (>40) present in those oils (Fig. 4c). The main sulfur-containing compounds in the oil from well H10, an example for condensate generated from kerogen, are benzothiophenes (DBE = 6), dibenzothiophenes (DBE = 9) and benzothiophenes (DBE = 12) containing carbon numbers ranging from 12 to 40 (Fig. 4d). The S_1 species with low DBE values (1–3) and S_1O_1, S_2 species in TSR-altered oil are more distinctly abundant than that in non-altered oil (Fig. 3a-b), which is contributed from the introduction of inorganic sulfur and generation of organic sulfur compounds as TSR reactions proceed.

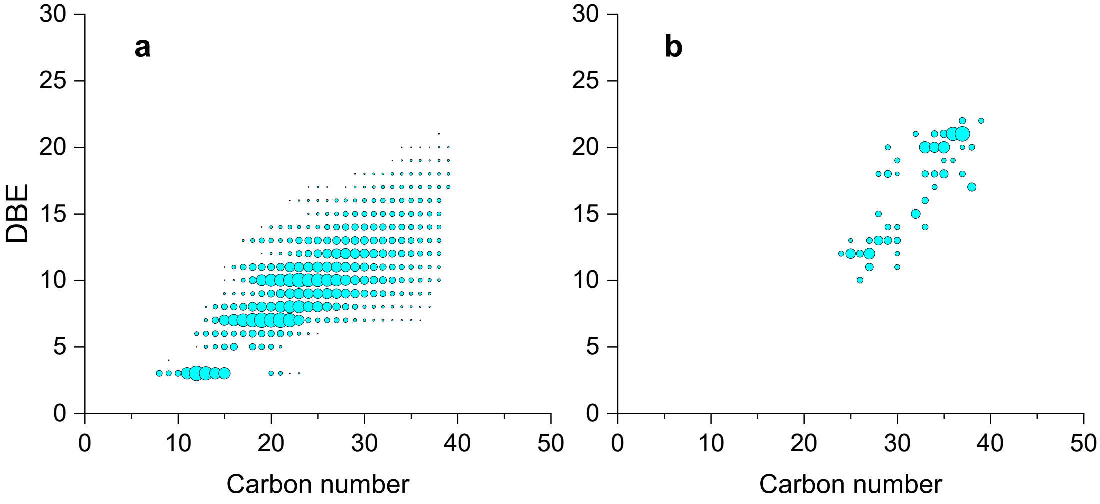


Fig. 5. Cross plots of DBE and carbon number showing the relative abundance of S_2 species in wells (a) LS2 from the Tarim Basin and (b) L19 from the Baiyun Sag (PRMB).

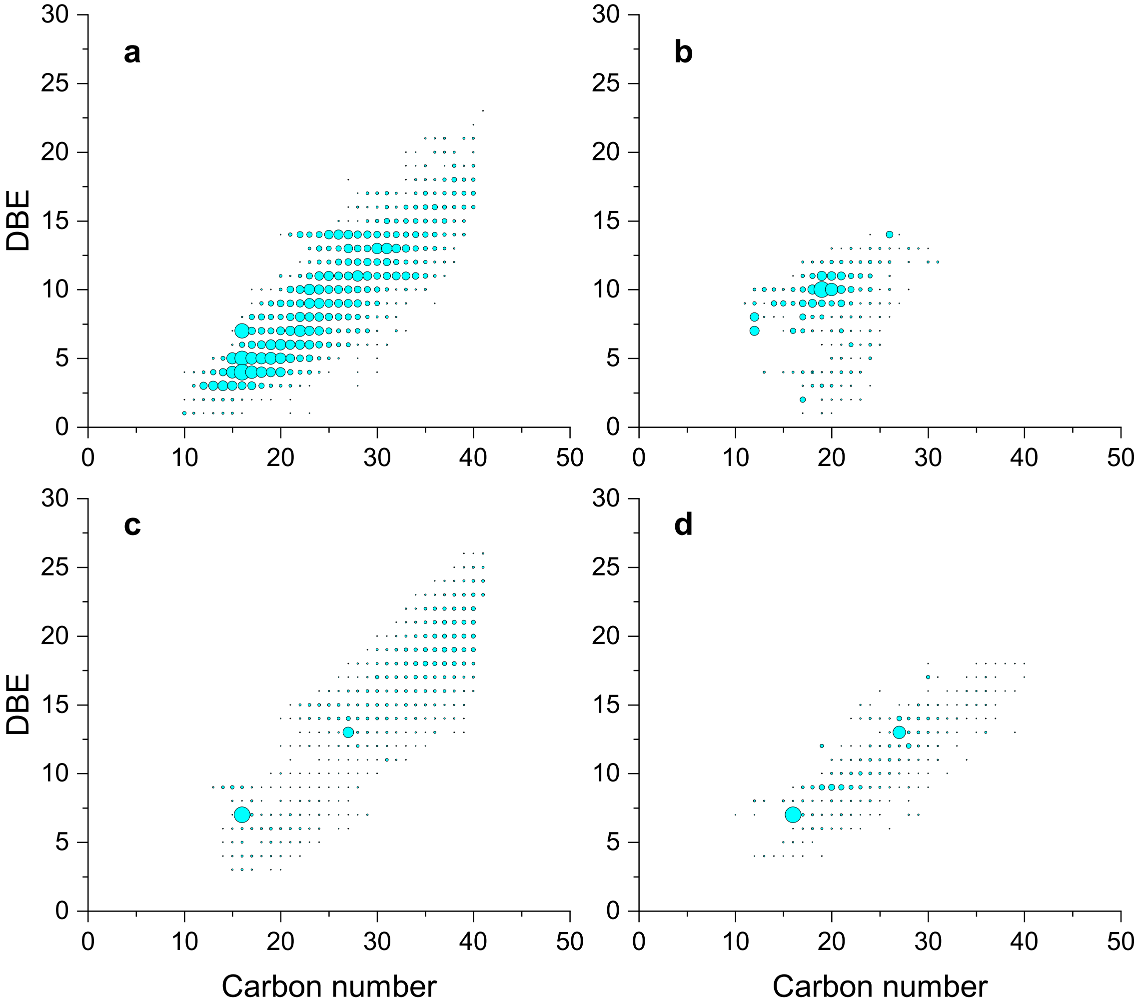


Fig. 6. Cross plots of DBE and carbon number showing the relative abundance of S_1O_1 species in wells (a) LS2 from the Tarim Basin; (b) S6 from the Tarim Basin; (c) L19 from the Baiyun Sag (PRMB); and (d) H10 from the Fushan Sag (Beibuwan Basin).

4.3. *S_2 species*

As shown in Fig. 3, the oils from wells LS2 and L19 altered by TSR and evaporative fraction contain low contents of S_2 species, while the primary condensates (e.g., wells S6 and H10) from the kerogen has very little those compounds. The TSR-altered oil contains a wide range of

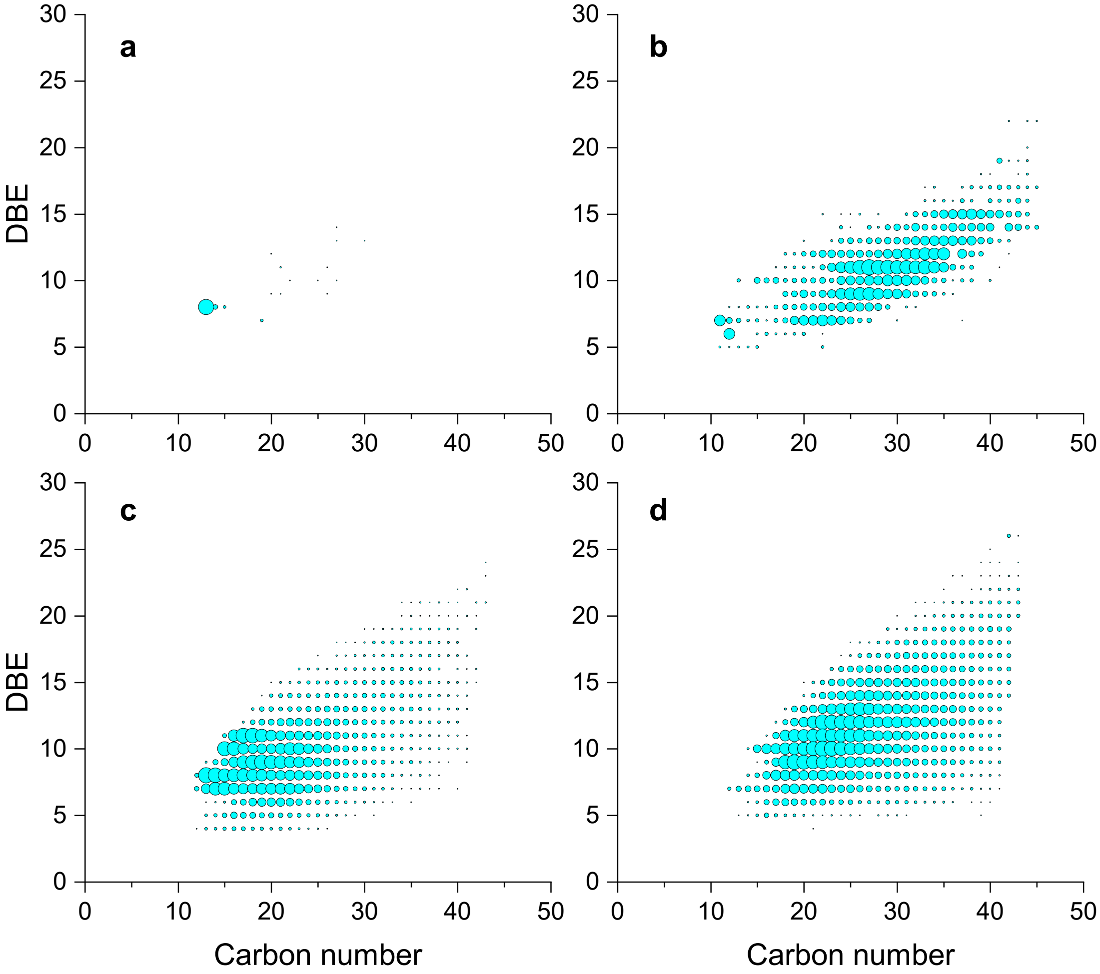


Fig. 7. Cross plots of DBE and carbon number showing the relative abundance of N_1 species in wells (a) LS2 from the Tarim Basin; (b) S6 from the Tarim Basin; (c) L19 from the Baiyun Sag (PRMB); and (d) H10 from the Fushan Sag (Beibuwan Basin).

DBE values and carbon number between 3 and 21 and 8–40, respectively (Fig. 5a). However, the DBE values and carbon number of S_2 species are limited ranging from 11 to 22 and 23–40 respectively (Fig. 5b).

4.4. O_1S_1 species

Fig. 6 shows that the distributions of DBE values and carbon number for S_2 species in different condensate types. In the LS2 oil altered by TSR, the DBE values for S_1O_1 species are in range from 1 to 21 and carbon number for the series compounds are in range from 10 to 40. The oil contains relatively high abundance of S1O1 species with low DBE values (1–3), corresponding to thiols compounds containing one oxygen atom, which appears to be consistent with that of S_1 species (Fig. 6a). Compared to TSR-altered oils, the S6 oil, a primary condensate from kerogen, has a limited range of DBE values and carbon number for S_2 species, between 2 and 14 and 10–30, respectively (Fig. 6b). In the L19 oil, an example for evaporative fraction alteration, is characterized by high content of highly concentrated S_2 species with high DBE values (17–22), and contains vary little low DBE values (1–3) for species (Fig. 6c). The relative abundances of S_2 species with high DBE values in the primary high mature condensate are limited relative to those in the evaporative fraction altered oil (Fig. 6d).

4.5. N_1 species

A very low abundance of N_1 species (Fig. 3a), covering a limited range of DBE values (6–14) and carbon number (11–30) (Fig. 7a), occur in Well LS2 oil, which were altered by TSR. In contract, a relatively complete N_1 series with DBE values ranging from 5 to 20 and carbon number ranging from 10 to 45 were observed in the non-TSR altered S6 oil (Fig. 7b), although those compounds also present in a low content overall (Fig. 7b). In Well L19 oil subjected by evaporative fraction alteration, the N1 species have a relatively broad range of DBE values (4–24) and carbon number (11–41) with a maximum at DBE value of 8 and carbon number of 19 (Fig. 7c). The range of DBE values in H10 oil are broader (4–27) than that in L19, and those of carbon number for N_1 species are similar (Fig. 7d).

4.6. Hydrocarbon species (CHs)

The LS2 oil contain a low content of CH_2s species (Fig. 3a), and appear to be enriched in those compounds with low DBE values (4–7) and carbon number (11–25) (Fig. 8a). The S6 condensate is characterized by a broad range of carbon number between 11 and 50 for CH_2s with DBE values ranging from 4 to 20 (Fig. 8b). In the oil sample from well L19, the DBE values and carbon number range in 6–20 and 15–38, respectively (Fig. 8c). A relatively abundant S_2 species with a DBE value range of 4–21 (mainly 7–9) and a carbon number range of 12–40 (mainly 15–20) in the well H10 crude oil (Fig. 8d). The carbon number and DBE for CH_2s species in the TSR-altered oil is limited due to their interactions with inorganic sulfur. However, the CH_2s species contents in non-TSR altered oils is high. In addition, by combination with the carbon number distributions for each compound class in TSR-altered, the oils in Baiyun and Fushan Sags contain low contents of S_1 species

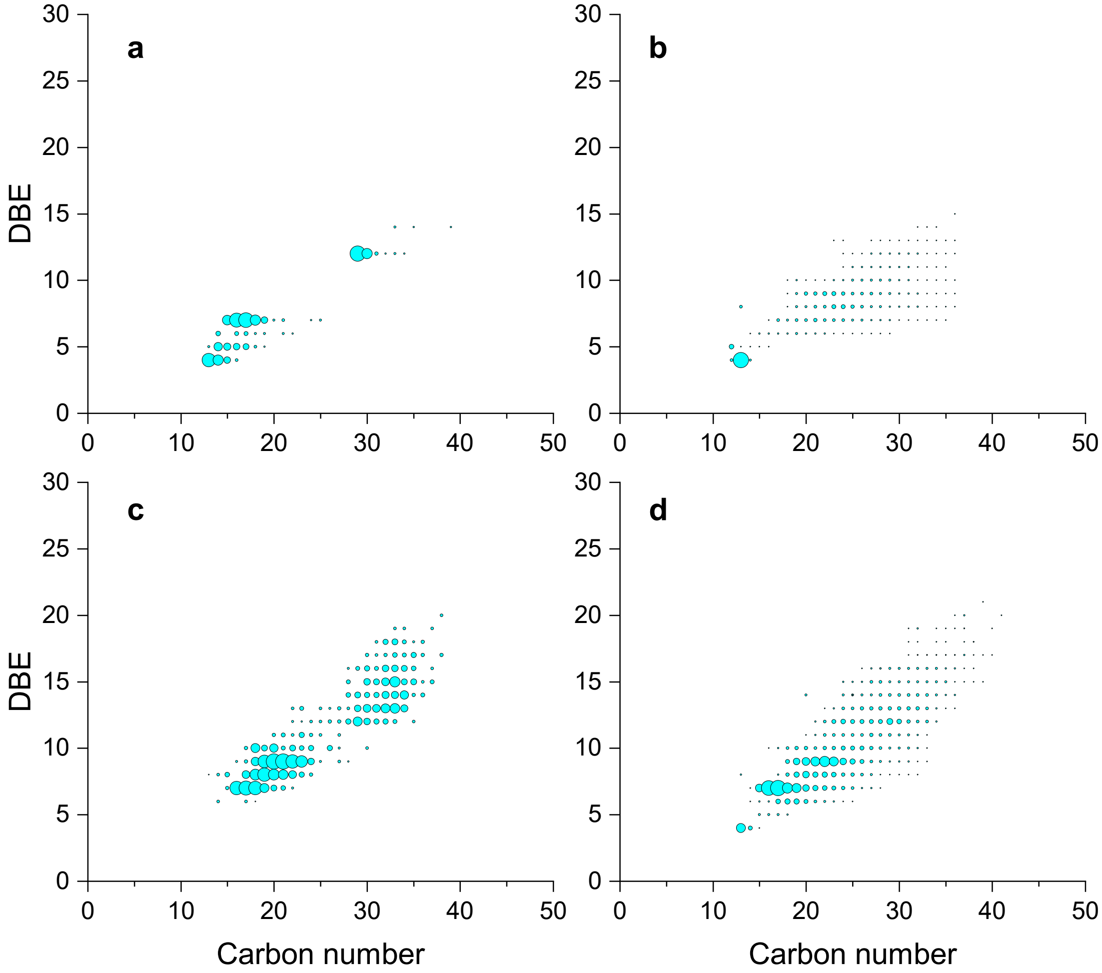


Fig. 8. Cross plots of DBE and carbon number showing the relative abundance of CH_2s species in wells (a) LS2 from the Tarim Basin; (b) S6 from the Tarim Basin; (c) L19 from the Baiyun Sag (PRMB); and (d) H10 from the Fushan Sag (Beibuwan Basin).

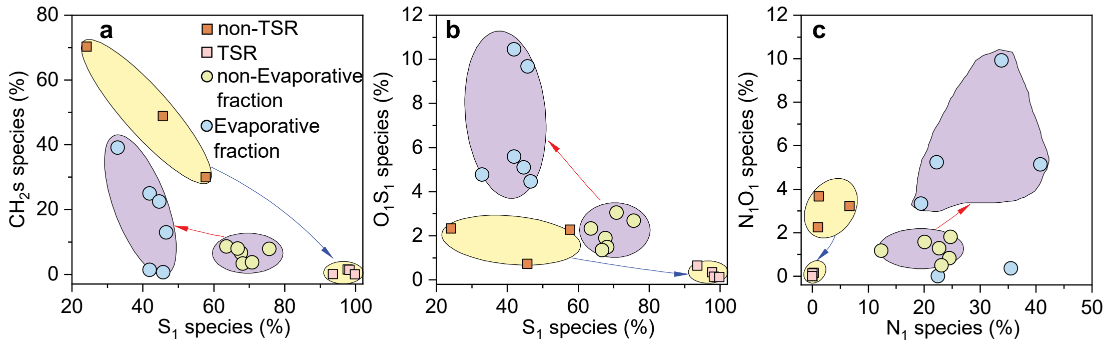


Fig. 9. Cross plots showing the relationship between the relative contents of S_1 species and (a) CH_2s species and (b) N_1 species in the condensates with different secondary alteration. The bule arrow shows the changes on molecular compositions during TSR, and the red one shows the changes on molecular compositions during evaporative fractionation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with low DBE values (1–3) (Fig. 3), S_2 species (Fig. 5), S_1O_1 species (Fig. 6) and high contents of N_1 (Fig. 7) and CH_2s species (Fig. 8).

4.7. Influence of TSR alteration on heteroatomic compound in condensates

Fig. 9 illustrates the relative contents of S_1, CH_2s and N_1 species and their oxides in different type oils to comprehensively show the influence of different secondary alteration on those compounds. It can be clearly seen that the relative contents of S_1 species in the TSR-altered oils are distinctly higher than that in non-TSR altered oils (Fig. 9a). The relative contents of CH_2s and O_1S_1 species in TSR-altered oils are distinctly lower than that in non-TSR altered oils. TSR-altered oils have a slight edge of N_1 species over non-TSR altered oils (Fig. 9a, b). The N_1 and N_1O_1 species are depleted in TSR-altered oils (Fig. 9c). During the TSR alteration, the hydrocarbon has an interaction with sulfur from sulfate and/or H_2S [6,12,15], which can be converted into sulfur-containing compounds, leading to a decrease of CH_2s species and an increase of S_1 and

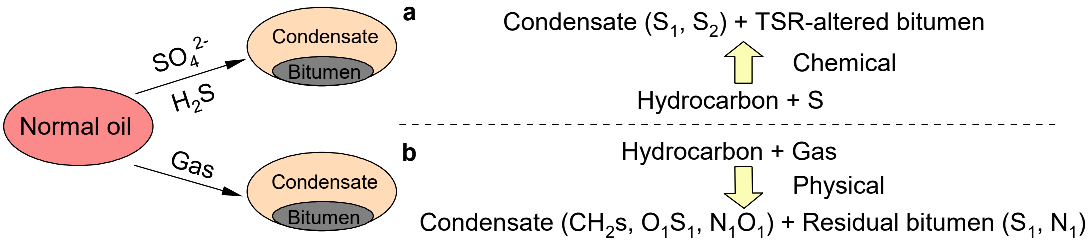


Fig. 10. A schematic diagram showing the compositional change mechanism in condensates with (a) TSR and (b) evaporative fraction alterations.

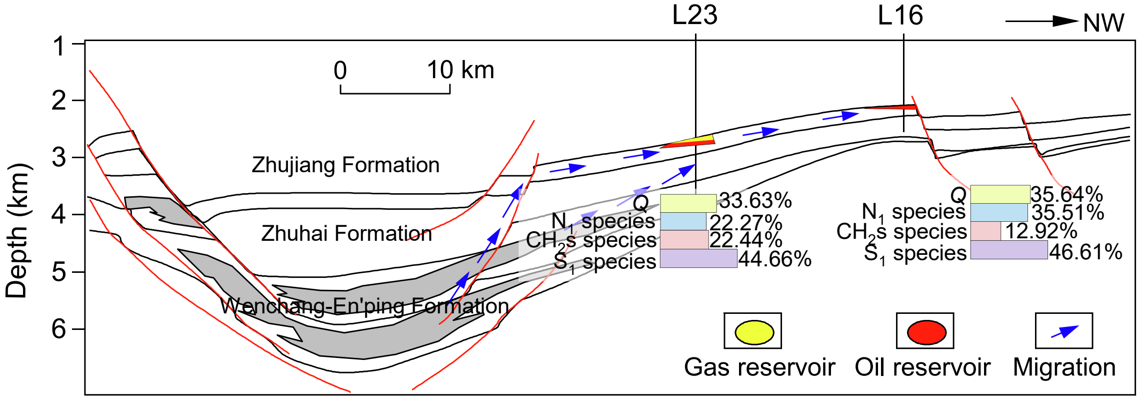


Fig. 11. Cross-sections showing hydrocarbon accumulation with evaporative fractionation during gas invasion in the Baiyun Sag. The location of profile is shown in Fig. 1. Q is the mass deletion of n-alkanes.

S_2 species (Fig. 10a) [42,50]. Therefore, TSR-altered condensate is characterized by high contents of labile organosulfur compounds such as thiol and thioether (Fig. 10a). Meanwhile, it can result in the precipitation of asphaltene molecules of primary oils generated from the kerogen due to a shift of the molecular distribution towards lighter compositions by TSR, and then form the TSR proto-solid bitumen species that are largely insoluble [24]. These proto-solid bitumen species are characterized to be highly condensed and not occurred in non-TSR altered oil with equivalent thermal stress [23]. In fact, an insufficient sulfur was present in the Ordovician oil reservoirs, where *in-situ* TSR reactions rarely occurred. However, abundant anhydrite has been observed in Cambrian strata in this area, which are considered as a favor sulfur source. Therefore, the TSR-altered oils and H_2S gas migrated from the Cambrian strata into Ordovician reservoirs and mixed the primary oils, which was supported by high H_2S centration in these S4 reservoirs and the correlated sulfur isotopic compositions between H_2S and Cambrian anhydrites in the south part of No.4 fault zone [52]. The relative contents of S_1 and CH_2s species could be an indicator for TSR determination, where the S1 species would be more than 95 % in TSR-altered oils.

4.8. Influence of evaporative fraction on heteroatomic compound in condensates

The relative abundances of S_1 species in the oils with evaporative fractionation are lower than that in the oils without evaporative fractionation (Fig. 9a). Compared to the primary condensate, a relatively elevated level of CH_2s, N_1, O_1S_1 and N_1O_1 species occur in the oils with evaporative fractionation (Fig. 9b, c). The oils are enriched in CH_2s species due to the easy dissolution of hydrocarbon when highly mature gas invades the priorly primary oil reservoir (Fig. 10b). However, the higher compositions, generally enriched S_1, N_1 and O_1S_1 species, are least dissolved and then precipitated, which formed residual bitumen in situ. The contents of N_1O_1 species in the oils experiencing evaporative fractionation are broad (Fig. 9c) possibly due to the unstable dissolution of these compounds into gas and irregular migration during fractionation, which leads to be an unavailable indicator for evaporative fractionation determination. Physical differentiation plays a key role in the formation of condensate and heavy oil reservoirs in the process. Fig. 11 shows a petroleum accumulation scenario during gas invasion and evaporative fractionation in the Baiyun Sag. Crude oil generated from kerogen in the early period of oil window migrated, trapped and accumulated in favorite structural zones along the slope. And then, natural gas generated from the source rock deposited in the deep region in the high mature stage migrated along the slope and displaced the early formed oil reservoirs, which consequently migrated to the marginal zones in the area. During this process, a trend in oils with an increased mass deletion of *n*-alkanes and the relative content of S_1 and N_1 species as well as a decreased CH_2s content occurred from the central to marginal areas. Therefore, the relative contents of S_1, N_1 and CH_2s species could be potential parameters for petroleum migration direction in this area.

5. Conclusions

In this work, we completed a comprehensive characterization of heteroatomic compounds in the condensates with different secondary alteration (TSR and evaporative fraction) by high-resolution mass spectrometry. Compared to the oils without TSR alteration, the TSR-altered oils are characterized by vary high contents of S_1 species (>90 %) and low contents of CH_2s species (<2%) attributed to the consumption of hydrocarbons. Those oils also have a relative abundance of low molecular S_1 species referring to thiols and thiophenes. However, the relative contents of CH_2s species in oils undergone evaporative fraction are high than that in non-altered oil, while those of S_1 and N_1 species are on the contrary, which may be due to the dissolving of hydrocarbons in gas. Therefore, in this study, it gives a good application of the heteroatomic compositions in oils to determine secondary alteration types and show a great potential for defining alteration extent, as well as the origin and formation of condensate.

CRediT authorship contribution statement

Dongyong Wang: Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. **Jianfa Chen:** Writing – review & editing, Resources, Investigation, Conceptualization. **Meijun Li:** Writing – review & editing, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Jianxun Wu:** Software, Methodology. **Quan Shi:** Resources, Methodology. **Wenqiang Wang:** Visualization. **Shuofan Li:** Software, Methodology. **Zichao Ran:** Visualization, Methodology, Investigation. **Zi'ao Geng:** Software, Investigation. **Xin Wang:** Resources, Investigation. **Huiqiang Qin:** Investigation. **Xianli Zou:** Resources, Project administration. **Sajjad Ali:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 42170354), Natural Science Foundation of Xinjiang Uygur Autonomous Region of China (Grant No. 2023D01A20) and China Scholarship Council (CSC202306440129) for the financial support provided to Dongyong Wang. We acknowledge the Northwest China Petroleum Bureau SINOPEC; Southern Oil Exploration and Development Company, PetroChina; and Shenzhen Branch Company, CNOOC for providing samples and allowing data to be published. We would like to express our great thanks for the editor, Dr. Yasushi Sekine and two anonymous reviews, whose comments have improved our manuscript quality. The authors also thanks to Shengbao Shi, Lei Zhu and Yahe Zhang for their experimental assistance.

Data availability

Data will be made available on request.

References

[1] Mccain WD. The Properties of Petroleum Fluids. Tulsa: Petroleum Publishing Company; 1973.
[2] Thompson KFM. Classification and thermal history of petroleum based on light hydrocarbons. Geochim Cosmochim Acta 1983;47:303–16.
[3] Hunt JM. Petroleum Geochemistry and Geology. 2nd ed. San Francisco: WH Freeman Company; 1995.
[4] Philippi GT. The deep subsurface temperature controlled origin of the gaseous and gasoline-range hydrocarbons of petroleum. Geochim Cosmochim Acta 1975;39:1353–73.
[5] Tissot BP, Welte DH. Petroleum Formation and Occurrence. Second Edition ed, New York: Springer-Verlag Berlin Heidelberg; 1984.
[6] Cai C, Li H, Li K, Wang D. Thermochemical sulfate reduction in sedimentary basins and beyond: A review. Chem Geol 2022;607:121018.
[7] Thompson KFM. Gas-condensate migration and oil fractionation in deltaic systems. Mar Pet Geol 1988;5:237–46.
[8] Thompson KFM. Fractionated aromatic petroleums and the generation of gas-condensates. Org Geochem 1987;11:573–90.
[9] Hill RJ, Tang Y, Kaplan IR, Jenden PD. The influence of pressure on the thermal cracking of oil. Energy Fuels 1996;10:873–82.
[10] Hill RJ, Tang Y, Kaplan IR. Insights into oil cracking based on laboratory experiments. Org Geochem 2003;34:1651–72.
[11] Orr WL. Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation—study of big horn basin paleozoic oils. AAPG Bull 1974;58:2295–318.
[12] Zhang T, Ellis GS, Wang K, Walters CC, Kelemen SR, Gillaizeau B, et al. Effect of hydrocarbon type on thermochemical sulfate reduction. Org Geochem 2007;38:897–910.
[13] Ma Q, Ellis GS, Amrani A, Zhang T, Tang Y. Theoretical study on the reactivity of sulfate species with hydrocarbons. Geochim Cosmochim Acta 2008;72:4565–76.
[14] Powell TG, Macqueen RW. Precipitation of sulfide ores and organic Matter: Sulfate reactions at Pine Point, Canada. Science 1984;224:63–6.
[15] Xia X, Ellis GS, Ma Q, Tang Y. Compositional and stable carbon isotopic fractionation during non-autocatalytic thermochemical sulfate reduction by gaseous hydrocarbons. Geochim Cosmochim Acta 2014;139:472–86.
[16] Amrani A, Zhang T, Ma Q, Ellis GS, Tang Y. The role of labile sulfur compounds in thermochemical sulfate reduction. Geochim Cosmochim Acta 2008;72:2960–72.
[17] Machel HG, Krouse HR, Sassen R. Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. Appl Geochem 1995;10:373–89.
[18] Wingert WS. GC–MS analysis of diamondoid hydrocarbons in Smackover petroleums. Fuel 1992;71:37–43.
[19] Wei Z, Moldowan JM, Fago F, Dahl JE, Cai C, Peters KE. Origins of thiadiamondoids and diamondoidthiols in petroleum. Energy Fuels 2007;21:3431–6.
[20] Wei Z, Mankiewicz P, Walters C, Qian K, Phan NT, Madincea ME, et al. Natural occurrence of higher thiadiamondoids and diamondoidthiols in a deep petroleum reservoir in the Mobile Bay gas field. Org Geochem 2011;42:121–33.
[21] Li J, Xie Z, Dai J, Zhang S, Zhu G, Liu Z. Geochemistry and origin of sour gas accumulations in the northeastern Sichuan Basin, SW China. Org Geochem 2005;36:1703–16.
[22] Hu A, Li M, Wong J, Reyes J, Achal S, Milovic M, et al. Chemical and petrographic evidence for thermal cracking and thermochemical sulfate reduction of paleo-oil accumulations in the NE Sichuan Basin, China. Org Geochem 2010;41:924–9.
[23] Walters CC, Qian K, Wu C, Mennito AS, Wei Z. Proto-solid bitumen in petroleum altered by thermochemical sulfate reduction. Org Geochem 2011;42:999–1006.
[24] Walters CC, Wang FC, Qian K, Wu C, Mennito AS, Wei Z. Petroleum alteration by thermochemical sulfate reduction – A comprehensive molecular study of aromatic hydrocarbons and polar compounds. Geochim Cosmochim Acta 2015;153:37–71.
[25] Ma K. Study on petroleum evaporative fractionation: A new mechanism for the generation of condensate. Adv Earth Sci 1995;10:567–71. in English with Abstract.
[26] Chen J, Deng C, Wang X, Ni Y, Sun Y, Zhao Z, et al. Formation mechanism of condensates, waxy and heavy oils in the southern margin of Junggar Basin, NW China. Sci China Earth Sci 2017;60:972–91.
[27] Khavari-Khorasani G, Dolson JC, Michelsen JK. The factors controlling the abundance and migration of heavy versus light oils, as constrained by data from the Gulf of Suez. Part I. The effect of expelled petroleum composition, PVT properties and petroleum system geometry. Org Geochem 1998;29:255–82.
[28] Matyasik I, Steczko A, Philp RP. Biodegradation and migrational fractionation of oils from the Eastern Carpathians, Poland. Org Geochem 2000;31:1509–23.
[29] Napitupulu H, Ellis L, Mitterer RM. Post-generative alteration effects on petroleum in the onshore Northwest Java Basin, Indonesia. Org Geochem 2000;31:295–315.
[30] Volk H, Horsfield B, Mann U, Suchý V. Variability of petroleum inclusions in vein, fossil and vug cements—a geochemical study in the Barrandian Basin (Lower Palaeozoic, Czech Republic). Org Geochem 2002;33:1319–41.
[31] Sharaf LM, El Nady MM. Application of light hydrocarbon (C7+) and biomarker analyses in characterizing oil from wells in the North and North Central Sinai. Egypt Pet Sci Technol 2006;24:607–27.
[32] Zhang S, Su J, Zhang B, Wang X, He K. Genetic mechanism and controlling factors of deep marine light oil and condensate oil in Tarim Basin. Acta Pet Sin 2021;42:1566–80. in English with Abstract.
[33] Chen C, Zhang X, Peng G, Long Z, Liu B, Wang X, et al. Controlling factors on the charging process of oil and gas in the eastern main sub-sag of the Baiyun Sag, Zhujiang River (Pearl River) Mouth Basin. Acta Oceanol Sin 2023;42:189–200.
[34] Fu J, Li M, Sun Y, Li Y, Yang Y, Lu X, et al. Thermal maturity of crude oils in the Baiyun sag, Pearl River Mouth basin, South China Sea: Insights from biomarkers, aromatic hydrocarbon and adamantane compounds. Mar Pet Geol 2023;155:106353.
[35] Zhu X, Chen J, Zhang C, Wang Y, Liu K, Zhang T. Effects of evaporative fractionation on diamondoid hydrocarbons in condensates from the Xihu Sag, East China Sea Shelf Basin. Mar Pet Geol 2021;126:104929.
[36] Müller H, Andersson JT, Schrader W. Characterization of high-molecular-weight sulfur-containing aromatics in vacuum residues using Fourier transform ion cyclotron resonance mass spectrometry. Anal Chem 2005;77:2536–43.
[37] Wu J, Ma C, Zhang W, Chang W, Zhang Y, Shi Q. Molecular characterization of non-polar sulfur compounds in the full boiling range crude oil fractions. Fuel 2023;338:127323.
[38] Lu H, Shi Q, Ma Q, Shi Y, Liu J, Sheng G, et al. Molecular characterization of sulfur compounds in some specieal sulfur-rich Chinese crude oils by FT-ICR MS. Sci China Earth Sci 2014;57:1158–67.
[39] Li S, Wu J, Wang Y, Zhang X, Zhang W, Zhang Y, et al. Isolation and characterization of thiols in petroleum using Ag+-silica solid phase extraction followed by gas chromatography-mass spectrometry and high-resolution mass spectrometry. Fuel 2024;363:130946.
[40] Li S, Shi Q, Pang X, Zhang B, Zhang H. Origin of the unusually high dibenzothiophene oils in Tazhong-4 Oilfield of Tarim Basin and its implication in deep petroleum exploration. Org Geochem 2012;48:56–80.
[41] Purcell JM, Hendrickson CL, Rodgers RP, Marshall AG. Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry for Complex Mixture Analysis. Anal Chem 2006;78:5906–12.
[42] Wang Y, Wu J, Li S, Zhang W, Wang P, Wang M, et al. Identification and Geological Implication of Thiols in the Condensate Oils. Energy Fuels 2023;37:11675–82.
[43] Zhu G, Wang M, Chi L, Li J, Wu Z, Zhang Z. Discovery and molecular characterization of organic caged compounds and polysulfanes in Zhongba81 Crude Oil, Sichuan Basin, China. Energy Fuels 2020;34:6811–21.
[44] Zhu G, Zhang Y, Wang M, Zhang Z. Discovery of High-Abundance Diamondoids and Thiadiamondoids and Severe TSR Alteration of Well ZS1C Condensate, Tarim Basin, China. Energy Fuels 2018;32:7383–92.

[45] Li D, Liang D, Jia C, Wang G, Wu Q, He D. Hydrocarbon Accumulations in the Tarim Basin, China. AAPG Bull 1996;80:1587–603.

[46] Jia C, Wei G. Structural characteristics and petroliferous features of Tarim Basin. Chin Sci Bull 2002;47:1–11.

[47] Zhang S, Huang H. Geochemistry of Palaeozoic marine petroleum from the Tarim Basin, NW China: Part 1. Oil family classification. Org Geochem 2005;36:1204–14.

[48] Zhang S, Huang H, Su J, Liu M. Ultra-deep liquid hydrocarbon exploration potential in cratonic region of the Tarim Basin inferred from gas condensate genesis. Fuel 2015;160:583–95.

[49] Zhu G, Zhang Z, Jiang H, Yan L, Chen W, Li T, et al. Evolution of the Cryogenian cratonic basins in China, paleo-oceanic environment and hydrocarbon generation mechanism of ancient source rocks, and exploration potential in 10,000 m-deep strata. Earth-Sci Rev 2023;244:104506.

[50] Zhu G, Li J, Zhang Z, Wang M, Xue N, He T, et al. Stability and cracking threshold depth of crude oil in 8000 m ultra-deep reservoir in the Tarim Basin. Fuel 2020; 282:118777.

[51] Huang H, Zhang S, Su J. Palaeozoic oil–source correlation in the Tarim Basin, NW China: A review. Org Geochem 2016;94:32–46.

[52] Wang D, Kutuzov I, Zhang H, Cao Z, Wang Q, Amrani A, et al. Application of sulfur isotopes of volatile organic sulfur compounds to determine the natural gas secondary alterations and possible sources in the Tarim Basin, NW China. Mar Pet Geol 2024;169:107078.

[53] Ma A, Qi L. Geochemical characteristics and phase behavior of the Ordovician ultra-deep reservoir fluid, No.4 fault, northern Shuntuoguole, Tarim Basin. Earth Science Frontiers 2023;30:247–62 (in English with Abstract).

[54] Bian J, Hou D, Cui Y, Zhu X. Geochemical characteristics and origin of the ultra-deep hydrocarbons from the Shunbei Oilfield in the Tarim Basin, China: Insight from molecular biomarkers and carbon isotope geochemistry. Mar Pet Geol 2023; 158:106542.

[55] Peng W, Deng S, Zhang J, Huang C, Qiu H, Li Y, et al. Genetic mechanism and main controlling factors of deep marine condensate reservoirs: A case study of the Shunbei No.4 fault zone in Tarim Basin, NW China. Nat Gas Geosci 2024 (in English with Abstract).

[56] Zhu X, Chen J, He L, Wang Y, Zhang W, Zhang B, et al. Geochemical characteristics and source correlation of hydrocarbons in the Well Luosi 2 of Maigaiti Slope, Tarim Basin, China. Natural Gas Geoscience 2017;28:566–74. in English with Abstract.

[57] Ma A, Jin Z, Zhu C, Gu Y, Li H, Lu Q. Effect of TSR on the crude oil in Ordovician reservoirs of Well Luosi-2 from Maigaiti Slope, Tarim Basin: Evidences from molecular markers. Oil Gas Geol 2018;39:730–7. in English with Abstract.

[58] Zhu G, Zhang Y, Zhou X, Zhang Z, Du D, Shi S, et al. TSR, deep oil cracking and exploration potential in the Hetianhe gas field, Tarim Basin. China Fuel 2019;236: 1078–92.

[59] Wang X, Qiu N, Peng G, Zhang X, Li K, Chang J, et al. Characteristics of geothermal field and tectono-thermal evolution in Baiyun Sag, Pearl River Mouth Basin, China. J Nat Gas Geosci 2024;9:99–109.

[60] Lu X, Li M, Li Y, Yang Y, Wang N, Ran Z, et al. Rearranged oleananes in Tertiary oils from the Baiyun Sag, Pearl River Mouth Basin, South China Sea: identification, distribution and geochemical significance. Org Geochem 2023;175:104525.

[61] Wang C, Zeng J, Zhang Z, Shi N, Lao M, Zhao Q, et al. Origin and distribution of natural gas and oil in the Baiyun Depression, Pearl River Mouth Basin, South China Sea. J Pet Sci Eng 2018;170:467–75.

[62] Lu X, Li M, Li Y, Yang Y, Yang H, Wang N, et al. Early Oligocene marine transgression and organic matter accumulation recorded in the upper Eocene to lower Oligocene Enping Formation of the Baiyun Sag, Pearl River Mouth Basin, South China Sea. J Asian Earth Sci 2024;259:105909.

[63] Fu J, Zhang Z, Chen C, Wang TG, Li M, Ali S, et al. Geochemistry and origins of petroleum in the Neogene reservoirs of the Baiyun Sag, Pearl River Mouth Basin. Mar Pet Geol 2019;107:127–41.

[64] Jiang W, Chen C, Long Z, Li Y, Yang C, Xiong Y. Geochemical characteristics and possible sources of crude oils in the Baiyun deep-water area of the Pearl River Mouth Basin, South China. Sea Mar Pet Geol 2022;135:105410.

[65] Liu E, Wang H, Li Y, Zhou W, Leonard ND, Lin Z, et al. Sedimentary characteristics and tectonic setting of sublacustrine fans in a half-graben rift depression, Beibuwan Basin, South China. Sea Mar Pet Geol 2014;52:9–21.

[66] Li M, Wang T, Liu J, Zhang M, Lu H, Ma Q, et al. Biomarker 17α(H)-diahopane: A geochemical tool to study the petroleum system of a Tertiary lacustrine basin, Northern South China Sea. Appl Geochem 2009;24:172–83.

[67] Gan H, Gong S, Tian H, Wang H, Chen J, Ma Q, et al. Geochemical characteristics of inclusion oils and charge history in the Fushan Sag, Beibuwan Basin, South China Sea. Appl Geochem 2023;150:105598.

[68] Li M, Wang T, Liu J, Zhang M, Lu H, Ma Q, et al. Total alkyl dibenzothiophenes content tracing the filling pathway of condensate reservoir in the Fushan Depression, South China Sea. Sci China Ser D Earth Sci 2008;51:138–45.

[69] Li M, Wang T, Shi S, Liu K, Ellis GS. Benzonaphthothiophenes and alkyl dibenzothiophenes: Molecular tracers for oil migration distances. Mar Pet Geol 2014;57:403–17.

[70] Gan H, Wang H, Shi Y, Ma Q, Liu E, Yan D, et al. Geochemical characteristics and genetic origin of crude oil in the Fushan sag, Beibuwan Basin, South China Sea. Mar Pet Geol 2020;112:104114.