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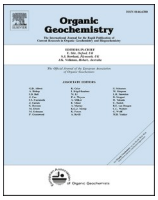

Rearranged oleananes in Tertiary oils from the Baiyun Sag, Pearl River Mouth Basin, South China Sea: identification, distribution and geochemical significance

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ABSTRACT

Three abundant rearranged oleananes detected in Tertiary oils from the Baiyun Sag, South China Sea, were designated as 5(4 → 3) *abeo*-3α(H), 5β(H), 18α(H)-oleanane (I), 3α, 5β-dimethyl-23α, 25-dinor-10β(H), 18α(H)-oleanane (II) and 1(10 → 5)*abeo*-3β-methyl-24β-nor-18α(H)-oleanane (III), using gas chromatography-mass spectrometry (GC–MS) and GC–MS–MS. The relative abundances of different rearranged oleananes correlated with each other, and also showed strong positive correlations with those of oleanane or des-A-oleanane. This is consistent with rearranged oleananes, oleanane (OL) and des-A-oleanane originating from functionalized oleanane triterpenoids, but by different formation processes. The distribution of rearranged oleananes in oils from the study area is controlled mainly by angiosperm inputs and the diagenetic conditions of their source rocks, rather than thermal maturity. Oligocene marine transgression in the study area may have played an important role in the expression of saturated oleanoids. Moreover, oxic and acidic peat swamp conditions in the Panyu Low Uplift favoured the formation of rearranged oleananes compared to oleananes. In addition, oils from the Baiyun Sag can be classified into two oil families, i.e., A and B, using the relative abundance of rearranged oleananes and other source-related indicators. The Family A oils in the eastern and northeastern portions of the sag are characterized by relatively low pristane/phytane (Pr/Ph) ratios, low rearranged oleananes/oleanane ((I + II + III)/OL) and bicadinane-T/C_{30} hopane (T/C_{30}H) ratios. The Family B oils in the Panyu Low Uplift and northeastern portion of the sag have higher Pr/Ph, (I + II + III)/OL and T/C_{30}H ratios. The related parameters of rearranged oleananes were therefore shown to be effective indicators for oil-oil or oil-source rock correlation in the study area.

1. Introduction

Oleanane is well known as an angiosperm biomarker which is found almost exclusively in Cretaceous and Tertiary rocks or related oils (Moldowan et al., 1994; Peters et al., 2005; Onojake and Abrakasa, 2021). Rearranged oleananes are a series of pentacyclic triterpanes that occur only in source rock extracts or oils containing oleanane (Nytoft et al., 2010, 2016). Multiple rearranged oleananes have been detected in Tertiary-sourced oils from many petroliferous basins around the world, like the Niger Delta Basin of Nigeria, Assam Basin of India, and Qiongdongnan Basin of China (Nytoft et al., 2010; Zhu et al., 2018; Mathur, 2014). Only three abundant rearranged oleananes (I, II, III) have been identified to date (Nytoft et al., 2010). Rearranged oleanane III was initially separated from Nigerian oil and was determined as 1(10 → 5) *abeo*-3β-methyl-24β-nor-18α(H)-oleanane by X-ray crystallography (Hills et al., 1968). Smith et al. (1995) identified another C_{30} triterpane (5(4 → 3) *abeo*-3α(H), 5β(H), 18α(H)-oleanane, i.e., rearranged oleanane I), by comparison with a synthetic standard. Subsequently, a novel rearranged oleanane (structure II) was identified in Niger Delta oil and was designated as 3α, 5β-dimethyl-23α, 25-dinor-10β(H), 18α(H)-

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oleanane on the basis of nuclear magnetic resonance spectroscopy data (Nytoft et al., 2010). Rearranged oleananes are considered to be the dehydration and rearrangement products of higher plant triterpenoids (Nytoft et al., 2014) and indicators of terrigenous organic matter inputs. Therefore, the relative abundances of rearranged oleananes have been used for oil family classification and oil-source correlations in many petroliferous basins (Zhu et al., 2018; Mathur, 2014). In addition, ratios of some rearranged oleananes might be useful maturity parameters (Mathur, 2014). However, few studies have focused on the factors affecting the abundance of rearranged oleananes. During early diagenesis, the precursors of oleananes in lakes or coal swamps are susceptible to aromatization, leading to pentacyclic hydrocarbons with aromatized rings (Poinsot et al., 1995; Ellis et al., 1996). Saturated oleanoids, including oleanane and rearranged oleananes, are considered to result from a small "leak" in the dominant diagenetic reactions producing aromatic oleanoids, like octahydropicenes, dimethylpicenes, 1,2,5- and 1,2,7-trimethylnaphthalenes (Murray et al., 1997a). Moreover, saturated oleananes in mature sediments or oils appear to be enhanced by marine influences during early diagenesis (Murray et al., 1997a, 1997b). Nytoft et al. (2010, 2016) proposed that clay catalysis might be an important factor controlling the formation of rearranged oleananes, because their relative abundances correlated well with those of diasteranes in oils from multiple basins.

Exploration efforts in the deepwater area of the Pearl River Mouth Basin, South China Sea, have led to the discovery of a series of light oil or condensate reservoirs in the Baiyun Sag. The oil and gas reservoirs are mainly located in the northern and eastern parts of the sag (Ping et al., 2019; Wang et al., 2018). Few indicators are available for oil-oil or oil-source correlation in the study area because of low concentrations of many biomarkers in light oils or condensates (Chang et al., 2018; Zhang et al., 2005). Oils from northern and eastern Baiyun Sag contain relatively abundant oleanane and bicadinanes and they belong to two distinct oil families (Fu et al., 2019). Jiang et al. (2022) suggested that oils from the northern and eastern portions of the sag can be divided into

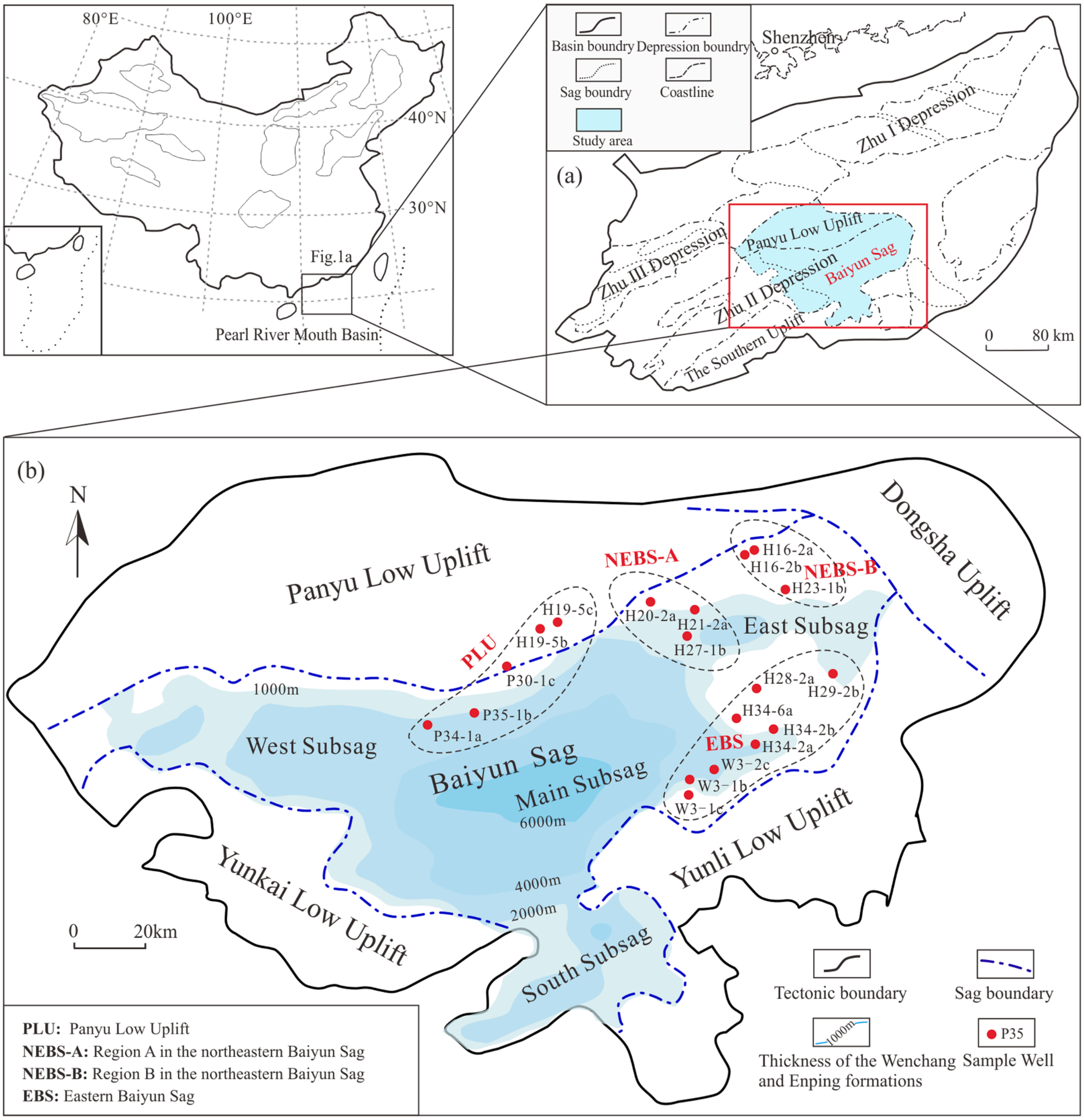

Fig. 1. Generalized geological map of the Pearl River Mouth Basin, South China Sea (a); Map of the Baiyun Sag (modified after Fu et al., 2019), with (b) sampled well locations and region name abbreviations used in this paper.

three groups on the basis of variations in their carbon isotope compositions and abundances of oleanane and bicadinanes. In this paper, rearranged oleananes (I, II, III) in Tertiary oils from the Baiyun Sag were determined based on gas chromatography-mass spectrometry (GC–MS) and gas chromatography-mass spectrometry-mass spectrometry (GC–MS–MS). This study also investigated the principal factors controlling the distribution of rearranged oleananes, and their significance for oil-source analysis in deepwater areas of the Pearl River Mouth Basin.

2. Geological setting

The Baiyun Sag of the Pearl River Mouth Basin is situated in the deepwater slope region of the South China Sea northern continental margin (Fig. 1a) where water depth varies from 200 to 3000 m (Fu et al., 2020). The Baiyun Sag is the largest sedimentary sag in this basin, surrounded by the Panyu Low Uplift, Dongsha Uplift, Yunli Low Uplift and Yunkai Low Uplift (Fig. 1b), with an area of more than 14,000 km^2 (Sun et al., 2020). Commercial reserves of oil and gas predominantly occur in the Panyu Low Uplift (PLU), and the northeastern (NEBS) and eastern Baiyun Sag (EBS) (Fu et al., 2019).

The tectonic evolution of the Baiyun Sag involved three main stages, including the *syn*-rift, transitional and post-rift subsidence stages (Fig. 2) (Clift et al., 2015; Zeng et al., 2019). The Paleogene Wenchang and Enping formations, deposited in the *syn*-rift stage (49–32 Ma), were principal source rocks for oil and gas accumulation in the study area (Ping et al., 2021). The Wenchang Formation was mainly deposited in a lacustrine environment. During the deposition of the Enping Formation, large-scale braided deltas developed in the north of the sag (Zeng et al., 2020). The formation of the Enping Formation source rocks might also have been affected by marine transgression (Zeng et al., 2019). The Nanhai Event, corresponding to the expansion of the South China Sea, marked the beginning of the transitional stage (32–23.8 Ma) (Briais et al., 1993). During this stage, the Oligocene Zhuhai Formation was dominated by marine and deltaic sediments comprising a set of sandstones with mudstone interbeds (Zhu et al., 2021; Tian et al., 2019). The major oil-producing reservoirs in the study area consist of deltaic sandstones of the Zhuhai Formation and deepwater fan sandstone or limestone of the overlying Zhujiang Formation (Ping et al., 2019). The Miocene Zhujiang Formation was deposited in the post-rift subsidence stage after the Baiyun tectonic event, and consists of sandstone and limestone in the lower member, and mudstones in the upper member (Jiang et al., 2022).

3. Samples and methods

Twenty-four light oils or condensates were collected from nineteen wells in the Baiyun Sag, including nine samples from eight wells in the EBS, six samples from three wells in the Northeastern Baiyun Sag region A (NEBS-A), four samples from three wells in region B (NEBS-B) and five samples of five wells from the Panyu Low Uplift (PLU, Fig. 1b, Table 1). The oils from the study area are characterized by low density

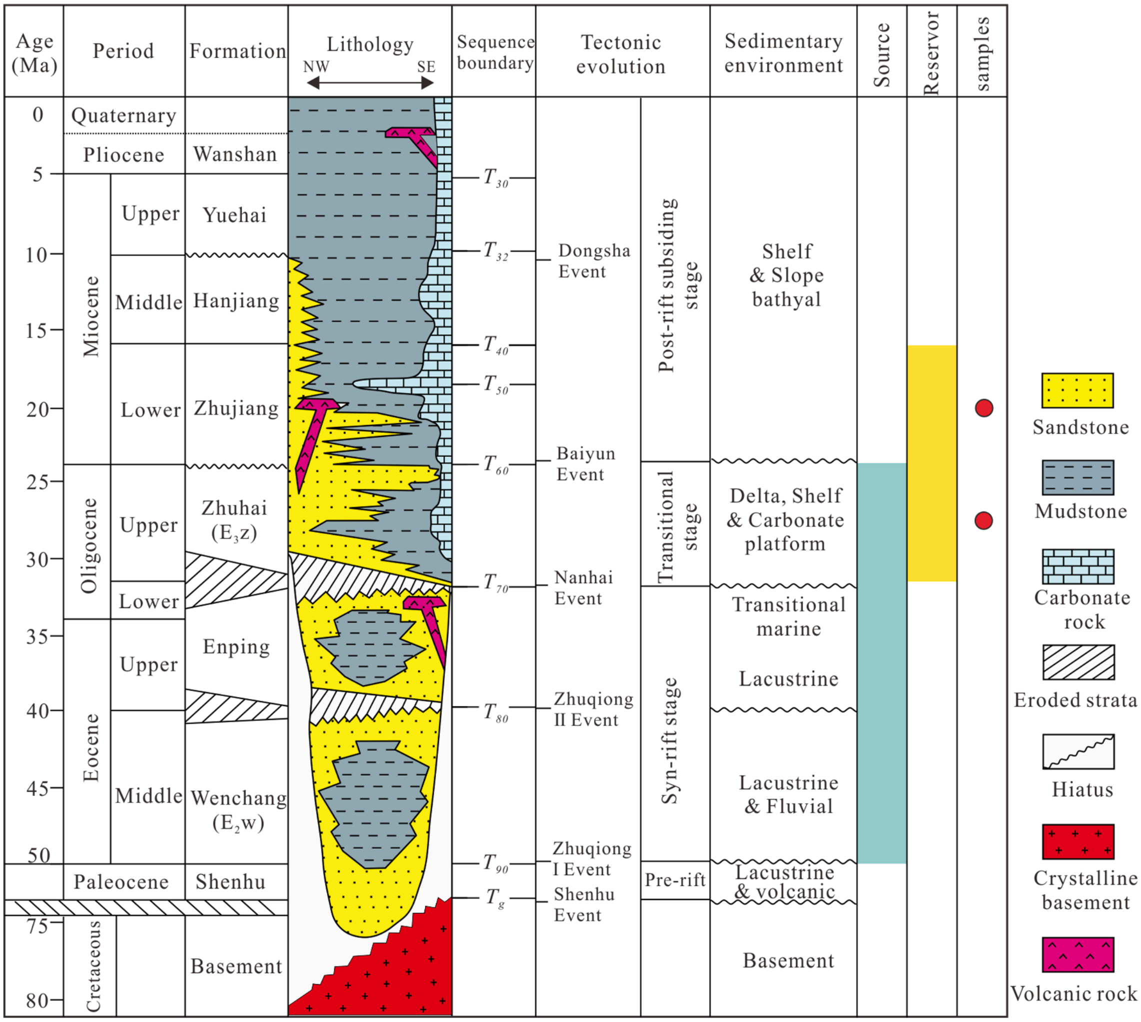

Fig. 2. Generalized stratigraphic column of the Baiyun Sag, Pearl River Mouth Basin (after Ping et al. 2021).

Table 1
Selected organic geochemical parameters of oils from the Baiyun Sag.

No.	Well	Depth (m)	Density (g/cm^3)	Gross composition (%)			I/ $C_{30}H$	II/ $C_{30}H$	III/ $C_{30}H$	(I + II + III)/ $C_{30}H$	(I + II + III)/ OL	OL/ $C_{30}H$	Y1/ C30H	Pr/ Ph	$C_{30}D$/ $C_{30}H$	C_{19+20}/ $C_{23}TT$	T/ $C_{30}H$	BMI-1
				SAT	ARO	NSO + ASPH												
1	W3-1b	3149–3154	0.8018	78.89	19.35	1.77	0.84	0.90	1.06	2.79	0.87	3.21	1.45	4.55	0.11	3.17	4.92	2.11
2	W3-1b	3111–3131	nd	82.46	13.53	4.01	0.62	0.81	0.63	2.05	0.86	2.40	1.16	4.24	0.07	3.17	3.53	2.29
3	W3-1c	3123–3127	nd	81.64	14.45	3.91	0.72	0.63	0.72	2.07	0.81	2.54	1.51	3.14	0.08	2.85	3.79	2.61
4	W3-2c	3396	0.8025	81.46	18.54	0.00	0.29	0.30	0.44	1.03	0.65	1.59	0.16	3.54	0.08	2.42	1.78	2.32
5	H34-2b	2976–2998	nd	82.56	8.32	9.12	0.48	0.55	0.60	1.63	0.89	1.83	0.58	4.22	0.09	2.76	3.64	2.23
6	H34-2a	3038	nd	80.13	17.50	2.37	0.32	0.41	0.47	1.20	0.72	1.67	0.21	3.32	0.09	1.67	2.31	2.41
7	H34-6a	3782	0.7867	85.46	9.69	4.85	0.10	0.40	0.54	1.04	0.57	1.81	0.12	3.72	0.12	3.29	4.57	2.71
8	H29-2b	2396	0.8410	73.83	20.68	5.49	0.42	0.33	0.46	1.21	0.72	1.68	0.24	3.89	0.09	2.05	2.03	2.15
9	H28-2a	2854	0.7943	78.53	13.45	8.03	0.34	0.37	0.40	1.11	0.57	1.96	0.17	4.63	0.07	2.68	1.63	2.04
10	H16-2a	2127–2136	0.7999	76.49	13.29	10.22	0.32	0.51	0.57	1.40	1.04	1.35	0.26	4.58	0.13	2.89	2.15	2.30
11	H16-2a	2157–2190	nd	77.40	17.49	5.11	0.22	0.43	0.54	1.19	1.06	1.12	0.25	4.21	0.12	1.54	2.07	2.05
12	H16-2b	2222	0.8060	82.86	13.43	3.71	0.21	0.49	0.50	1.20	0.98	1.23	0.17	4.66	0.12	3.76	1.85	2.51
13	H23-1b	2646	0.7702	73.20	18.86	7.93	0.21	0.41	0.60	1.22	1.11	1.10	0.16	4.68	0.10	1.62	2.15	2.74
14	H20-2a	2575	0.7803	77.85	13.47	8.68	0.29	0.75	0.72	1.75	1.44	1.22	0.82	6.27	0.14	6.23	4.38	2.23
15	H20-2a	2616	nd	82.24	10.18	7.58	0.79	0.88	1.08	2.74	2.20	1.25	0.81	6.27	0.17	5.50	4.69	1.89
16	H21-2a	2636	nd	79.94	13.37	6.68	0.45	0.59	0.75	1.80	1.53	1.18	0.66	5.49	0.14	5.71	5.50	2.35
17	H21-2a	2646	nd	82.56	13.91	3.53	0.43	0.61	0.69	1.73	1.15	1.50	0.45	5.66	0.13	4.38	5.84	2.28
18	H21-2a	2678	nd	77.90	17.33	4.77	0.47	0.57	0.84	1.88	1.32	1.42	0.48	6.22	0.12	5.02	5.97	2.38
19	H27-1b	2873–2910	nd	80.04	18.30	1.65	0.49	0.65	1.08	2.22	1.75	1.27	0.75	6.15	0.12	3.73	5.50	2.19
20	P35-1b	3180–3271	0.8206	74.32	18.02	7.65	0.73	0.74	1.40	2.86	2.34	1.22	1.06	5.36	0.23	3.76	6.20	2.15
21	H19-5c	2467–2480	0.7603	83.67	10.00	6.34	0.35	0.49	0.76	1.60	1.66	0.96	0.87	7.51	0.19	7.14	6.13	2.10
22	H19-5b	2725–2748	0.7715	81.16	9.32	9.52	0.22	0.32	0.36	0.91	1.21	0.75	0.41	6.40	0.10	5.84	3.76	2.52
23	P30-1c	2711–2726	nd	77.67	16.29	6.04	0.48	0.42	0.61	1.52	1.93	0.79	0.95	5.58	0.12	5.61	5.16	2.42
24	P34-1a	3612–3638	0.8227	68.72	24.68	6.60	0.13	0.27	0.85	1.25	1.98	0.63	0.54	6.58	nd	4.25	4.20	2.18

Note: All oils were collected from the Zhujiang Formation. Density was measured at 0.101 Mpa and 20 °C. SAT, ARO and NSO + ASPH represent saturated, aromatic, NSO and asphaletene fractions of oils. I, II and III are rearranged oleananes; OL = 18α(H)-oleanane; $C_{30}H$ = C_{30} 17α(H)-hopane; Y1 = des-A-oleanane; Pr/Ph = pristane/phytane; $C_{30}D$ = C_{30}-diahopane; TT = tricyclic terpane; W, T, T1 and R are C_{30} bicadinanes with different configurations. BMI-1 = Bicadinanes-T/(T1 + R) (Mathur, 2014). nd = not determined.

(0.7603–0.8227 g/cm^3), according to the bulk properties of the fluids provided by the China National Offshore Oil Corporation (CNOOC). All oils were deasphaltened by filtering using petroleum ether. The residual solutions were treated with standard column chromatography (silica gel/alumina 3:1, w/w), sequentially using petroleum ether, a mixture of dichloromethane and petroleum ether (2:1, v/v), and a mixture of dichloromethane and methanol (9:1, v/v) as elution solvents to obtain saturated, aromatic and NSO fractions. The contents of saturated hydrocarbons for oils from the Baiyun Sag are significantly higher than the sum of asphaltenes and NSOs, with an average of 79.21 % and 5.56 %, respectively (Table 1).

Gas chromatography (GC) analyses of saturated hydrocarbons were performed on a Shimadzu GC-2010 instrument equipped with a HP-5 elastic quartz capillary column (30 m × 0.25 mm × 0.25 μm). The oven temperature was initially set at 100 ℃, then increased to 300℃ at 4 ℃ per minute, finally held at constant temperature for 25 min.

The saturated hydrocarbons were pretreated with molecular sieves (5 Å) to increase the relative concentrations of biomarkers before performing GC–MS analysis, in view of the low concentration of biomarkers in light oils or condensates. GC–MS analyses for saturated and aromatic hydrocarbons of the oils were carried out on an Agilent 6890GC/5975iMSD instrument coupled with a HP-5MS (60 m × 0.25 mm i.d., 0.25 μm film thickness) fused silica capillary column. The GC–MS analyses for saturated fractions were performed under the following conditions. The GC split injector temperature was set at 300 ℃. The temperature of the GC oven was initially set at 50 ℃ (hold 1 min), then ramped up to 120 ℃ at 20 ℃/min, and then to 310 ℃ at 3 ℃/min, finally maintained at 310 ℃ for 25 min. For GC–MS analysis of the aromatic hydrocarbons, the oven temperature was ramped up from 50 ℃ to 310 ℃ at the rate of 3 ℃/min and then kept isothermal for 16 min.

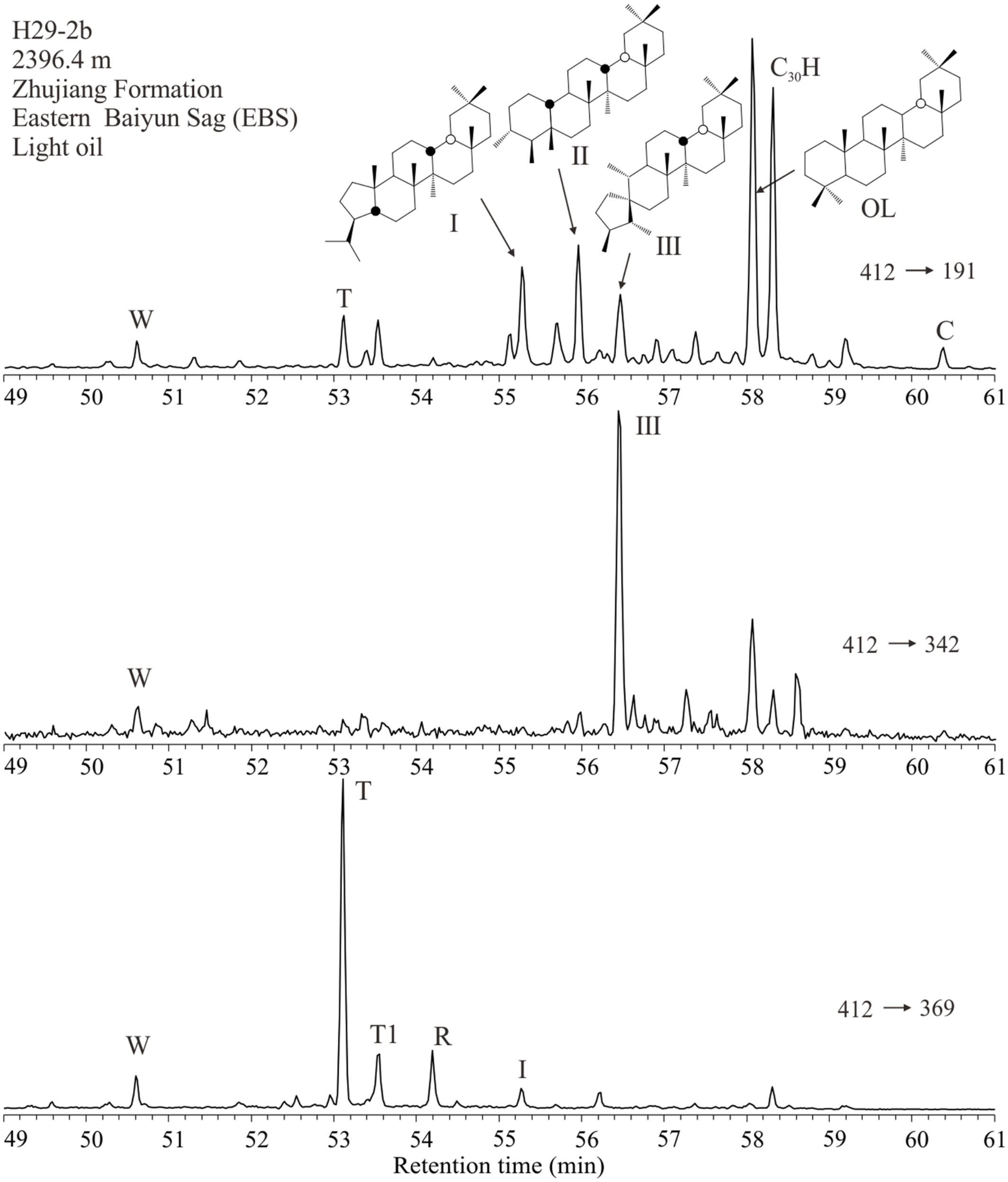

Fig. 3. Gas chromatography-mass spectrometry-mass spectrometry transitions m/z 412 to 191, 342 and 369 showing the presence of C_{30} triterpanes in a representative oil sample from the Baiyun Sag. I, II and III are rearranged oleananes; I = 5(4 → 3) *abeo*-3α(H), 5β(H), 18α(H)-oleanane; II = 3α, 5β-dimethyl-23α, 25-dinor-10β(H), 18α(H)-oleanane; III = 1(10 → 5) *abeo*-3β-methyl-24β-nor-18α(H)-oleanane; OL = 18α(H)-oleanane; C_{30}H = C30 17α(H)-hopane; C = 19α(H)-taraxastane. W is a C_{30} bicadinane with *cis*-cis–trans configuration. The compounds T, T1 and R are C_{30} bicadinanes with trans–trans–trans configuration.

The mass spectrometer (MS) was equipped with an electron ionization (EI) source at an ionization energy of 70 eV.

The GC–MS–MS analyses for selected saturated hydrocarbons were performed using a Thermo Fisher TSQ8000 Evo instrument coupled with a HP-5MS (60 m × 0.25 mm i.d., 0.25 μm film thickness) fused silica capillary column. The temperature of the GC oven was initially set at 50 ℃ (1 min), then increased to 120 ℃ at 20 ℃/min, and to 250 ℃ at 4 ℃/min, and ramped up to 310 ℃ at 3 ℃/min, and finally kept isothermal for 30 min. The carrier gas was helium at a flow rate of 1 mL/min. Argon was utilized as collision gas for GC–MS–MS analysis at a pressure of 0.6 mTorr.

4. Results and discussion

4.1. Occurrence and identification

Rearranged oleananes I, II and III were detected previously in Niger Delta oils and Assam Basin oils by GC–MS–MS (Nytoft et al., 2010, 2014). The results of GC–MS–MS analyses with parent-to-daughter transitions of 412 → 191, 412 → 342 and 412 → 369 are diagnostic for C_{30} triterpanes in representative Tertiary oils from the Baiyun Sag (Fig. 3). The mass chromatograms exhibit a series of rearranged oleananes (I, II and III) and bicadinanes (W, T, T1 and R). The distribution pattern of rearranged oleananes in Baiyun Sag oils is similar with that of Niger Delta oils, with a predominance of I, II and III structures, eluting in an orderly pattern between *T*-bicadinane and oleanane. Moreover, rearranged oleananes I and III can also be identified on 412 → 369 and 412 → 342 transitions because of their specific *m/z* 369 and 342 diagnostic fragments.

A number of C_{30} triterpanes, including bicadinanes (W, T, T1 and R), rearranged oleananes (I, II and III), oleanane (OL) and taraxastane (C), were also identified by comparison of their elution sequence and relative retention time in *m/z* 412 and 191 mass chromatograms with those published in the literature (Lu et al., 2019; Ding et al., 2021) (Fig. 4). Bicadinanes were first detected in Far Eastern oils (Grantham et al., 1983), and were considered to originate from angiosperms (Peters et al., 2005). The *m/z* 412 mass chromatograms show that bicadinane W and T are more abundant than the other isomers in oils from the study area.

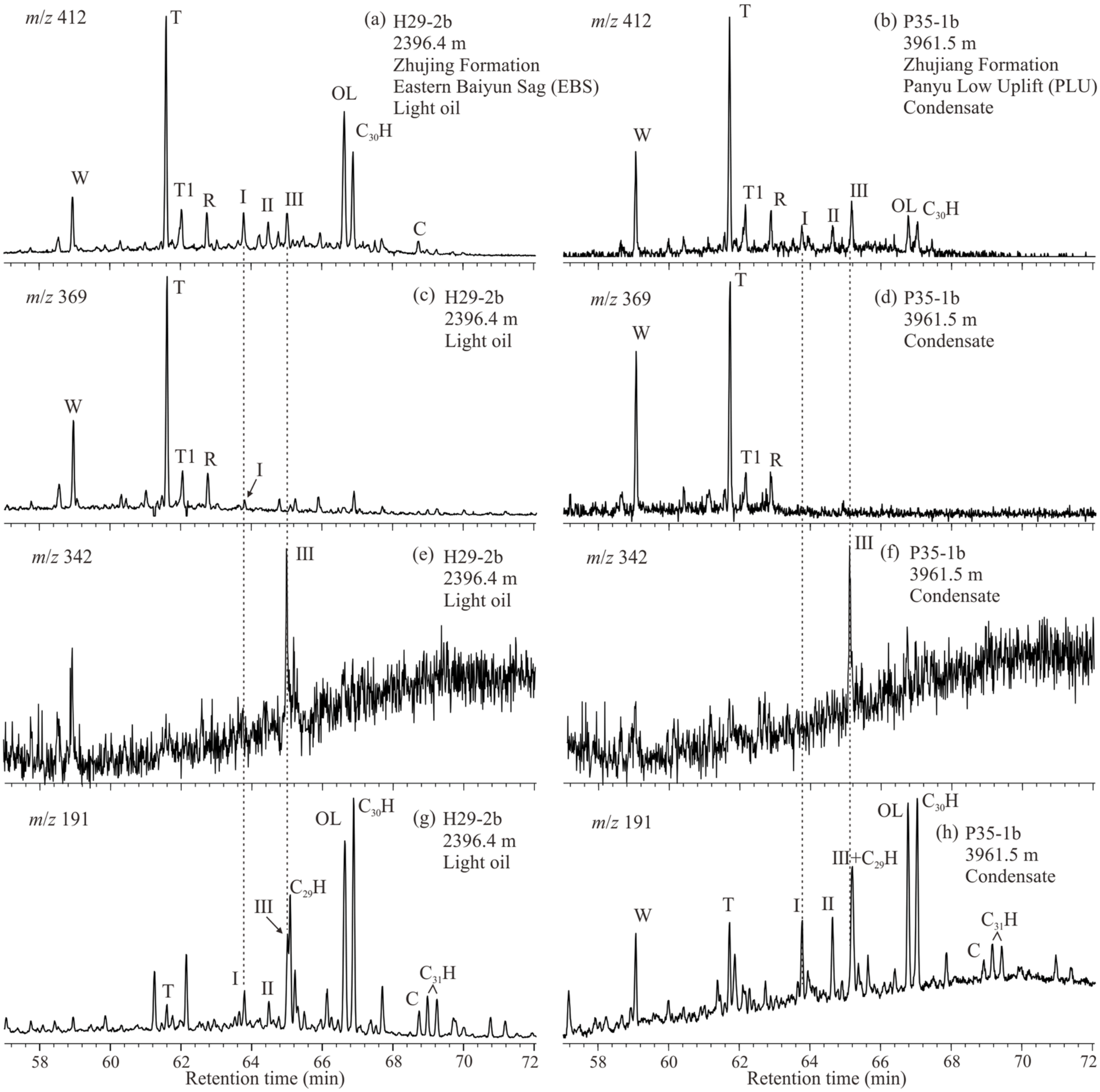

Fig. 4. Representative *m/z* 412, 369, 342 and 191 mass chromatograms show the distribution of rearranged oleananes in oils from the Baiyun Sag. Compounds I, II and III are rearranged oleananes. Compounds W, T, T1 and R are bicadinanes. OL = 18α(H)-oleanane; $C_{30}H$ = C_{30} 17α(H)-hopane.

Rearranged oleananes I, II and III elute systematically between bicadinane R and oleanane in m/z 412 mass chromatograms (Fig. 4a, b). Moreover, rearranged oleananes I and III can also be recognized in m/z 369 and 342 mass chromatograms respectively (Fig. 4c, d). Due to the coelution of rearranged oleanane III and C_{29} hopane in the m/z 191 mass chromatogram (Fig. 4g, h) (Faraj et al., 2017), C_{30} triterpanes were quantified using their peak areas on m/z 412 mass chromatograms. The des-A-oleanane (Y1) is a kind of tetracyclic terpane of terrigenous origin (Xiao et al., 2018), and is commonly present in oleanane-containing oils, such as oils from the Taranaki Basin of New Zealand and Niger Delta (Woolhouse et al., 1992; Samuel et al., 2010). In addition to oleanane and rearranged oleananes, abundant des-A-oleanane was detected in m/z 191 mass chromatograms of oils from the Baiyun Sag in this study (Fig. 5a, b). As shown in the Fig. 5c, d, des-A-oleanane elutes after the C_{24} tricyclic terpane in the m/z 191 mass chromatogram, and can also be detected in the m/z 330 mass chromatogram, due to its specific m/z 330 diagnostic fragment.

The mass spectrum of oleanane has a molecular ion at $M^{+\cdot}$ 412, and a base peak ion at m/z 191, with diagnostic fragment ions at m/z 397, 259, 274 and m/z 177 (Fig. 6). Mass spectra of rearranged oleananes and 19α(H)-taraxastane show characteristics similar to that of oleanane, with a base peak of m/z 191 and a $M^{+\cdot}$ 412 molecular ion. The isopropyl group on the A-ring gives the fragment at m/z 369 for rearranged oleanane I. The m/z 342 ion in the mass spectrum of rearranged oleanane III originates by cleavage of its 5-membered spiro A-ring (Woolhouse et al., 1992). Thus, the abundance of the m/z 342 ion in its mass spectrum distinguishes the spectrum of rearranged oleanane III from those of the other isomers. Moreover, mass spectra of rearranged oleananes obtained from the Baiyun Sag oil were similar to those of purified compounds (Nytoft et al., 2010). The mass spectrum of des-A-oleanane exhibits a molecular ion at $M^{+\cdot}$ 330, with a base peak of m/z 191, which corresponds to a C_{24} tetracyclic terpane (Fig. 6).

4.2. Distribution and relationships between rearranged oleananes

Ratios of rearranged oleananes and C_{30} hopane for oils from different parts of the Baiyun Sag are shown in Fig. 7. The systematic variation of $I/C_{30}H$, $II/C_{30}H$ and $III/C_{30}H$ ratios indicate that rearranged oleananes I, II and III have similar biological precursors. Oils from EBS and NEBS-B are characterized by relatively high $OL/C_{30}H$ and low $(I + II + III)/C_{30}H$ values, with an average of 1.74 and 1.38, respectively. By contrast, oils from the NEBS-A and PLU have lower values of $OL/C_{30}H$ (average 1.00) and higher $(I + II + III)/C_{30}H$ (average 1.74), suggesting a different source to that of the EBS and NEBS-B oils (Fu et al., 2019).

The relative abundances of the different rearranged oleananes correlated well for oils from the Baiyun Sag. The slope of the linear equation for a plot of $I/C_{30}H$ vs $II/C_{30}H$ is similar to that of the $III/C_{30}H$ vs $II/C_{30}H$ plot, suggesting similar biological origins or diagenetic conditions for these rearranged oleananes (Fig. 8a, b). Rearranged oleananes were only detected in oleanane-bearing sediments or oils (Nytoft et al., 2010). A positive relationship was observed between the relative abundances of rearranged oleananes and oleanane in this study. Nevertheless, the linear equation in the plot of $OL/C_{30}H$ vs $II/C_{30}H$ for the EBS and NEBS-B oils differs from that for PLU and NEBS-A oils, with a slope of 2.57 and 1.17, respectively (Fig. 8c). Although oleanane in the oil from well H34-2b is more abundant than that from well H19-5C (Table 1), the relative abundances of rearranged oleananes in these oils exhibit little variation, with $(I + II + III)/C_{30}H$ ratios with a mean of 1.62. Therefore, the abundance of rearranged oleananes may be influenced by multiple factors, not just the inputs of angiosperms. In addition, both rearranged oleananes and des-A-oleanane may have the same biological origins, and are likely derived from higher-plant triterpenoids (Nytoft et al., 2010; Woolhouse et al., 1992), which is supported by the strong positive relationship between the $Y1/C_{30}H$ ratios and $II/C_{30}H$ ratios in this study (Fig. 8d).

A probable diagenetic pathway for rearranged oleananes (I, II, III) was proposed by Nytoft et al. (2010) and has been modified here to show the relationship between rearranged oleananes and des-A-oleanane during diagenesis (Fig. 9). Des-A-oleanane likely forms by degradation of an oleanane triterpenoid (such as β-amyrin). β-amyrone, one of natural constituents of angiosperms, can also form by oxidative transformation of β-amyrin (Dutta et al., 2014). Despite the relative low stability of β-amyrone, higher abundance of β-amyrone were detected in some fossil resins compared to β-amyrin, implying that β-amyrin is susceptible to oxidation (Dutta et al., 2014). The degradation of the β-amyrone A-ring is initiated by microorganisms under reducing conditions (Huang et al., 2008; Trendel et al., 1989), and can also be accelerated by photochemical alteration under an oxidative

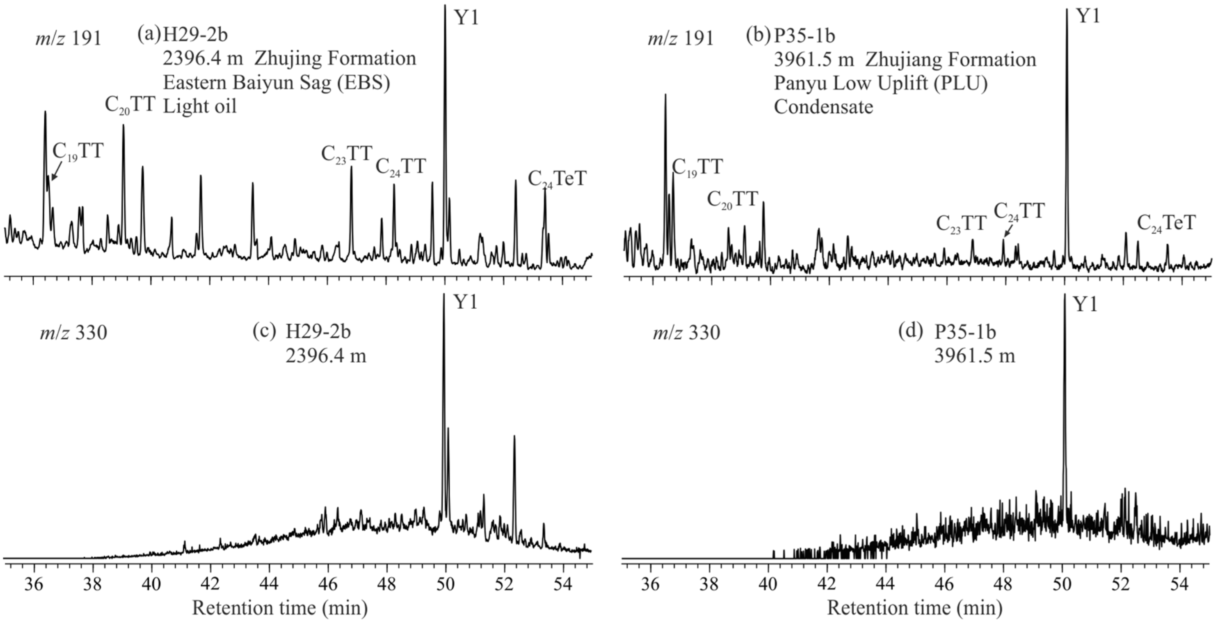

Fig. 5. Representative m/z 330 and 191 mass chromatograms showing the distribution of des-A-oleanane in oils from the Baiyun Sag. Y1 = des-A-oleanane; TT = tricyclic terpane; TeT = tetracyclic terpane.

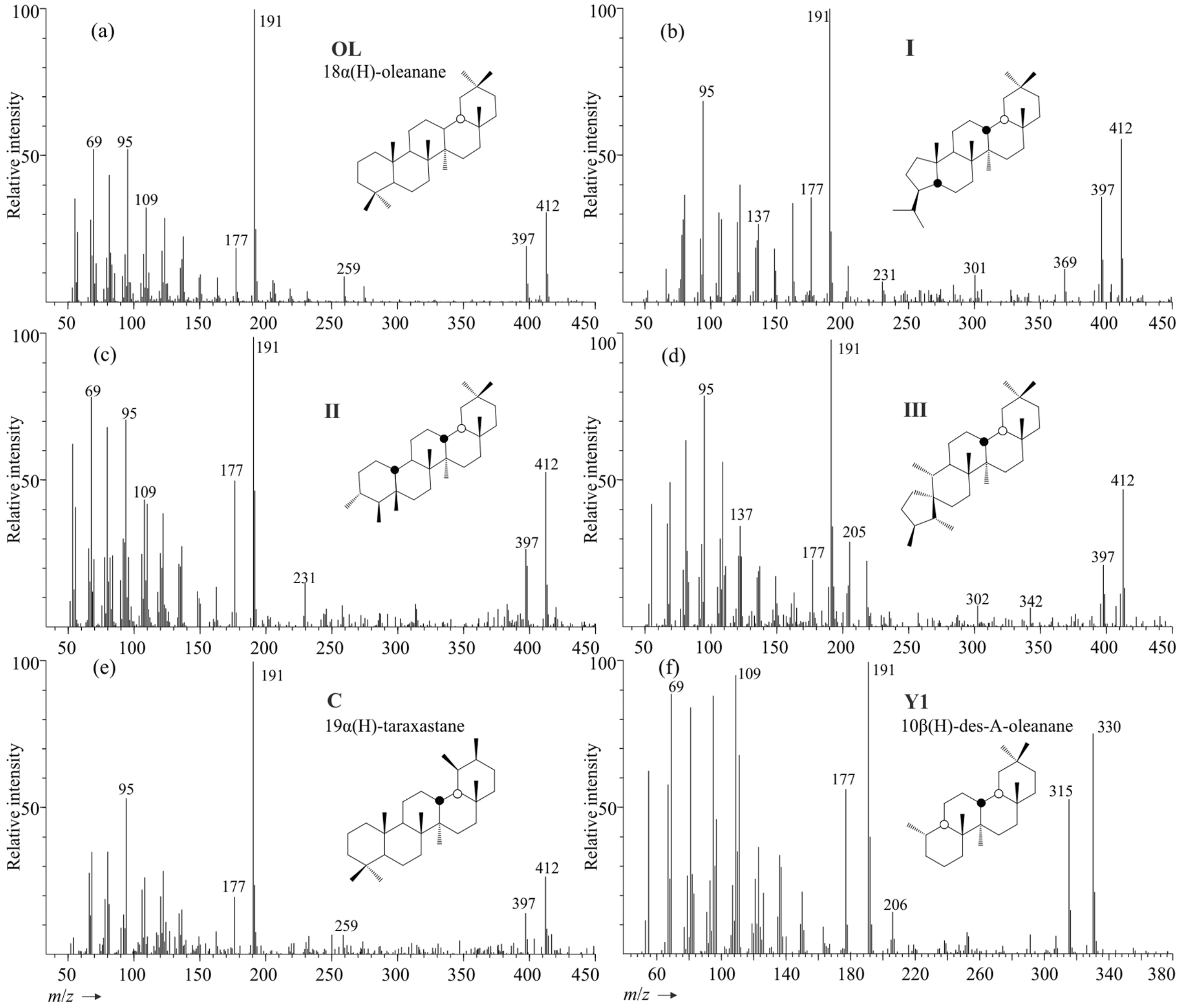

Fig. 6. Mass spectra of 18α(H)-oleanane (a), rearranged oleananes (b, c, d), 19α(H)-taraxastane (e) and des-A-oleanane (f), from full-scan GC–MS analysis of an oil sample (H29-2b, 2396.4 m) from the eastern Baiyun Sag.

environment. (Simoneit et al., 2009). 3, 4-Seco-olean-12-en-3-olic acid, which is a precursor of des-A-oleanane, forms during this reaction. Des-A-oleanane can form after further degradation of the 3, 4-seco-triterpenoidal acid (Samuel et al., 2010). In contrast, rearranged oleananes are thought to be dehydration and rearrangement products of oleananoid triterpenoid functionality at C-3, like β-amyrin (olean-12-en-3β-ol). As shown in Fig. 9, the dehydration of β-amyrin leads to generation of oleana-2, 12-diene, which is the precursor of oleanane. Contraction of ring A for oleana-2, 12-diene would produce 5(4 → 3) *abeo*-3α(H), 5β(H), 18α(H)-oleanane (rearranged oleanane I). Subsequently, the 3α, 5β-dimethyl-23α, 25-dinor-10β(H), 18α(H)-oleanane (rearranged oleanane II) and 1(10 → 5) *abeo*-3β-methyl-24β-nor-18α(H)-oleanane (rearranged oleanane III) could form by further rearrangement and hydrogenation during diagenesis (Nytoft et al., 2014). Overall, both des-A-oleanane and rearranged oleananes originate from functionalized oleanoid triterpenoids (such as β-amyrin), but by markedly different formation processes.

4.3. *Factors influencing the abundance of rearranged oleananes*

4.3.1. *Source of organic matter*

As shown in the gas chromatograms of the saturated hydrocarbons, oils from the Baiyun Sag have *n*-alkanes ranging from *n*-C_{11} to *n*-C_{33}, with a predominance of short-chain *n*-alkanes (Fig. 10). Moreover, the oils do not exhibit any unresolved complex mixtures (UCMs) in the gas chromatograms, suggesting little or no biodegradation. A pristane/*n*C_{17} vs phytane/*n*C_{18} plot can be used to determine organic matter types and depositional conditions of source rocks or related oils (El Diasty et al., 2022; Shanmugam, 1985). Fig. 11 shows that the oils from the Baiyun Sag originated from source rocks dominated by terrigenous organic matter deposited under oxidizing conditions. Evidence suggests that oils from many basins worldwide containing rearranged oleananes originated from source rocks rich in terrigenous organic matter, such as oils from the Qiongdongnan Basin of China, Upper Assam Basin of India, and Niger Delta Basin of Nigeria (Nytoft et al., 2010; Zhu et al., 2018; Mathur, 2014). The relative abundance of rearranged oleananes and oleanane exhibit a positive correlation (Fig. 8c). High inputs of angiosperms must be an important factor affecting the abundance of rearranged oleananes.

4.3.2. *Depositional and diagenetic conditions*

The dibenzothiophenes/phenanthrene (DBT/Phen) vs pristane/phytane (Pr/Ph) plot is useful to illustrate the depositional environment and lithology of source rocks (Rabbani et al., 2014; Hughes et al., 1995). The oils from the Baiyun Sag fall into the same zone typical of fluvial/deltaic environments, with the DBT/Phen ratios less than 1.0 (Fig. 12a). The distribution pattern of tricyclic terpanes (TT) can also provide important information on source-rock organic composition and depositional environment. A ternary diagram of C_{19+20}TT, C_{21}TT and C_{23}TT was proposed to determine the sedimentary environments of source rocks or related oils based on hundreds of samples from different basins

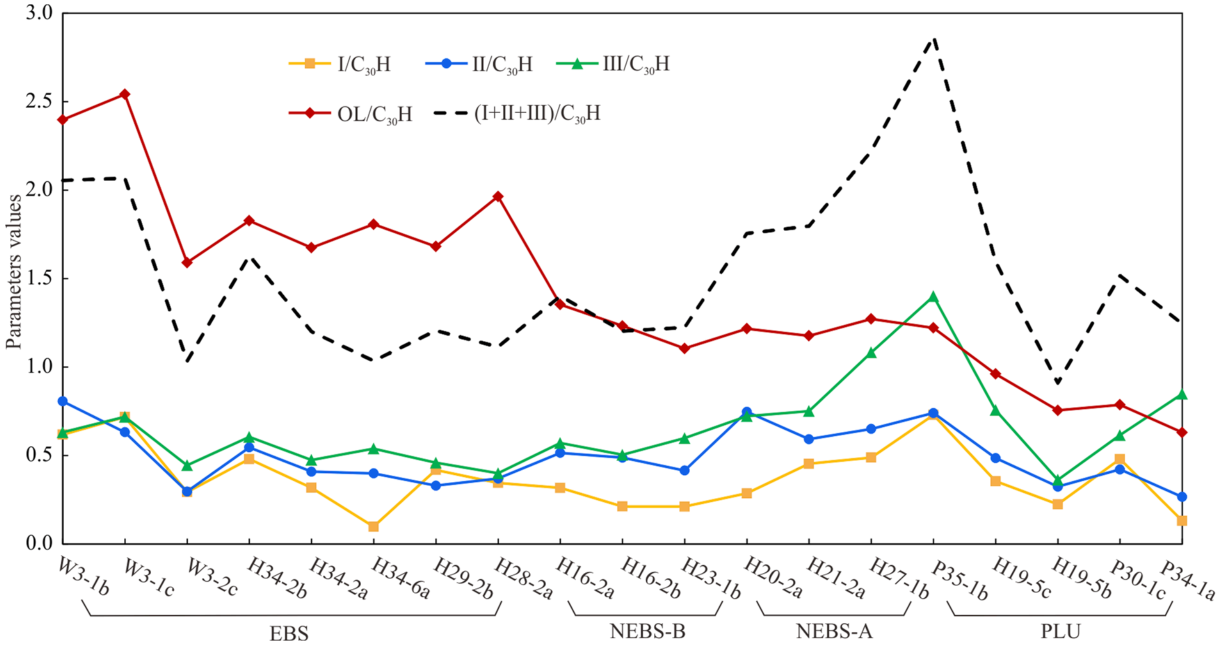

Fig. 7. Distributions of oleanane and rearranged oleananes in oils from the Baiyun Sag.

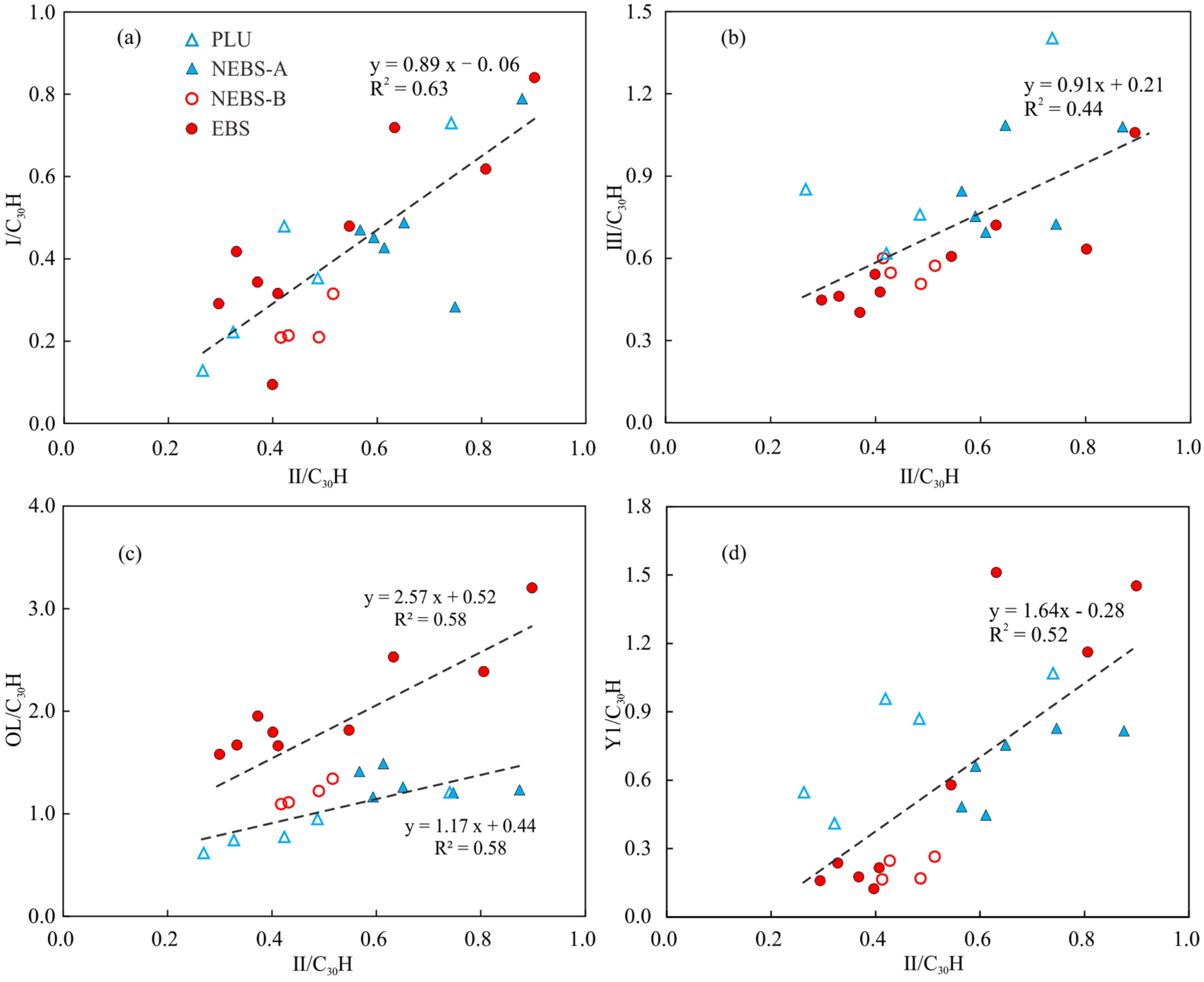

Fig. 8. Correlation between the relative abundance parameters: (a) $I/C_{30}H$ vs $II/C_{30}H$; (b) $III/C_{30}H$ vs $II/C_{30}H$ (c) OL/ $C_{30}H$ vs $II/C_{30}H$; (d) $Y1/C_{30}H$ vs $II/C_{30}H$. The upper linear equation in (c) was obtained by fitting the samples in the EBS and NEBS-B. The lower equation was obtained by fitting the PLU and NEBS-A oils. The linear equations in (a), (b) and (d) were obtained on the basis of 24 oils from the Baiyun Sag.

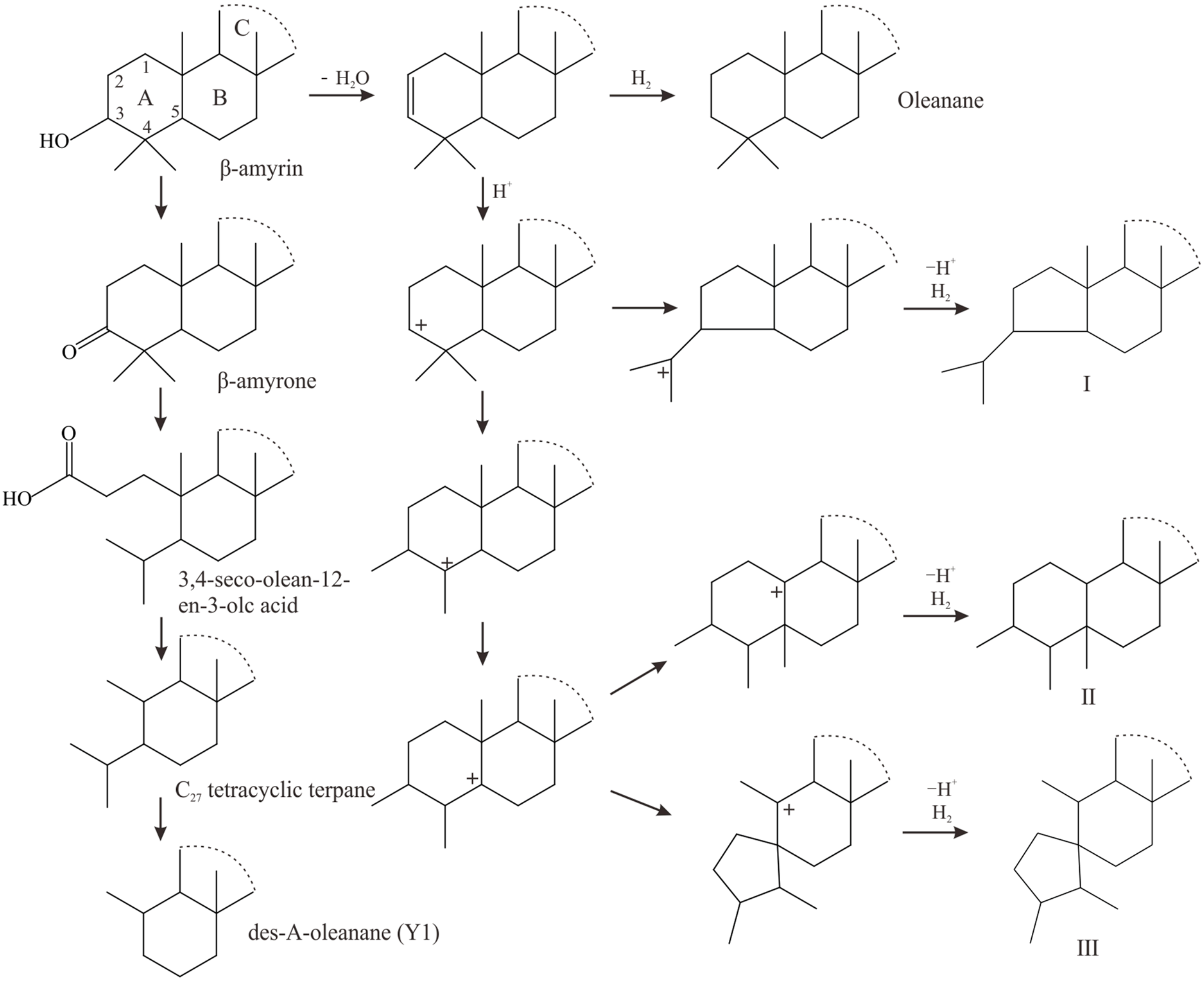

Fig. 9. Possible modes for the formation of rearranged oleananes and des-A-oleanane from β-amyrin (modified from Nytoft et al. 2010, 2014; Samuel et al. 2010).

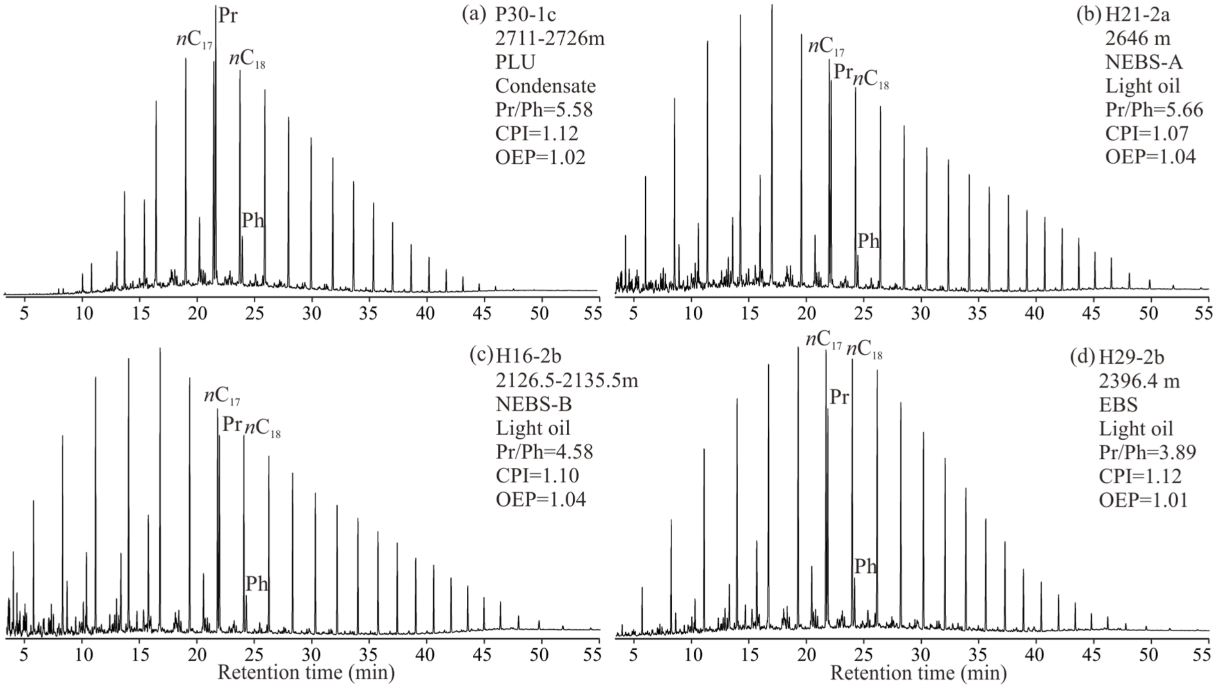

Fig. 10. Representative gas chromatograms of saturated hydrocarbons in oils from the Baiyun Sag showing the distribution of *n*-alkanes.

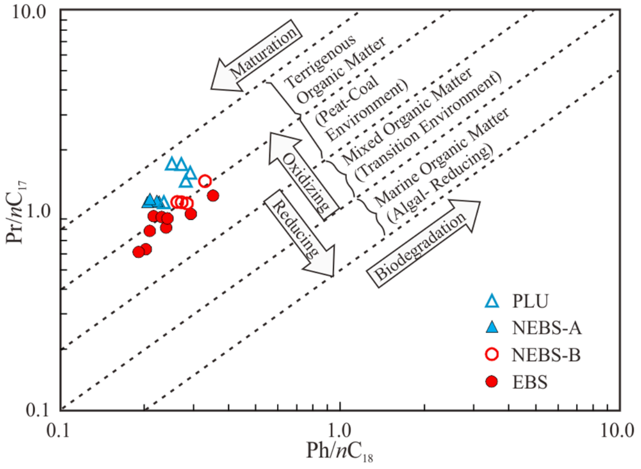

Fig. 11. Pr/nC_{17} vs Ph/nC_{18} plot (after Shanmugam 1985) for oils from the Baiyun Sag.

(Xiao et al., 2019a). C_{19}TT and C_{20}TT are generally more abundant in deltaic or swamp source rocks and related oils (Ekweozor and Strausz, 1983), while, marine or salt water lacustrine source rocks are usually characterized by a predominance of C_{23}TT (Aquino Neto et al., 1983). The Tertiary oils from the Baiyun Sag show consistent C_{19} to C_{23}TT distribution patterns, with a dominance of C_{19}TT and C_{20}TT (Fig. 5a, b). As shown in Fig. 12b, the NEBS-B and EBS oils fall within the fluvial or deltaic source rock zone, while the PLU and NEBS-A oils are likely derived from source rocks formed under a coal-swamp environment. During deposition of the upper member of the Enping Formation (Early Oligocene), large scale coal-bearing braided deltas developed in the PLU with the drainage evolution of the paleo-Pearl River (Zeng et al., 2019). Moreover, a marine transgression is believed to have started at this time (Zeng et al., 2020), which is supported by the occurrence of marine dinoflagellates in mudstones from the upper member of the Enping Formation (Sun et al., 2020). These coal-bearing deltas apparently played a significant role in the formation of source rocks in the Baiyun Sag. High abundances of rearranged oleananes were also detected in oils from the Qiongdongnan Basin, which originated from coastal plain-swamp and shallow marine source rocks (Zhu et al., 2018). Rearranged oleananes are thought to be a sign of autochthonous deposition of terrigenous organic matter (Nytoft et al., 2010; Murray et al., 1994), and are rare in source rocks deposited under deep water conditions.

Saturated oleanoids are the result of a small leak in the dominant diagenetic reactions leading to aromatic oleanoids (Murray et al., 1997a), and their abundance is sensitive to the degree of marine influence (Murray et al. 1997b). The proportion of oleanane vs hopane for sediments from the South Sumatra Basin correlated well with indicators of marine influence (Murray et al., 1997a). The PLU oils originated from Enping Formation coal-bearing source rocks in the Panyu Low Uplift (Fu et al., 2019), while the EBS oils are mainly from shallow marine or marine influenced lacustrine source rocks of the Enping Formation in the east of the Main Subsag (Jiang et al., 2021, 2022; Guo et al., 2014). OL/C_{30}H values for EBS oils are much higher than those of the PLU oils (Table 1). The Oligocene marine transgression appears to be an important factor limiting the abundance of saturated oleanoids in oils from the study area. Sulphur is thought to have played a critical role in hindering oleanoid aromatization (Murray et al., 1997a), because of the absence of aromatic oleanoids in evaporitic carbonate samples with abundant sulphurised plant triterpenes (Poinsot et al., 1995). Additionally, depositional environments with high pH or/and special microbial communities, similar to that found in evaporitic systems, may have hindered aromatization of oleananes (Murray et al., 1997a). The Oligocene marine transgression may have enhanced the expression of saturated oleanoids by affecting these environmental conditions in the study area.

As for the saturated oleanoids, the relative abundance of rearranged oleananes *vs* oleananes largely depends on diagenetic conditions. The diagenetic reactions for generation of rearranged oleananes start with acid-catalysed, or microbially mediated, dehydration of precursor molecules (ten Haven et al., 1992). Because of the typically low pH of tropical peat swamps (Sikora and Keeney, 1983), the generation of rearranged oleananes is enhanced by deposition of plant organic matter in marine influenced peat swamp conditions. The PLU oils are characterized by relatively abundant rearranged oleananes compared to oleanane (Fig. 7), with average (I + II + III)/C_{30}H and OL/C_{30}H ratios of 1.63 and 0.87, respectively (Table 1). The peat swamp environment of the Panyu Low Uplift must favour generation of rearranged oleananes. In contrast, abundant oleanane with low rearranged oleananes was expected in deep-water settings where plant matter was directly transported to the deposition site and underwent diagenesis under alkaline conditions (Murray et al., 1997a). The EBS oils, which originated from shallow marine or marine influenced lacustrine source rocks, therefore exhibit a higher abundance of oleanane than rearranged oleananes (Fig. 7), with average OL/C_{30}H and (I + II + III)/C_{30}H ratios of 2.08 and 1.57, respectively. In addition, as shown in Fig. 8c, the different linear equations in plots of OL/ C_{30}H *vs* II/C_{30}H for the PLU and EBS oils probably result from their differing diagenetic conditions.

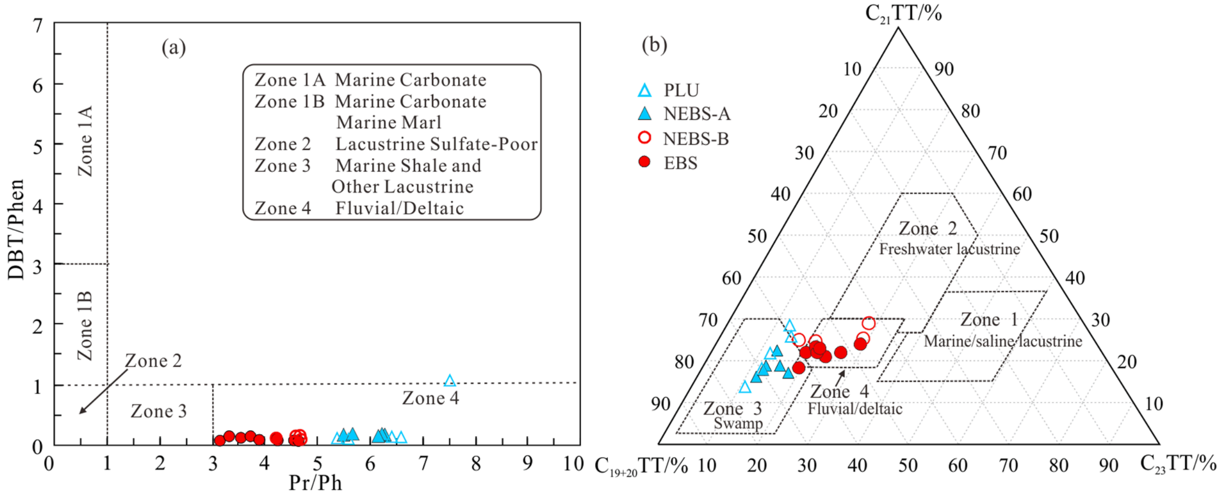

Fig. 12. Plot of DBT/Phen vs Pr/Ph (a) (after Hughes et al., 1995) and ternary diagram of C_{19}-C_{23}TT (b) (after Xiao et al. 2019a) showing the sedimentary environment of source rocks for oils from the Baiyun Sag. Note: DBT/Phen = dibenzothiophenes/phenanthrene; Pr/Ph = pristane/phytane; TT = tricyclic terpanes.

The sedimentary environments leading to high relative abundance of diasteranes (oxic and clay-rich conditions) appear also to favour generation of rearranged oleananes (Nytoft et al., 2010). The results of this study support this view, since the proportion of rearranged oleananes to oleananes correlated well with the abundance of 17α-diahopane in oils (Fig. 13). 17α-Diahopane was considered to originate from hopanoid precursors (like bacteriohopanetetrol and diplopterol), undergoing clay-mediated acidic catalysis and rearrangement in sub-oxic to oxic conditions (Xiao et al., 2019b; Li et al., 2015; Moldowan et al., 1991). Furthermore, the concentration of 17α-diahopane in rock or oil samples is also associated with thermal maturity, particularly in the late oil window (Li et al., 2009). Despite containing a higher relative abundance of 17α-diahopane (Fig. 13), the PLU and NEBS-A oils are not necessarily thermally more mature than the EBS and NEBS-B oils (Fig. 14a). Thermal maturity is obviously not the main factor controlling the abundance of 17α-diahopane in oils from the study area. The linear correlation between the relative abundance of rearranged oleananes and 17α-diahopane must result from their similar diagenetic conditions. The ratios of rearranged oleananes/oleanane strongly correlate with the diasteranes/steranes ratios for oils from many basins (Nytoft et al., 2010). The generation of diasteranes is facilitated by oxic and acidic conditions during diagenesis (Moldowan et al., 1986). Diasteranes/steranes ratios are often applied to differentiate crude oils from carbonate and argillaceous source rocks. However, van Kaam-Peters et al. (1998) proposed that the diasteranes/steranes ratio correlated well with the proportion of clay minerals *vs* organic matter content, rather than the content of clay mineral for source rocks from several areas. The enrichment of rearranged oleananes in oils from the PLU therefore is favoured by oxic and acidic conditions. Clay minerals may also enable rearranged oleananes formation. Nevertheless, the rearranged oleananes do not necessarily increase with enhanced clay content.

4.3.3. Maturity

The carbon preference index (CPI) (Bray and Evans, 1961) and odd-to-even predominance (OEP) (Scalan and Smith, 1970) can be applied to roughly estimate the maturity of crude oil. Oils from the Baiyun Sag show a full distribution of n-C_{11} to n-C_{33} n-alkanes, with n-C_{13} to n-C_{19} short-chain n-alkanes in predominance. Moreover, the CPI and OEP values are close to 1.0 (Fig. 10), suggesting that these oils are thermally mature. The thermal maturity of oils can also be measured by the Methyl-Phenanthrene Distribution Fraction (MPDF), which is less influenced by kerogen types or lithology and thought to be a reliable thermal maturity indicator (Fu et al., 2019; Kvalheim et al., 1987; Bao et al., 1992). MPDF parameters (F_1 and F_2) are based on the equation proposed by Kvalheim et al. (1987) using peak areas of methylphenanthrenes in the m/z 192 mass chromatograms of aromatic hydrocarbon fractions. Calibrations between vitrinite reflectance (R_o) and the MPDF parameters were performed by Bao et al. (1992). As shown in Fig. 14a, oils from the Baiyun Sag reached the mature (0.7–1.1 %, R_o) to high mature stage (R_o greater than 1.1 %), with the F_1 values more than 0.45. No significant correlation was observed between (I + II + III)/OL ratios and F_1 values for oils from the study area, implying that the relative abundance of rearranged oleananes may not be influenced by thermal maturity (Fig. 14b). Molecular mechanics calculations and geochemical data indicated that the 4-/1-MDBT ratio is a valid maturity indicator, even at high maturity (Yang et al., 2019). Due to the low impact of biodegradation and diagenetic effects, the bicadinane maturity indicator (BMI-1) was considered to be a reliable maturity index for oils (Sosrowidjojo et al., 1996; Mathur, 2014). Neither 4-/1-MDBT nor BMI-1 showed correlation with (I + II + III)/OL ratios in these oils (Fig. 14c, d). This observation further suggests that thermal maturity is not a major factor controlling the relative abundance of rearranged oleananes in oils from the Baiyun Sag.

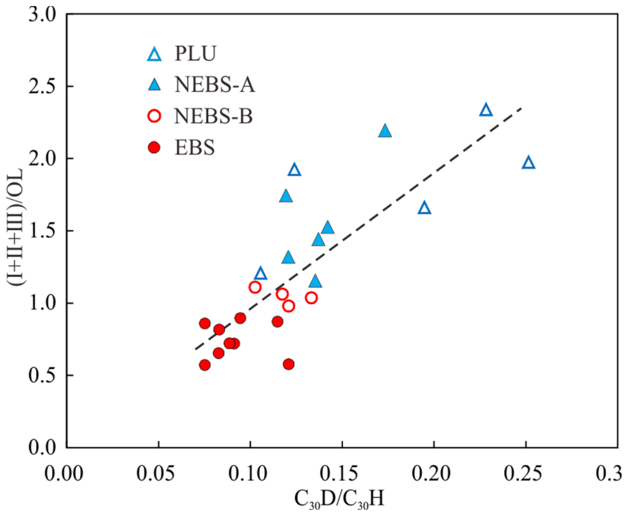

Fig. 13. Plot of (I + II + III)/OL vs $C_{30}D/C_{30}H$ for oils from the Baiyun Sag. $C_{30}D$ = C_{30} 17α(H)-diahopane; $C_{30}H$ = C_{30} 17α(H)-hopane.

4.4. Application in oil-oil correlations

The relative abundance of rearranged oleananes in oils is principally controlled by the source of organic matter and the depositional environment, rather than thermal maturity of their source rocks. The abundance of rearranged oleananes relative to oleanane therefore may offer a robust indicator for oil family classification and oil-source correlation. As shown in Fig. 15a, the plot of bicadinane (I + II + III)/OL and Pr/Ph can differentiate the PLU and NEBS-A oils from EBS and NEBS-B oils. Oils from the PLU and NEBS-A are characterized by relatively high Pr/Ph and (I + II + III)/OL ratios compared to EBS and NEBS-B oils (Fig. 15a), consistent with different origins of these oils. Furthermore, two oil groups can be distinguished depending on plots of (I + II + III)/OL *vs* $C_{19+20}TT/C_{23}TT$ and $T/C_{30}H$ vs (I + II + III)/OL (Fig. 15b, c), which is in accordance with the result of $T/C_{30}H$ vs $OL/C_{30}H$ plot (Fig. 15d). The relative abundance of rearranged oleananes therefore is a reliable indicator for oil family classification in the study area. The oil families of the Baiyun Sag include Family A and Family B. Family A oils, including the EBS and NEBS-B oils, are characterized by relatively low Pr/Ph, $T/C_{30}H$, (I + II + III)/OL ratios, and relatively high $OL/C_{30}H$ values. In contrast, Family B oils consist of the PLU and NEBS-A oils, which have relatively high Pr/Ph, $T/C_{30}H$, (I + II + III)/OL ratios, and relatively low $OL/C_{30}H$ values. As discussed above, the different groups of crude oils in the study area may mainly result from the diversity of diagenetic conditions during source rock deposition.

Considering the variation of formation processes for oleanane, rearranged oleananes and des-A-oleanane, a ternary diagram of relative abundances of these compounds was proposed to show the genetic relationship between oils from the study area (Fig. 16a). Relative abundances of oleanane, rearranged oleananes and des-A-oleanane for oils also reveal two oil families. The Family A oils have more abundant oleanane, comprising EBS and NEBS-B oils. In contrast, the Family B oils include the PLU and NEBS-A oils, and are rich in rearranged oleananes and des-A-oleanane. Bicadinanes are known as a class of pentacyclic triterpanes of terrigenous origin (Van Aarssen et al., 1990, 1992), and their relative abundances do not co-vary with that of oleanane in discovered oils (Lu et al., 2019; Peters et al., 2005). Hopanes are pentacyclic triterpanes that originated from precursors in bacterial membranes (Ourisson et al., 1979). Because of the different biological precursors and/or diagenetic processes for oleanane, bicadinanes and C_{30} hopane, the relative abundances of these pentacyclic triterpanes appear to be effective for oil family classification and oil-source correlation (Pearson and Alam, 1993). The ternary diagram of relative abundances of oleanoid triterpanes, bicadinanes and C_{30} hopane was applied for oil-oil correlation in this study, using the proportion of peak areas quantified from m/z 412 mass chromatograms (Fig. 16b). This

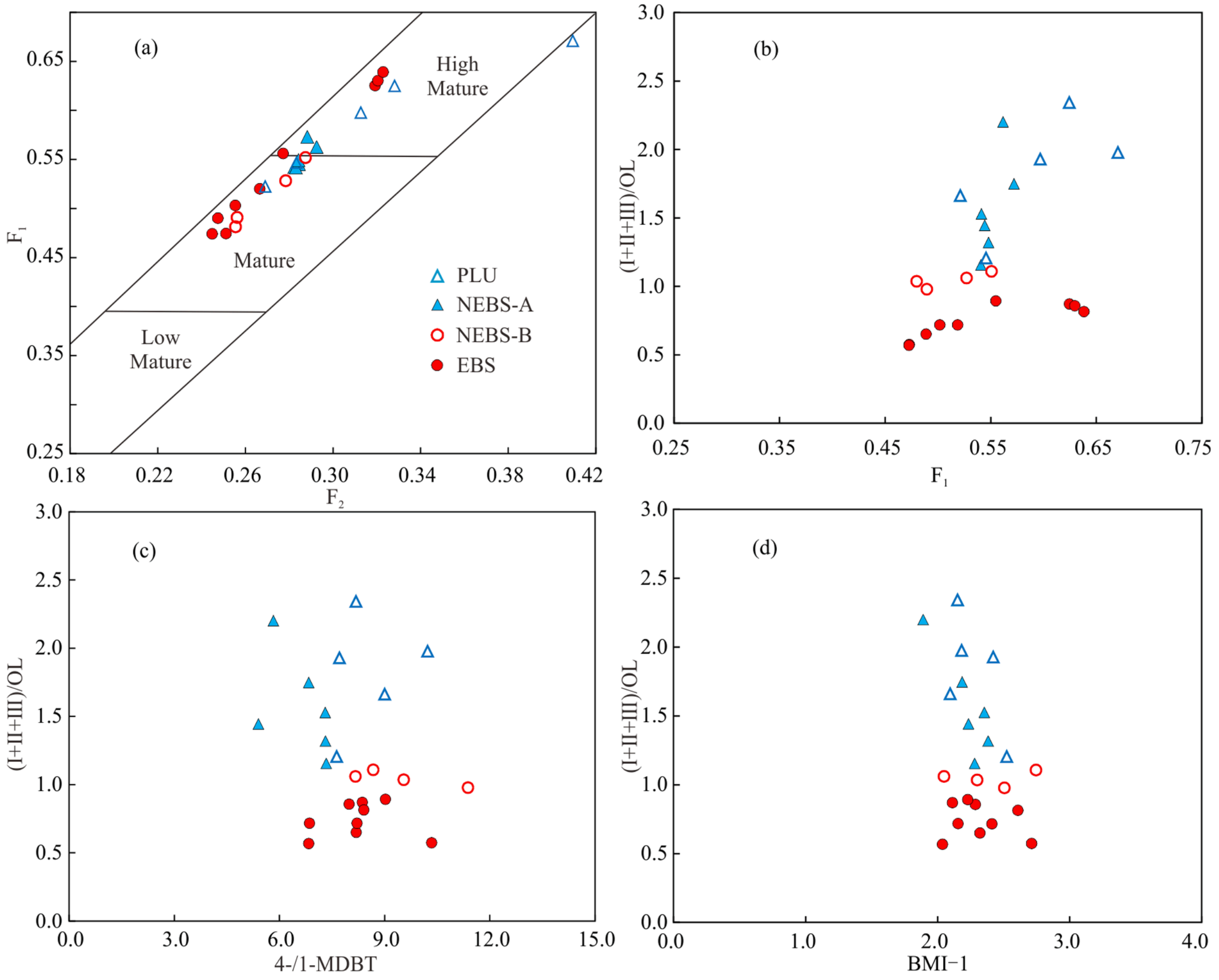

Fig. 14. Plots of (a) the Methyl-Phenanthrene Distribution Fraction (MPDF) F_1 vs F_2; (b) (I + II + III)/OL vs F_1; (c) (I + II + III)/OL vs 4–1-MDBT; (d) (I + II + III)/OL vs BMI-1 for oils from the Baiyun Sag. Note: F_1= (2-MP + 3-MP)/(2-MP + 3-MP + 1-MP + 9-MP); F_2 = 2-MP/(2-MP + 3-MP + 1-MP + 9-MP) (Kvalheim et al., 1987); the measured vitrinite reflectance (R_o) were used to calibrated the high mature (R_o greater than 1.1 %), mature (0.7 %-1.1 %, R_o) and low mature (R_o less than 0.7 %) boundaries in Fig. 13a (Bao et al., 1992); MP = methylphenanthrenes; 4-/1-MDBT = 4-/1-methyldibenzothiophene; BMI-1 = Bicadinane T/(T1 + R).

ternary diagram classifies oils from the Baiyun Sag into two oil families, which is in agreement with the result of Fig. 16a. Therefore, the ternary diagram of relative abundances of oleanane, rearranged oleananes and des-A-oleanane in oils offers an effective and convenient approach for oil-oil correlation.

5. Conclusions

Three major rearranged oleananes I, II and III were identified in Tertiary oils from the Baiyun Sag using GC–MS and GC–MS–MS. The relative abundances of the different rearranged oleananes linearly correlate with each other for the 24 oil samples. The relative abundances of rearranged oleananes also exhibit strong positive correlations with those of oleanane and des-A-oleanane. The investigation of diagenetic pathways indicates that rearranged oleananes, oleanane and des-A-oleanane originate from functionalized oleanane triterpenoids, by apparently different formation processes. The relationships of rearranged oleananes and other biomarkers suggest that source of organic matter and diagenetic conditions of their source rocks are the principal factors affecting the abundance of rearranged oleananes in oils, rather than thermal maturity. High input of angiosperms is a vital factor for the enrichment of rearranged oleananes in sediments or related oils. Although oleanane precursors are vulnerable to aromatization leading to aromatic oleanoids, the Oligocene marine transgression in the study area may have enhanced the expression of saturated oleanoids. Within saturated oleanoids, the relative abundance of rearranged oleananes *vs* oleanane is largely determined by diagenetic conditions. The PLU oils are characterized by high abundance of rearranged oleanane compared with oleanane. On the contrary, the EBS oils have higher content of oleanane than that of rearranged oleananes. The formation of rearranged oleananes appears to be facilitated by oxic and acidic peat swamp conditions in the PLU. Two oil families in the Baiyun Sag were identified using the relative abundance of rearranged oleananes and many other source-related indicators. Family A oils, including the EBS and NEBS-B oils, are mainly distributed in the eastern and northeastern Baiyun Sag. Family B oils include the PLU and NEBS-A oils, and are principally located in the Panyu Low Uplift and northeastern part of the sag. The results of oil-oil correlation by the relative abundance of rearranged oleananes are consistent with those using the other source-related indicators. Rearranged oleananes are therefore effective tools for oil-oil correlation. The triangular plot of relative abundances of oleanane, rearranged oleananes and des-A-oleanane and the ternary diagram of relative abundances of oleanoid triterpanes, bicadinanes and C_{30} hopane are proposed to be effective means for oil-oil correlation or oil source analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

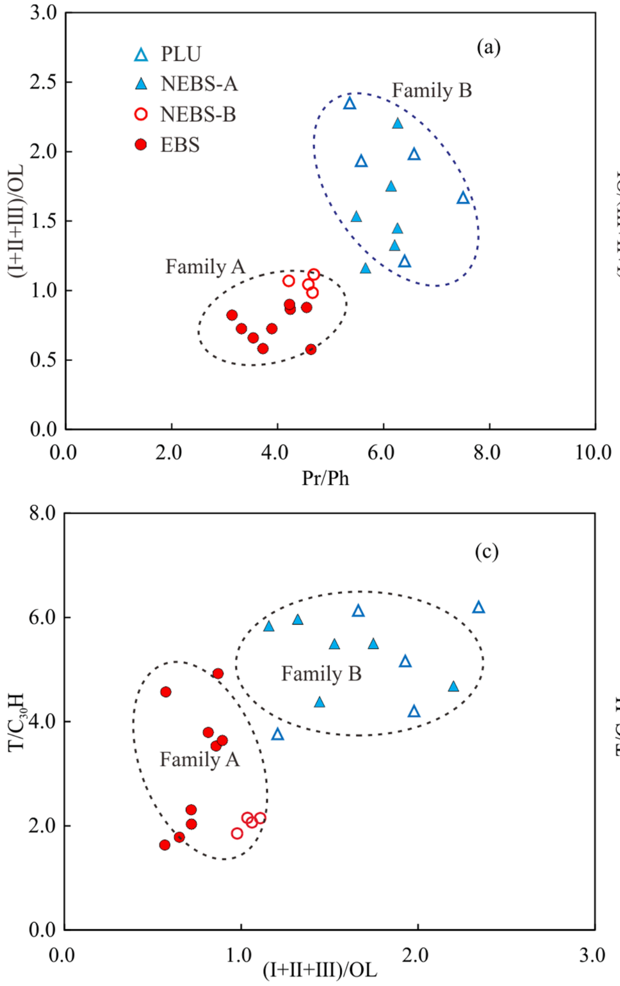

Fig. 15. Plots of (a) (I + II + III)/OL vs Pr/Ph, (b) (I + II + III)/OL vs C_{19+20}TT/C_{23}TT, (c) bicadinane T/C_{30}H vs (I + II + III)/OL, (d) bicadinane T/C_{30}H vs OL/C_{30}H for oils from the Baiyun Sag, showing that oils from the study area can be divided into two groups.

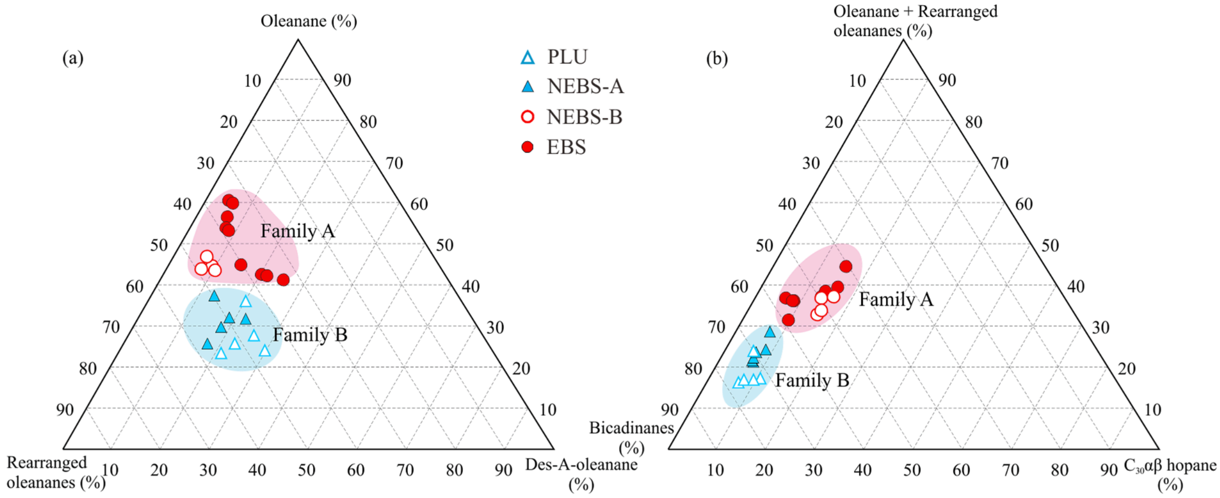

Fig. 16. Ternary diagram of oleanane, rearranged oleananes and des-A-oleanane (a), and ternary diagram of oleanane + rearranged oleananes, bicadinanes and C_{30} hopane (b) in oils from the Baiyun Sag. Rearranged oleananes include I, II and III compounds; bicadinanes include bicadinane W and T.

the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

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Appendix A. Supplementary data

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