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Molecular organic geochemistry and origin of oil in the Potwar Basin, Pakistan

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ABSTRACT

The Potwar Basin (PTB) is a prominent geological feature located in northern part of Pakistan, and is considered as one of the active and productive regions for petroleum and gas exploration in Pakistan. In this study, eight crude oil specimens originating from three distinct fields within the PTB were comprehensively examined to decipher the environmental conditions, source of organic matter (OM) and oil-oil correlations using gas chromatography coupled with flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GC–MS). The molecular marker and hierarchical cluster analysis of PTB oils reveal two different crude oil families. Family-I showed relatively low values of Pr/Ph, C_{19}TT/C_{23}TT and C_{25}TT/C_{24}TeT, C_{27}-C_{29} regular steranes, dibenzothiophene (DBT), fluorene (FL) and dibenzofuran (DBF), as well as C_{26}/C_{28} TAS (20S) and C_{27}/C_{28} TAS (20R). These results suggest that Family-I crude oils derived from marine environment of suboxic water bodies with higher contribution from green algae or planktonic microbes. However, Family II contains comparatively high values of the aforementioned molecular parameters, indicating that crude oils mainly originated from a lacustrine environment with a higher contribution of plant organisms under oxidizing conditions. Saturated hydrocarbon maturity parameters such as CPI and OEP, and C_{31}22S/(C_{31}22S + C_{31}22R) and C_{32}22S/(C_{32}22S + C_{32}22R) indicate PTB crude oils are thermally mature, while aromatic indices reveal that Family-II crude oils are high mature. The present research defines that PTB crude oils contributed from mixed organic matter sources of marine and lacustrine majorly from marine sedimentary environment with the bloom of algae and/or higher plants.

1. Introduction

The PTB, located in Pakistan, is a geologically imperative region within the Indian plate, characterized by tectonic deformation and the overthrust of the Sub-Himalayas on its northern and northwest sides. It serves as an active and productive area for the exploration of hydrocarbon resources in Pakistan, encompassing various stratigraphic sequences ranging from the Cambrian to the Miocene periods (Khan et al., 1986; Kadri, 1995). Numerous oil and gas fields, varying in size from small to medium, have been successfully identified within the PTB. Notably, the Dhurnal oil field, extracting oil from the Eocene Sakessar Formation, stands as the largest among these discoveries (Jaswal et al., 1997; Wandrey et al., 2004a; Fazeelat et al., 2011).

The PTB has been extensively studied by the USGS (United States Geological Survey), which has identified multiple distinct petroleum systems within the basin. These systems have been classified as Eocambrian-Miocene TPS (Total Petroleum Systems), where petroleum of varying characteristics is generated at different depths within a distance of a few kilometers (Wandrey et al., 2004a). The basin exhibits a complex structural style and contains numerous stacked sources and reservoirs, leading to the mixing of hydrocarbons (Ahmed and Alam, 1990; Wandrey et al., 2004a). This complexity presents challenges when conducting studies on the migration of oil between different reservoirs and source rocks. While the predominant source of hydrocarbons within the basin is attributed to the Patala Formation of the Paleocene age, which is characterized by kerogen types II and III, there are indications

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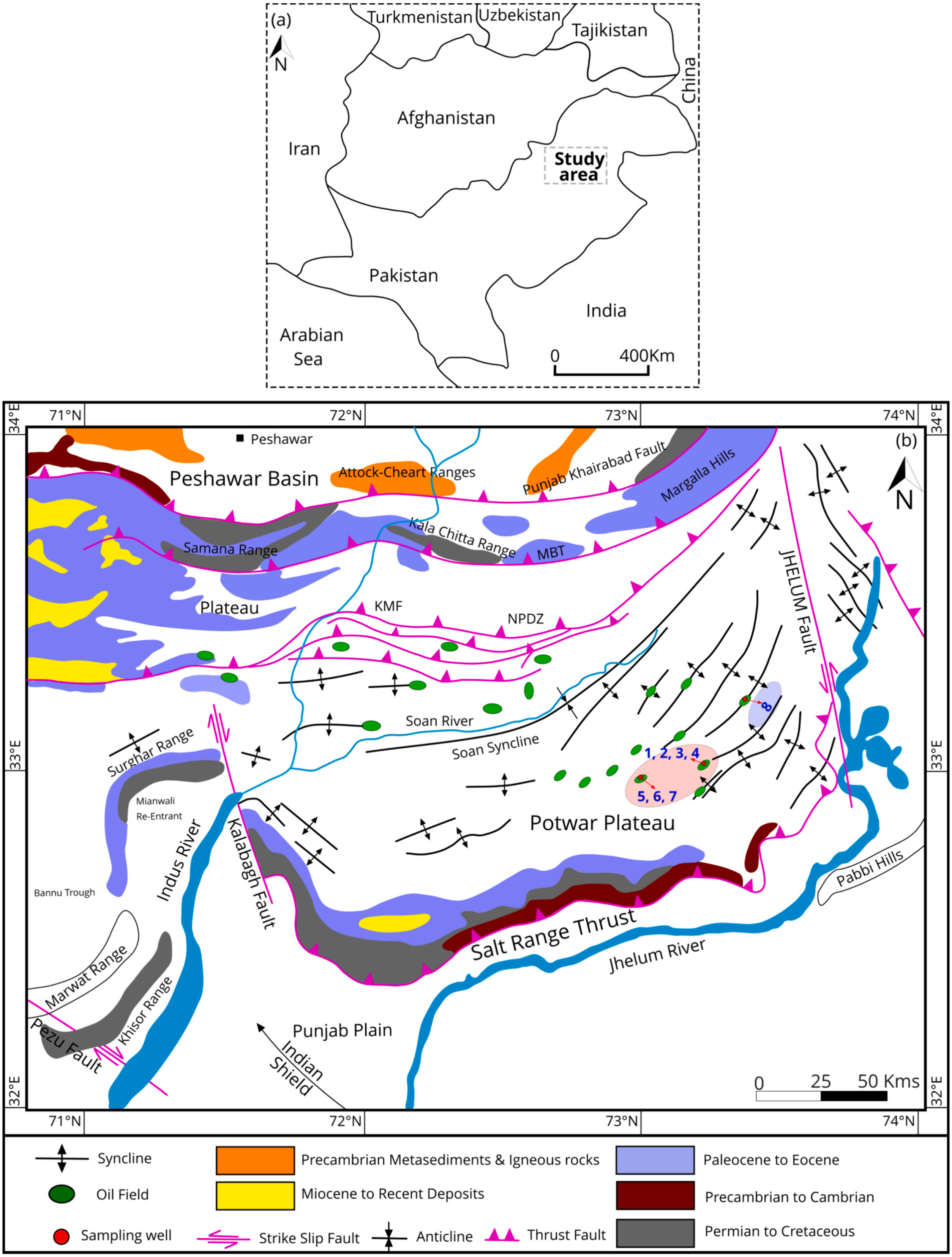

Fig. 1. Map showing the location of the study area (a), geological map showing the studied crude oils and structural features of PTB, Pakistan (b) (after modified wandrey et al. 2004;and references therein).

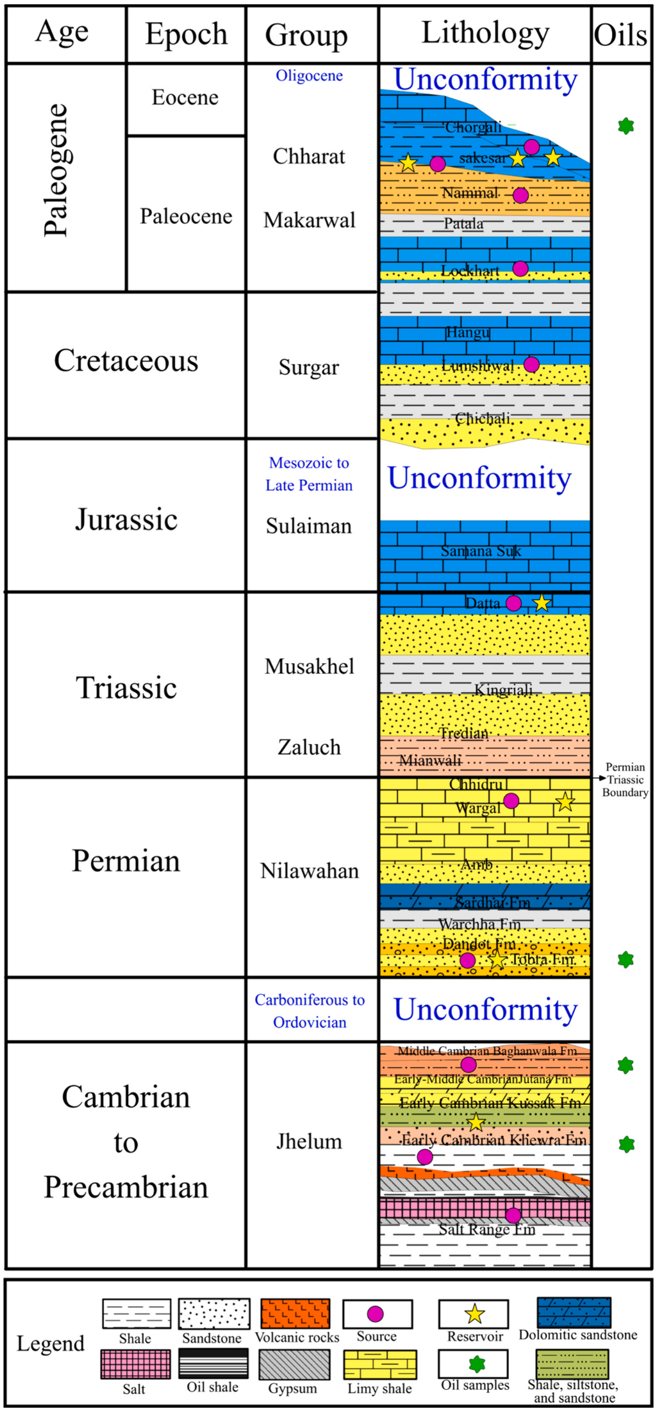

Fig. 2. Lithostratigraphic columnar section showing the PTB formations, reservoirs and source rocks.

that alternative source rock formations might have contributed to hydrocarbon generation across diverse regions within the PTB. (Ahmad and Alam, 2007; Zaidi et al., 2012; Craig et al., 2018). The oldest organically rich Ediacaran Salt Range Formation (ESRF) comprised of clastic, carbonate, and evaporitic sequence containing type I to II kerogen, is regarded as the main potential source rock, also Sardhai and Chidru formations from the Permian age appeared to be the possible source rock with a higher abundance of organic matter (Quadri and Quadri, 1997; Wandrey et al., 2004a; Ahmad and Alam, 2007).

The PTB contains possible source rock layers from the Precambrian, Permian, and Paleocene periods that possess sufficient total organic carbon content (TOC), as evidenced by their thermal evolution reaching the level of early to peak stage of oil generation. Earlier research was done on the source rocks of the PTB utilizing conventional geochemical methods (Khan et al., 1986; Ahmad and Alam, 2007; Fazeelat et al., 2010; Zaidi et al., 2012; Khan et al., 2020). Moreover, research on oil classification was conducted utilizing saturated and polycyclic aromatic hydrocarbons as well as stable isotopes of carbon and hydrogen (Asif et al., 2009; Muhammad Asif et al., 2011; Fazeelat et al., 2011; Asif and Fazeelat, 2012). Their findings reveal that the PTB contains a mixture of light and heavy oils sourced from marine, terrigenous, and mixed OM origins. To deepen our understanding regarding the molecular characteristics of PTB oils and oil classification, their OM source and associated depositional environment, we have obtained crude oils from three different oil fields with different depths (not previously reported) (Muhammad Asif et al., 2011; Asif and Fazeelat, 2012) (Fig. 1).

Biomarkers like steranes and terpanes are key in oil classification, being more resistant to biodegradation than *n*-alkanes and acyclic isoprenoids. These compounds, indicative of eukaryotic and prokaryotic origins, are important for identifying oil and source families, and assessing paleo-environments and thermal maturity (Summons and Walter, 1990; Jinggui et al., 2005; Grice et al., 2009; Fang et al., 2015; Huang et al., 2016; Xiao et al., 2022). However, their reliability decreases with increased biodegradation. Beyond a biodegradation level of 5 on the Peters and Moldowan (1993) scale, even these robust biomarkers, including steranes, terpanes, and aromatic hydrocarbons, can be significantly altered (Peters and Moldowan, 1993; Peters et al., 2005). Additionally, the applicability of certain aromatic hydrocarbons, including DBT, FL, DBF, triaromatic steroids, and triaromatic dinosteroids, extends to correlation studies involving both oils and their source rocks (Chen et al., 2018). In molecular marker research especially for complex oils, multiple methods are recommended to assess the geochemical heterogeneities between oil to oil and/or oil to source rocks, therefore, this study presents a comprehensive molecular marker analysis employing GC-FID and GC–MS and hierarchical cluster (HC) analysis to achieve oil-oil correlation, the origin of OM source and depositional environments of the Paleozoic and Paleogene crude oils from specific fields within the PTB, Pakistan.

2. Geological setting

The PTB in the northern part of Pakistan, constitutes approximately half of the Upper Indus Basin. Geographically located along the western foothills of the Himalayas, this region lies at the northern periphery of the Indian plate (Fig. 1). Within the basin, there is a diverse assemblage of rock formations from Precambrian to Tertiary ages. Notably, three major unconformities can be observed at the boundaries between the Ordovician and Carboniferous periods, the Mesozoic and Late Permian periods, as well as the Eocene and Oligocene periods (Kazmi and Jan, 1997; Aamir and Siddiqui, 2006).

The sedimentary succession in the PTB commenced with substantial Precambrian evaporite formations which were subsequently overlain by comparably thinner deposits ranging from the Cambrian to Eocene times (Kadri, 1995; Wandrey et al., 2004b), these were then succeeded by extensive deposits from the Miocene to Pliocene periods (Fig. 2). Severe tectonic activities during the Himalayan Orogeny, particularly between the Pliocene and middle Pleistocene times, led to the partitioning of the Eocene to Cambrian rock succession, a process facilitated by the presence of Precambrian salt deposits. As a consequence of compressional forces acting on this Eocene to Cambrian sequences within the PTB, numerous folds and faults have been developed in the region (OGDC, 1996; Quadri and Quadri, 1996; Aamir and Siddiqui, 2006). Consequently, the presence of multiple overlapping hydrocarbon sources and reservoirs, coupled with intense tectonic activity, resulted in the intermingling of petroleum derived from various sources. This poses a significant challenge in classifying the oils present within the region due to their complex and diverse composition resulting from these geological

Table 1
Physical characteristics of the crude oils and sleeted parameters based on *n*-alkanes and isoprenoids using GC-FID.

Oils	Reservoir Formation	Depth	Age	API	Max-Peak	C_{21}^{-}/C_{22}^{+}	$C_{(21+22)}/C_{(28+29)}$	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	CPI	OEP	SAT (%)	ARO (%)	ASP (%)	NSO (%)	SAT/ARO	C_{30}H/(Pr + Ph)
Paleozoil-1	Tobra/Jutana Formation	3518	Permian-middle Cambrian	22	C_{17}	1.04	1.59	1.32	0.90	0.69	1.07	1.00	35.16	28.64	26.47	9.73	1.23	0.32
Paleozoil-2	Tobra Formation	3505	Permian	24	C_{17}	1.08	1.68	1.38	0.90	0.65	1.04	1.00	41.64	31.59	16.64	10.13	1.32	0.32
Paleozoil-3	Khewra Formation	3580	Early Cambrian	25	C_{18}	1.08	1.64	1.33	0.92	0.69	1.04	0.98	44.07	29.00	14.88	12.05	1.52	0.31
Paleozoil-4	Tobra Formation	3534	Permian	26	C_{17}	1.12	1.68	1.51	0.90	0.62	0.99	1.01	41.59	31.88	15.14	11.40	1.30	0.35
Paleozoil-5	Tobra/Khewra Formation	2493	Permian-Early Cambrian	18	C_{18}	1.01	1.56	1.17	0.85	0.71	0.97	0.98	36.11	28.16	27.10	8.63	1.28	0.30
Eocoil-6	Sakessar Formation	2223	Eocene	12	C_{18}	0.81	1.60	0.84	0.88	0.88	1.00	0.91	16.12	28.90	46.96	8.02	0.56	0.28
Paleozoil-7	Khewra Formation	2279	Early Cambrian	18.5	C_{18}	1.03	1.55	1.12	0.85	0.72	0.99	0.96	29.33	30.96	30.36	9.35	0.95	0.29
Eocoil-8	Sakessar Formation	1840	Eocene	–	C_{15}	2.08	2.58	2.39	0.65	0.32	1.06	1.09	65.02	24.25	2.44	8.29	2.68	0.40
Eocoil-9	Sakessar Formation	1840	Eocene	–	C_{15}	1.62	2.20	1.83	0.72	0.40	1.06	1.05	65.21	25.25	5.15	9.22	2.58	0.41

Note: Pr/Ph: Pristane/Phytane; CPI = $\{(C_{25} + C_{27} + C_{29} + C_{31} + C_{33})[1/(C_{24} + C_{26} + C_{28} + C_{30} + C_{32}) + 1/(C_{26} + C_{28} + C_{30} + C_{32} + C_{34})]\}/2$; (OEP) index is measured as $(nC_{25} + 6{*}nC_{27} + nC_{29})/(4{*}nC_{26} + 4{*}nC_{28})$; Paleozoil = Paleozoic oil; Eocoil = Eocene oil.

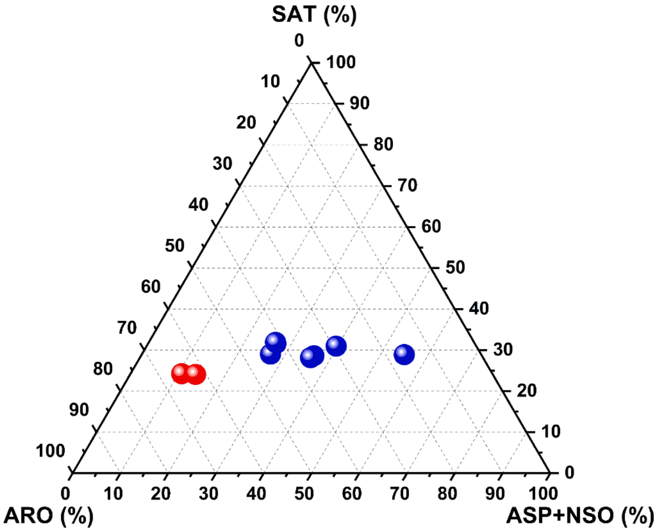

Fig. 3. Ternary diagram shows the bulk characteristics of PTB crude oils. Saturated fraction (SAT); Aromatic fraction (ARO); Non hydrocarbon fraction (NSO); Asphaltene fraction (ASP).

processes (Fazeelat et al., 2011). Within the basin, shallow marine shales of the Paleocene Patala Formation, with thicknesses varying between 20 and 180 m, could potentially function as a source rock. These shales possess OM type II to III, boasting an average TOC content of 1.4 wt.%. However, it’s conceivable that various other potential source rocks could have played a role in hydrocarbon generation across distinct areas of the PTB (Raza, 1973; Khan et al., 1986). The basin’s oldest potential source rock is the ESRF, featuring type II kerogen and an exceptionally high TOC content surpassing 30 wt.% (Ahmad and Alam, 2007; Khan et al., 2020). The ESRF comprises a thick deposition of rock-salt, marl, gypsum, carbonate, and dark oil shales, along with an igneous band known as the “Khewra Trap” (Jan et al., 1992). It is noted that the oil shales present in the ESRF have generated hydrocarbons deep within the subsurface, which have subsequently migrated and charged the upper reservoir (Ahmad and Alam, 2007; Craig et al., 2018). These geological formations have given rise to multiple small reservoirs within the PTB, resulting in the discovery of crude oil originating from various formations (Quadri and Quadri, 1996). The Cambrian succession (Khewra, Kussak, Jutana, Baghanwala formations) in the Salt Range, PTB underneath the ESRF, this sequence is locally called as “Jhelum Group”. The early Cambrian Khewra Formation, which is primarily composed of sandstone, has been found producing oil in fields A (1, 2, 3 and 4 wells) and B (5, 6 and 7 wells). In addition, oil production in field C (8 well) has been observed in the early middle Cambrian Kussak Formation (comprising sandstone and siltstone), as well as the Choragali and Sakesser formations (consisting of limestone and sandy shale) from the Eocene period (Kadri, 1995). Furthermore, field A has shown oil production in the early Middle Cambrian Jutana Formation (consisting of sandy carbonates and sandstones) and the overlying Permian Tobra Formation (composed of glacial conglomerate). Consequently, we have collected crude oil samples from these three fields (Table 1), which represent reservoirs from the Cambrian, Permian, and Eocene periods (refer to Fig. 2). Tobra, Amb, and Wargal formations of the Permian, Datta Formation from the Jurassic, Lumshiwal Formation from the Cretaceous period, and the Hangu, Lockhart, Patala, and Namal formations from the Paleocene period. Additionally, the Chorgali Formation and Margala Hill Limestone from the Eocene period, as well as the Murree Formation from the Miocene period, have also been significant contributors to petroleum and gas exploration and production in the PTB (Wandrey et al., 2004b; Craig et al., 2018).

The Late Cretaceous period marked the beginning of hydrocarbon generation in the PTB, originating from source rocks ranging from the

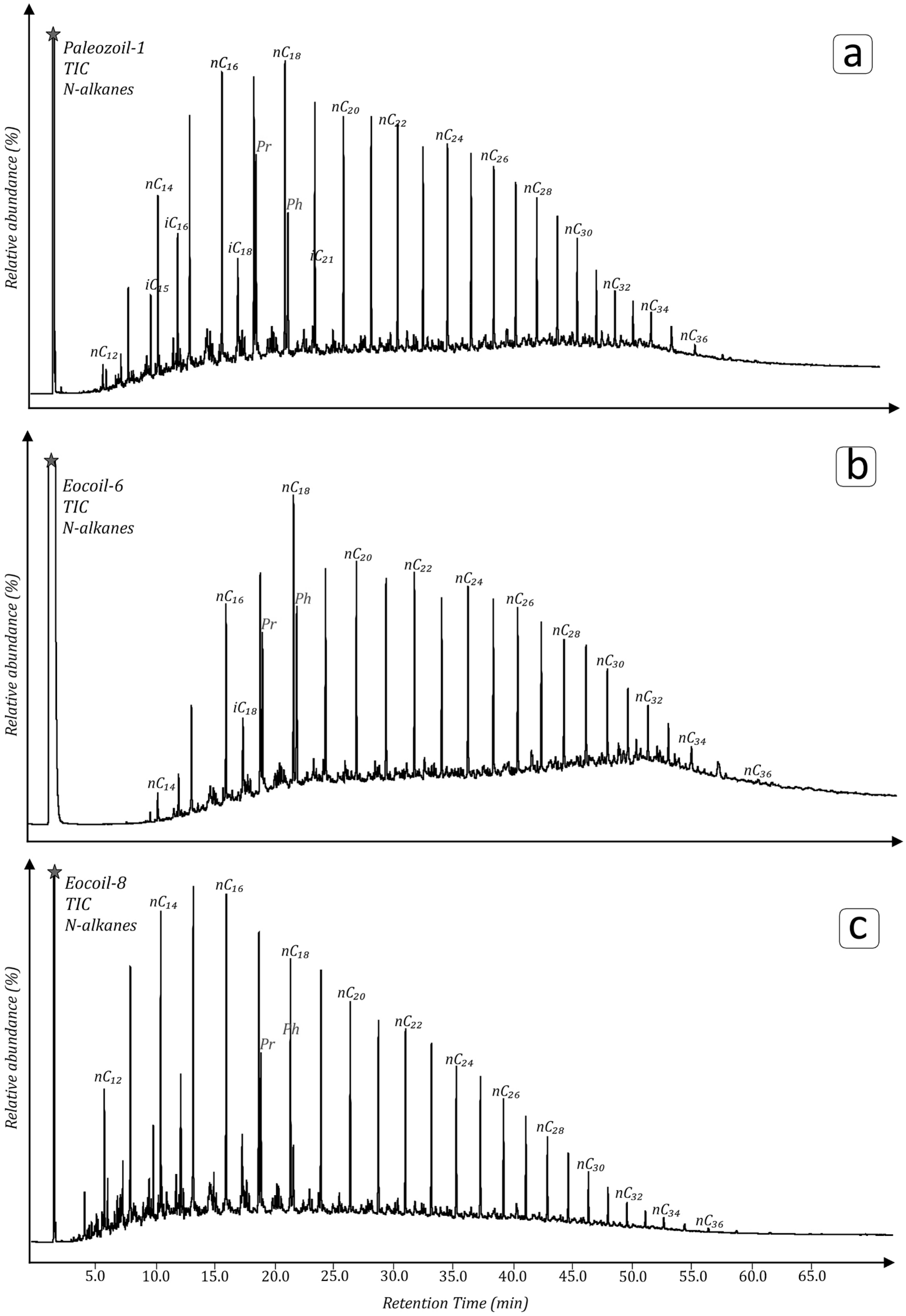

Fig. 4. Mass chromatograms of GC-FID showing *n*-alkane and isoperenoid distributions of Potwar crude oils. The red star represents the internal standard added into crude oil fractions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Cambrian to the Lower Cretaceous, and this continued with the involvement of younger source rocks from the Pliocene to recent. (OGDC, 1996; Fazeelat et al., 2010). The hydrocarbon generation and migration within the PTB initiated about 30 Ma which is regarded as the late or second hydrocarbon generation period from 20-15 Ma. This geological process is still ongoing (Law et al., 1998; Wandrey et al., 2004b). It is postulated that migration took place over relatively limited distances in an up-dip and vertical manner into neighboring reservoir formations as a result of plate collision, faults and thrusting. Sealing mechanisms primarily encompass the fault truncations, intercalated shales, thick shale deposits, and ultimately the clay-rich strata within the Miocene-Pliocene deposits, which are locally referred to as the Siwalk

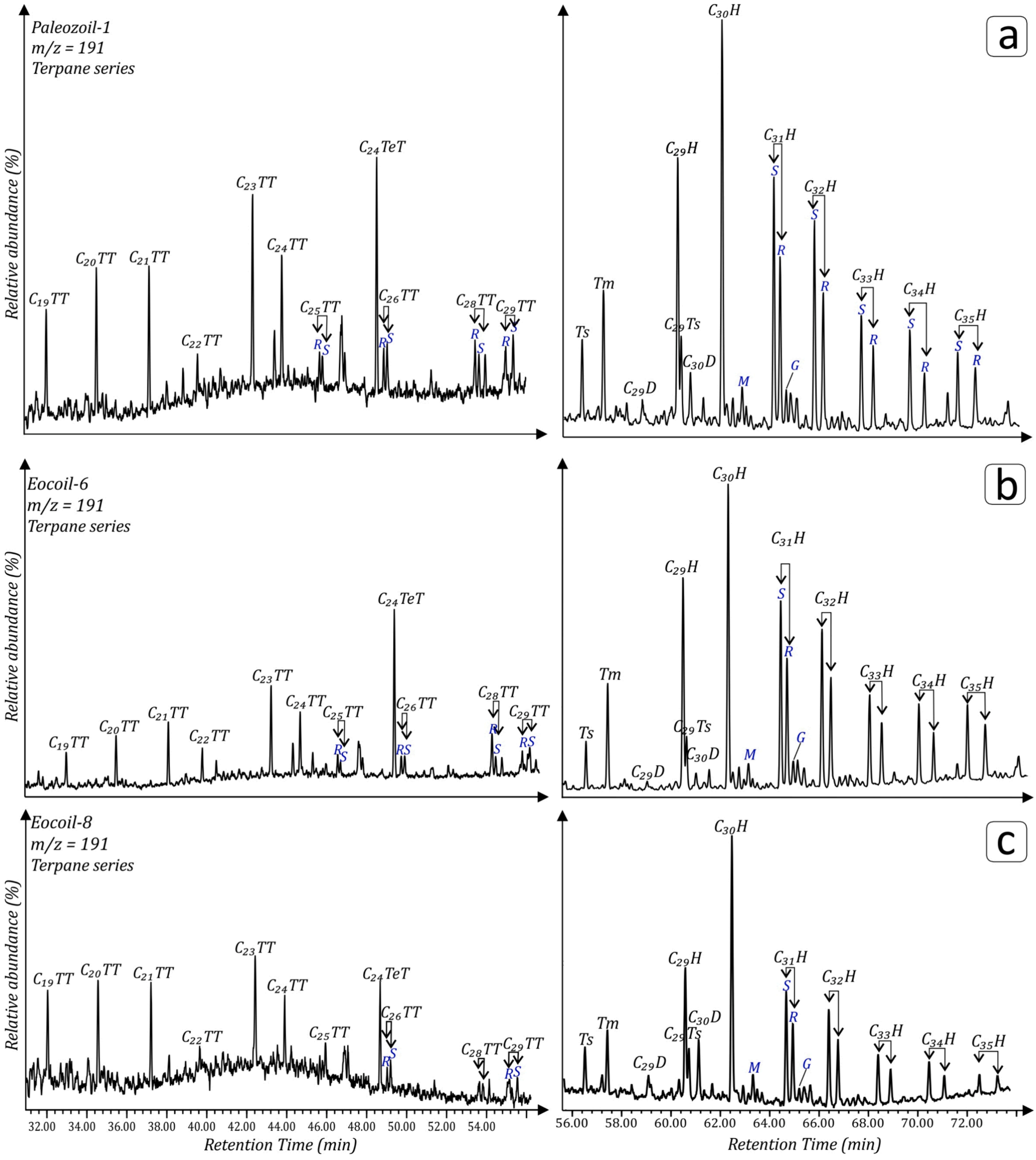

Fig. 5. Mass chromatograms (*m/z* 191) sowing the distribution of terpane series in crude oils from PTB. Abbreviations: G: Gammacerane; M: Moretane; H: Hopane; D: Diahopane.

Group.

3. Sample and analytical methods

Eight oil samples from three different fields of PTB were obtained, where two samples belong to the Eocene age and six from the Paleozoic age. The sample Eocoil-8 was analyzed twice in order to get precision for oil to oil correlation analysis (Table 1). All the reservoir samples, locations and depth information are provided in Table 1 and Fig. 1. The analysis of the PTB crude oils involved the utilization of GC-FID and GC–MS techniques to examine the saturated and aromatic hydrocarbon fractions. All the experiments were completed at the National Key Laboratory of Petroleum Resources and Engineering, China University of Petroleum, Beijing, 102249, China. The crude oil samples were

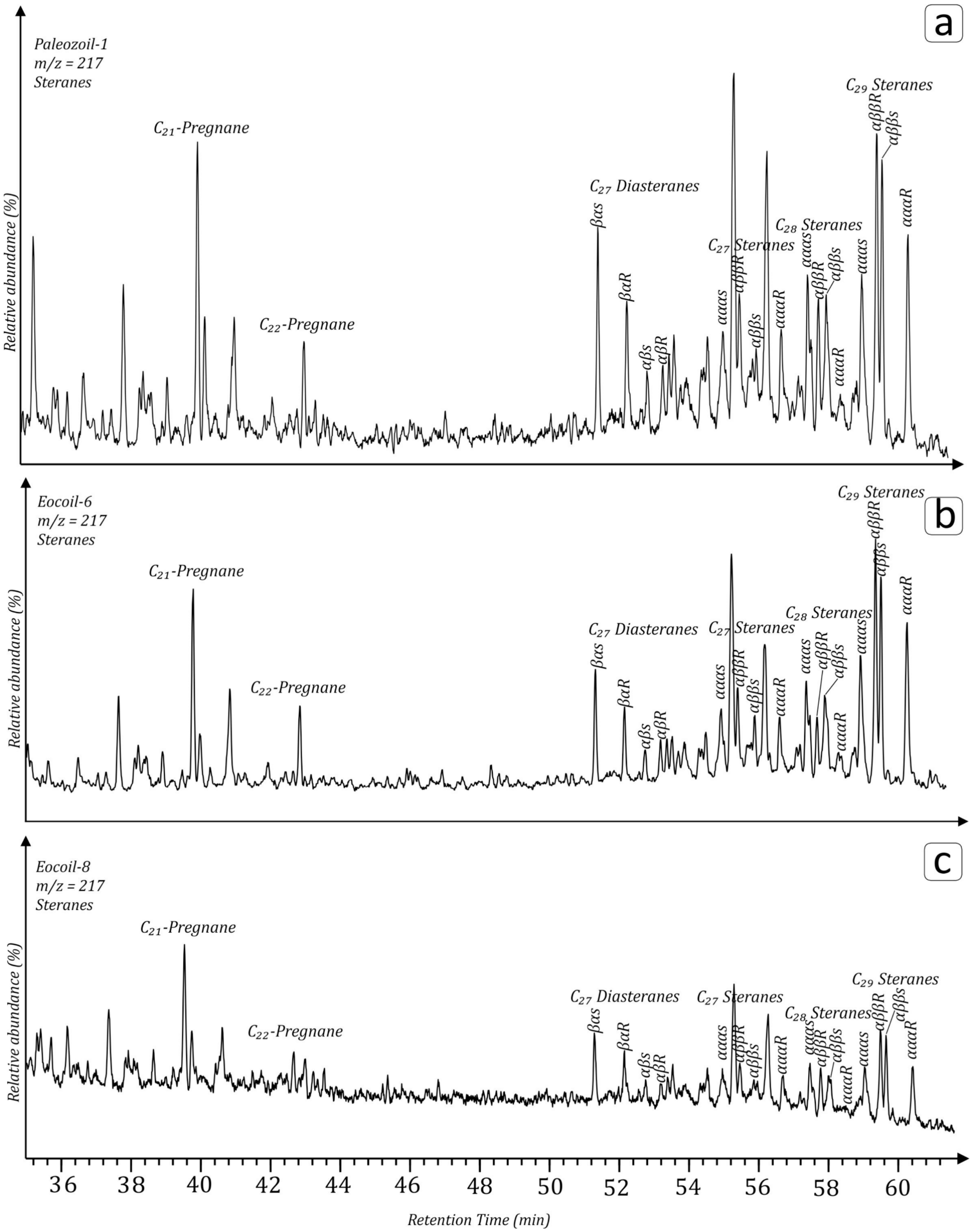

Fig. 6. Mass chromatograms (*m/z* 217) showing the distribution of C_{21}-C_{22} pregnanes, C_{27} diasteranes and C_{27}-C_{29} regular steranes in crude oils from the PTB.

deasphaltened utilizing petroleum ether, and individual fractions (saturated, aromatic, aspheltene and non-hydrocarbons) were fractioned by column chromatography using silica gel/alumina with the ratio of (3:2) columns. The *n*-hexane, dichloromethane and *n*-hexane (2:1) were used as sequential eluents.

The Initial analysis of the *n*-alkanes and acyclic isoprenoids of saturated hydrocarbon fraction of oils began with GC-FID. This process was conducted using the Shimadzu GC-2010 instrument coupled with FID. Chromatographic separation was achieved through the utilization of the silica capillary column HP-5MS (30 m × 0.25 mm, 0.25 μm film thickness). The carrier gas was Helium (He) and the initial temperature of the oven was set at 100 °C for 1 min and then elevated to 300 °C at a rate of 4°C per minute, and finally, it was maintained at 300 °C for a duration of 25 min.

Table 2
Thermal maturity indicators related to saturated and aromatic biomarkers in crude oils from PTB.

Oils	MPI-1	MDR	MPR	%Rc (MPI-1)	%Rc (MDR)	%Rc (MPR)	MNR	F1	F2	$C_{29}\alpha\alpha\alpha$20S /(20S + 20R)	$C_{29}\beta\beta$/ ($\beta\beta$ + $\alpha\alpha$)	Moretane/ Hopane	Ts/ Tm	C_{31}22S/ (C_{31}22S + C_{31}22R)	C_{32}22S/ (C_{32}22S + C_{32}22R)
Paleozoil-1	0.87	5.85	1.37	0.92	0.94	0.36	0.99	0.51	0.29	0.53	0.53	0.10	0.58	0.58	0.59
Paleozoil-2	0.92	6.59	1.48	0.95	0.99	0.38	1.07	0.52	0.30	0.53	0.54	0.11	0.63	0.57	0.59
Paleozoil-3	0.87	5.80	1.48	0.92	0.93	0.38	0.93	0.52	0.30	0.49	0.54	0.11	0.60	0.57	0.58
Paleozoil-4	0.95	6.88	1.43	0.97	1.01	0.37	0.83	0.52	0.29	0.53	0.54	0.12	0.69	0.57	0.59
Paleozoil-5	0.87	4.95	1.29	0.92	0.87	0.34	0.97	0.50	0.28	0.51	0.52	0.10	0.51	0.57	0.58
Eocoil-6	0.83	4.33	1.19	0.90	0.83	0.33	0.79	0.49	0.28	0.49	0.53	0.10	0.43	0.58	0.58
Paleozoil-7	0.89	4.80	1.31	0.93	0.86	0.35	0.87	0.50	0.29	0.51	0.53	0.10	0.49	0.58	0.58
Eocoil-8	1.25	9.49	2.00	1.15	1.20	0.46	1.80	0.61	0.34	0.53	0.53	0.12	0.78	0.57	0.58
Eocoil-9	1.25	9.98	1.99	1.15	1.24	0.46	1.81	0.61	0.34	0.53	0.53	0.12	0.76	0.60	0.57

%Rc (MPI-1) % = 0.6*MPI-1 + 0.4; MDR = 4-MDBT/1-MDBT; % R_C(MDR) = 0.073*MDR + 0.51; MPR = 2-MP/1-MP; %R_C (MPR) = 0.99*log(MPR + 0.94); MNR = 2-methylnaphthalene/1-methylnaphthalene; Ts/Tm (Ts:18α(H)–22,29,30-trisnorneohopane; Tm: 17α(H)–22,29,30-trisnorhopane).

Table 3
Selected molecular parameters for oil to oil correlation analysis for PTB crude oils.

No.	Parameters	Group I (average values)	Group II (average values)
1	C_{21}/C_{22}^{+}	1.02	1.85
2	$C_{(21+22)}/C_{(28+29)}$	1.61	2.39
3	Pr/Ph	1.24	2.11
4	Pr/nC_{17}	0.89	0.68
5	Ph/nC_{18}	0.71	0.36
6	CPI	1.01	1.06
7	OEP	0.98	1.07
8	C_{29}Diahopane/C_{29} Hoppane	0.10	0.19
9	C_{30} Diahopane/C_{30} Hopane	0.15	0.28
10	C_{25}TT/C_{24}TeT	0.61	0.98
11	C_{19}TT/C_{23}TT	0.52	0.71
12	C_{26}/C_{28} TAS(20S)	0.62	1.38
13	C_{27}/C_{28} TAS(20R)	0.51	0.59
14	DBT/Phen	0.58	0.13
15	C_{21}/C_{22} Methyltriaromatic steroid	2.71	1.22
16	G/C_{30}H	0.08	0.06
17	DBT (%)	61.60	29.76
18	DBF (%)	12.01	10.07
19	FL (%)	26.39	61.66
20	C_{27}%	24.48	33.85
21	C_{28}%	23.98	22.35
22	C_{29}%	51.54	43.81
23	$(C_{19} + C_{20})/(C_{23} + C_{24})$TT	0.75	1.03
24	HHI	0.13	0.08
25	C_{26} TAS (%)	28.46	46.78
26	C_{27} TAS (%)	25.01	19.28
27	C_{28} TAS (%)	46.53	33.95
28	MDBT (%)	64.53	16.07
29	MDBF (%)	9.45	58.37
30	MF (%)	26.02	25.57

The examination of the saturated and aromatic components of crude oils was conducted using (GC–MS). The analytical instrumentation consisted of a (GC-Agilent 6890) equipped with an Agilent 595i mass detector, and chromatographic separation was carried out employing a fused silica capillary column, specifically a 60m HP-4MS column with dimensions measuring 0.25 mm in diameter and 0.25 μm in thickness. Commencing at 50 °C and held for one minute, the temperature was then elevated to 120 °C, increasing by 20 °C per minute. Ultimately, the temperature ascended to 310 °C, progressing at a rate of 3 °C per minute, and was maintained at this constant temperature for 25 minute. Throughout this process, He was utilized as the carrier gas. The mass spectrometer functioned for dual mode selected ion monitoring (SIM) and fully scanning mode from (*m/z* 50–600 Da) with an ionized energy of 70 eV.

4. Results

4.1. Physical properties of crude oils

The geochemical and bulk properties of PTB oils are listed in Table 1. Both light and heavy oils were discovered from study area, their API values range from 12 to 26°. The main exemption of biodegraded oils is the loss of *n*-alkanes and presence of few immature oils enriched in naphthenic aromatic fractions (Tissot and Welte, 1984). The saturate fractions in PTB crude oils were relatively higher than aromatic, asphaltene and non-hydrocarbon fractions (Table 1). These bulk compositions show significant change in relative contents of SAT (%), ARO (%) and ASP + NSO (%) in Group I and Group II oils (Fig. 3). The SAT/ARO ratio was higher in Eocoil-8 and Eocoil-9 crude oils > 2 compared to other samples (>1) (Table 1).

4.2. n-Alkanes and acyclic isoprenoids (GC-FID) analysis

The total ion chromatogram illustrates a prevalence of *n*-alkanes within the analyzed crude oils, ranging from nC_{15} to nC_{32}, and are slightly differ (Fig. 4). The normalized *n*-alkanes and acyclic isoprenoids of the crude oils show that Group II is dominated by *n*-alkanes maximizing at nC_{16} with relatively higher pristane over phytane (Pr/Ph) values (Fig. 10a), however, the Group I oils have *n*-alkanes from nC_{12}-nC_{36} with lower pristane and phytane values compared to Group II. The existence of waxy alkanes, as well as lower Pr/Ph, Ph/nC_{18}, and Pr/nC_{17} values in Group I crude oils, provides robust support for the influence of marine OM source, distinguishing it from Group II. In addition, the majority of these oils belong to Cambrian reservoirs, hence there should be no land plants during this geological time. The mid-chain monomethyl alkanes (MMAs) compounds are also observed in crude oils, predominantly in Paleozoil-2 and Paleozoil-5 crude oil samples. Prior investigations have reported the presence of MMAs in Neoproterozoic oils from various regions, including India, Siberia, Russia, and Oman, these oil reserves originated from the source rocks of the lower Paleozoic to Precambrian age (Kelly et al., 2011; Bhattacharya et al., 2017).

Table 4
Selected biomarker parameters for oil classification based on depositional environment and organic matter source.

Oils	G/ $C_{30}H$	$C_{19}TT$/ $C_{23}TT$	$(C_{19} + C_{20})/(C_{23} + C_{24})$ TT	$C_{25}TT$/ $C_{24}TeT$	C_{30} Diahopane/ C_{30} Hopane	C_{29}Diahopane/ C_{29} Hopane	DBT/ Phen	C_{27}%	C_{28}%	C_{29}%	HHI	DBT (%)	DBF (%)	FL (%)	MDBT (%)	MDBF (%)	MF (%)	C_{26}/ C_{28} TAS (20S)	C_{27}/ C_{28} TAS (20R)	C_{21}/C_{22} Methyltriaromatic steroid	C_{26} TAS (%)	C_{27} TAS (%)	C_{28} TAS (%)
Paleozoil-1	0.08	0.55	0.77	0.67	0.14	0.10	0.47	22.34	29.84	47.82	0.12	59.10	12.59	28.31	58.49	11.54	29.98	0.62	0.53	2.43	28.29	26.10	45.62
Paleozoil-2	0.08	0.56	0.78	0.76	0.22	0.11	0.44	24.98	23.66	51.36	0.12	55.63	14.02	30.35	56.75	13.81	29.44	0.67	0.51	2.25	30.27	24.31	45.43
Paleozoil-3	0.08	0.54	0.76	0.35	0.18	0.15	0.53	25.94	23.88	50.18	0.12	66.33	15.19	18.47	64.57	14.18	21.26	0.68	0.52	2.16	30.53	24.31	45.15
Paleozoil-4	0.07	0.56	0.83	0.75	0.19	0.15	0.36	23.86	24.94	51.20	0.11	53.50	11.74	34.76	56.68	11.77	31.55	0.78	0.49	1.99	34.26	21.60	44.15
Paleozoil-5	0.09	0.54	0.80	0.66	0.11	0.08	0.63	26.53	21.24	52.24	0.15	63.69	10.93	25.38	69.27	6.21	24.52	0.58	0.53	2.74	27.17	25.74	47.09
Eocoil-6	0.09	0.41	0.58	0.53	0.07	0.05	0.97	23.94	22.14	53.93	0.15	66.23	10.53	23.24	75.88	2.60	21.52	0.40	0.52	4.34	20.18	28.92	50.90
Paleozoil-7	0.08	0.49	0.71	0.57	0.11	0.08	0.68	23.79	22.17	54.04	0.15	66.69	9.09	24.22	70.09	6.03	23.87	0.60	0.50	3.08	28.52	24.12	47.36
Eocoil-8	0.06	0.73	1.01	0.92	0.27	0.18	0.13	33.91	22.28	43.81	0.08	29.26	9.57	61.16	16.04	58.49	25.48	1.37	0.50	1.21	46.87	18.87	34.26
Eocoil-9	0.06	0.68	1.05	1.03	0.29	0.19	0.13	33.79	22.41	43.80	0.08	30.26	10.57	62.16	16.09	58.25	25.65	1.39	0.68	1.23	46.68	19.68	33.64

Note: Regular C_{27}(%) = ($C_{27}\alpha\alpha\alpha20S$ + $C_{27}\alpha\alpha\alpha20R$ + $C_{27}\alpha\beta\beta20S$ + $C_{27}\alpha\beta\beta20R$) / Total Steranes * 100, C_{28} (%) and C_{29} (%) regular steranes are similarly defined as C_{27} (%); DBT (%) = DBT/(DBT + FL + DBF)*100 and MDBT (%) = MDBT/(MF + MDBF + MDBT) *100, relative percentage of DBF (%) and FL (%), and MDBF (%) and MF (%) was similarly calculated; C_{26} TAS (%) = C_{26} TAS /(C_{26} TAS + C_{27} TAS + C_{28} TAS) *100, relative abundance of C_{27} TAS and C_{28} TAS was measured following C_{26} TAS; HHI = $C_{35}H/(C_{31}H\text{-}C_{35}H)$*100.

4.3. Terpanes

A complete series of terpanes (C_{19}TT-C_{35}HH) compounds were detected in the PTB crude oils. The hopanes are enriched relative to tricyclic terpanes and the most prominent peak appears as C_{30}H in the PTB oils. Fig. 5 displays the representative chromatograms of tricyclic terpanes (TT) and hopane (H) series compounds identified from *m/z* 191. The tricyclic terpanes and hopanes usually derived from bacteria and algae, have been extensively detected in PTB oils (Fig. 5). The analysis of these compounds exhibits similarities between two field samples, while the terpanes and hopane series compounds from field A (1, 2, 3 and 4 wells) and B (5, 6 and 7 wells) reservoirs showing comparable distributions, but field C (8 well) crude oils reveal different origin (Table 4). The series of C_{19}TT-C_{29}TT compounds were consistently observed in the oil samples, with C_{24}TeT being dominant peak (Fig. 5). The mean values of $C_{19}TT/C_{23}TT$ and $(C_{19} + C_{20})/(C_{23} + C_{24})$TT in Group I and Group II oils are (0.52 and 0.71; 0.75 and 1.03). Moreover, the average ratios of $C_{25}TT/C_{24}TeT$ in Group I and Group II oils vary between 0.61 and 0.98 (Table 3). The distribution of hopane compounds, including Ts, Tm, C_{29}D and C_{29}H with C_{29}Ts and C_{30}D followed by C_{30}H, and C_{31} to C_{35} homohopanes were recognized in the studied oils (Fig. 5). The C_{30}H peak dominantly appears in all the samples. The ratios of G/C_{30}H, $C_{29}D/C_{29}H$ and $C_{30}D/C_{30}H$ in the crude oils range from 0.06-0.09, 0.05–0.19 and 0.07–0.29, respectively (Table 4). The maturity related parameters based on pentacyclic series such as Ts/Tm, $C_{31}22S/(C_{31}22S + C_{31}22R)$ and $C_{32}22S/(C_{32}22S + C_{32}22R)$ for studied oils ranging from 0.43–0.78, 0.57–0.60, and 0.57–0.59, accordingly. The average values of the calculated homohopane index (HHI) in Group-I and Group-II oils are 0.13 and 0.08 (Table 4).

4.4. Steranes

The steranes are the ubiquitous compound class in oils and can be identified from selected *m/z* 217 mass chromatogram (Fig. 6). However, the steranes are not found in prokaryotic organisms but they are commonly observed in higher plants and algae (Volkman, 1986).

A complete distribution of steranes, including C_{21} and C_{22} pregnanes, C_{27} diasterane, and C_{27}, C_{28} and C_{29} regular steranes, along with their R and S isomers was identified (Fig. 6). The relative proportion of regular steranes are generally applied to identify the primary OM source. Most of the crude oils have a preeminence of C_{29} sterane (Fig. 10a). The relative abundance of C_{27}%-C_{29}% steranes are diverse within the ranges of 22.34–33.91 %, 21.24–29.84 % and 43.80–54.04 %, respectively (Table 4). The calculated ratio of $C_{29}\alpha\alpha\alpha20S/(20S + 20R)$ and $C_{29}\beta\beta/(\beta\beta + \alpha\alpha)$ in the oils appears consistent, ranging from 0.49 to 0.53 and 0.52–0.54, accordingly (Table 2).

4.5. Aromatics

The abundant aromatic hydrocarbons were detected from PTB oils (Fig. 8). The major aromatic hydrocarbons including their methylated derivates such as phenanthrene (P), naphthalenes (N), DBT, DBF, and FL were observed in studied oils. Besides, the triaromatic steroids (TAS) and triarmatic dinosteriods (TADS) series were also detected. The average values for C_{26}, C_{27}, and C_{28} TAS in Group I oils are 28.46, 25.01, and 46.53, whereas in Group II, they are 46.78, 19.27, and 33.95, respectively (Table 4). These average values clearly highlight significant disparities in the compositional profiles between the two groups.

The indicators of thermal maturity, namely MPI-1, MPR, MDR, and MNR, in the analyzed crude oils exhibit ranges of 0.83–1.25, 1.19–2.00, 4.33–9.98, and 0.79–1.81, respectively. The calculated vitrinite reflectance values, denoted as %Rc, for MPI-1, MDR, and MPR in PTB crude oils are observed within the intervals of 0.90–1.15, 0.83–1.24, and 0.33–0.46, respectively (Table 2). The normalized phenanthrene and its alkylated homologs series maximizes at the P and 2, 10-+1,3-+3,10-

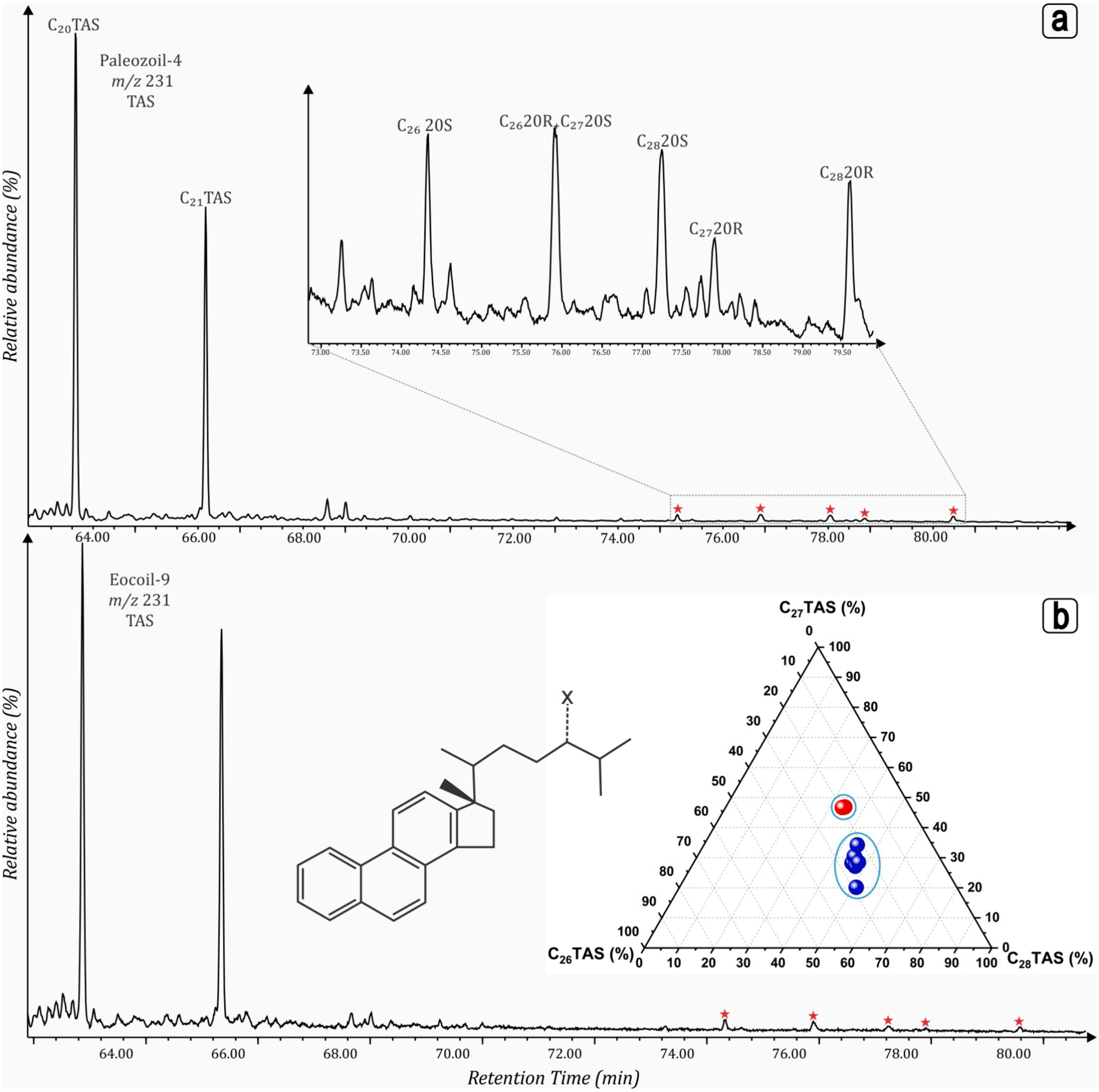

Fig. 7. Mass chromatograms of *m/z* 231 showing triaromatic steroids of representative oil samples (a), triangular plot indicates the relative abundance of C_{26}, C_{27} and C_{28} triaromatic steroids in PTB crude oils (b).

+,39 DMP compounds in crude oils (Fig. 9b).

5. Discussions

5.1. Biodegradation and thermal maturity of PTB crude oils

Petroleum biodegradation is caused by microbial activity resulting in the alteration of crude oil. This secondary mechanism leads to the modification of the chemical and physical attributes of oil reservoirs over time, resulting in the selective depletion of saturated hydrocarbons and the accumulation of higher molecular weight polar and asphaltene constituents. (Asif et al., 2009; Connan, 1984; Milner et al., 1977). In the present investigation, the degree of crude oil biodegradation is evaluated using the procedure outlined by Peters et al. (2005). To estimate the biodegradation level, we employed various bulk properties such as API gravity and the relative proportions of saturated hydrocarbons (SAT %), aromatic compounds (ARO %), asphaltenes (ASP %), and non-hydrocarbon compounds (NSO %), along with the analysis of saturated hydrocarbons via GC-FID and GC–MS (Table 1). The presence of a clear distribution of *n*-alkanes (C_{12}-C_{35}) with specific ratios like Pr/nC_{17}, Ph/nC_{18}, Pr/Ph, and $C_{30}H/(Pr + Ph)$ suggests that the PTB crude oils are non-biodegraded or may have been influenced by very slight biodegradation. Numerous investigations have demonstrated that the microbial demethylation of hopanes plays a fundamental role as a precursor for 25-norhopanes in heavily biodegraded oils (Moldowan and McCaffrey, 1995; Volkman et al., 1983). Consequently, the presence of

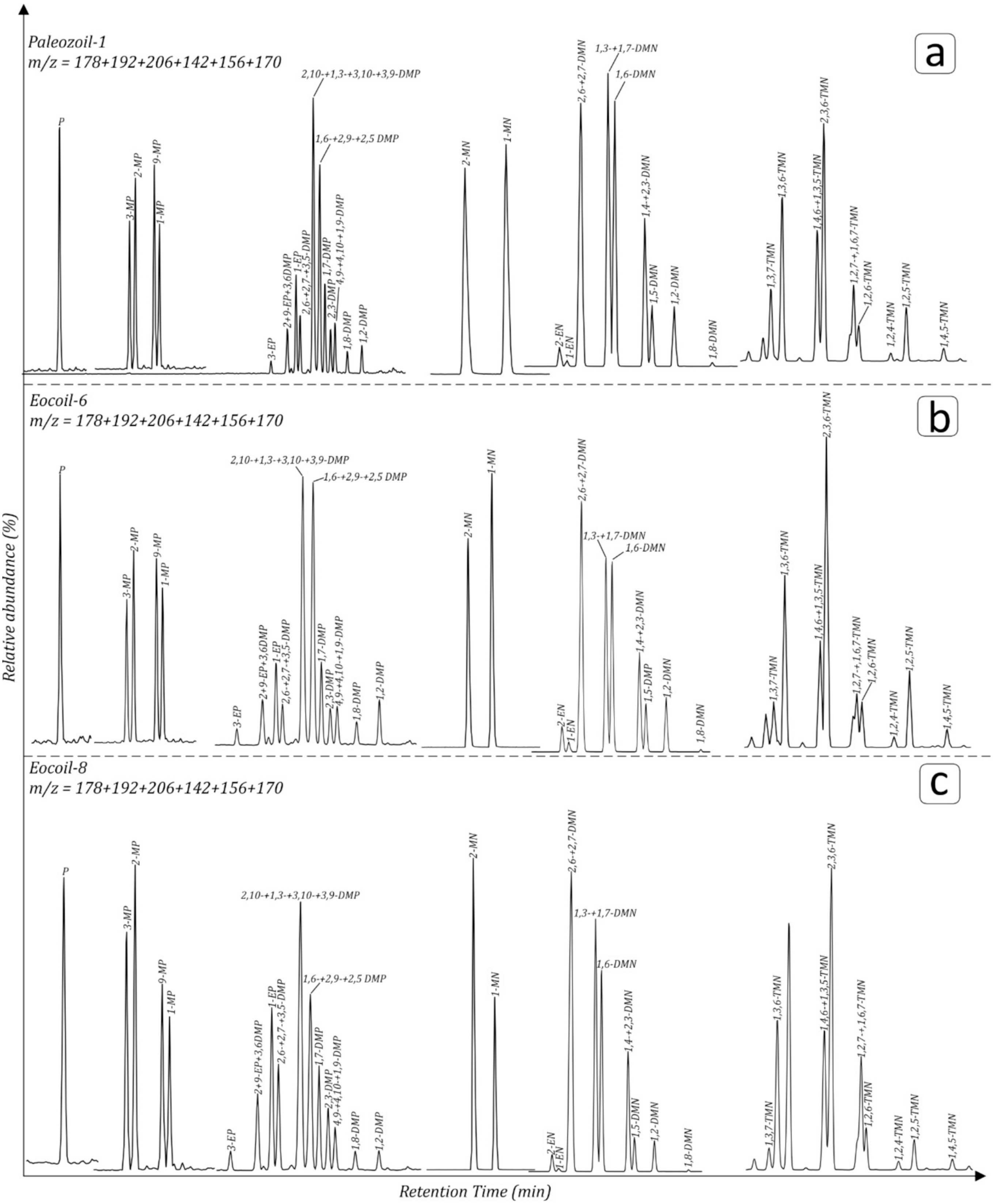

Fig. 8. Representative chromatograms of aromatic hydrocarbons in crude oils of PTB. Compound abbreviations: P: phenanthrene; MP: methylphenanthrene; DMP: dimethyl methylphenanthrene; MN: methylnaphthalene; DMN: dimethylnaphthalene; TMN: trimethylnaphthalne.

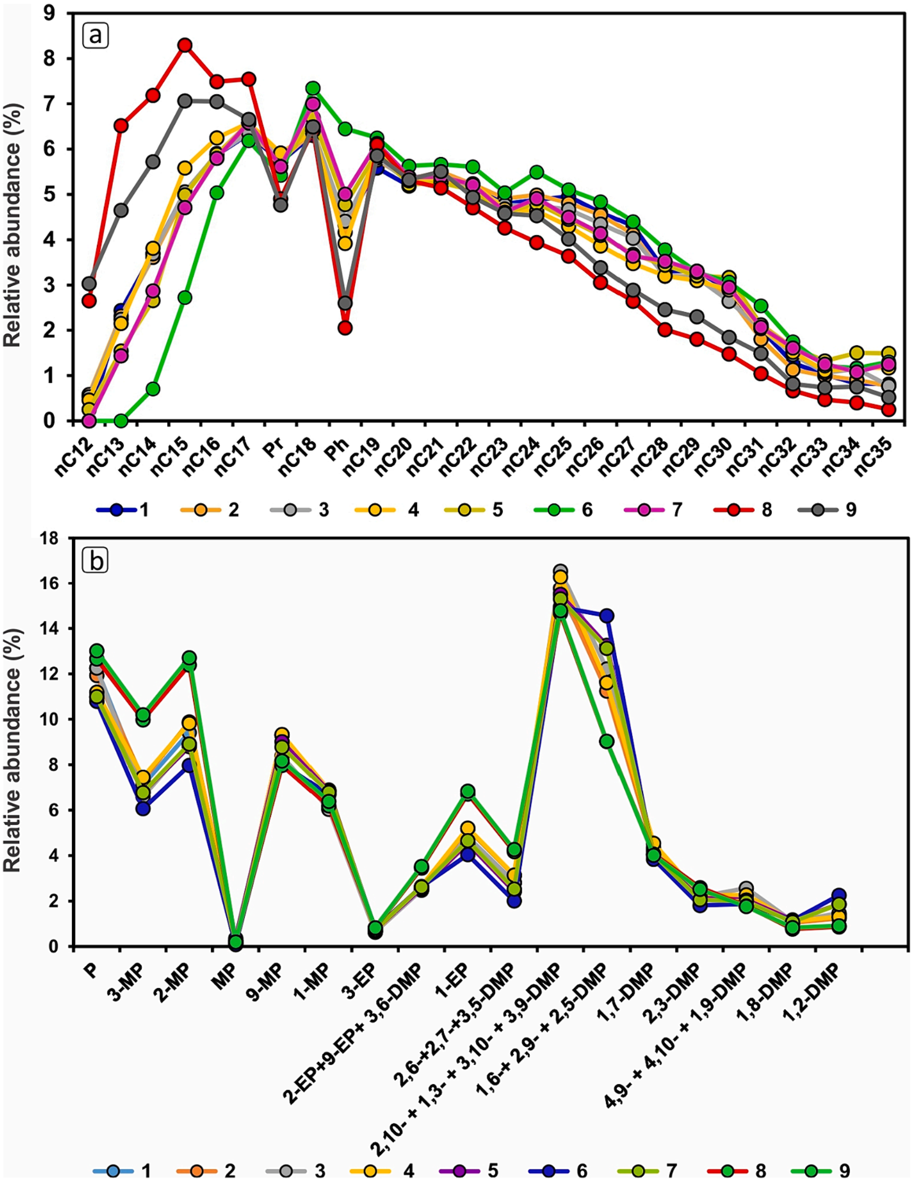

Fig. 9. Normalized concentration of *n*-alkanes including isopernoids (a) and Phanenthereane series with their alkylated homologues (b).

25-norhopane homologues is considered a significant indicator of severe biodegradation, initiating at the advanced stage of alteration (Peters et al., 2005; Volkman et al., 1983). The identification of the 25-norhopane series can be achieved through *m/z* 177. In our research, the absence of the 25-norhopane series affirms that the examined PTB crude oils have not undergone severe biodegradation (Fig. 5).

CPI and OEP values commonly demonstrate the thermal maturity assessment, their values around 1 indicate a thermally mature state and values more than 1 exhibit a lower maturation level (Peters et al., 2005). In the PTB oils, both the CPI and OEP display values close to 1, indicating thermally mature oils (Table 1; Fig. 13b). The ratio of 18α(H)–22,29,30-trisnorneohopane (Ts) to 17α(H)–22,29,30-trisnorhopane (Tm), a hopanoid-based metric, is widely employed as an indicator for evaluating the thermal maturity of both oil and source rocks. For examined PTB oil samples, the Ts/Tm ratio ranges from 0.43 to 0.69 in Group I oils and from 0.76 to 0.78 in Group II oils (Table 2). These ratios show differences in oil generation for example, Group I oils are predominantly situated in the primary phase of hydrocarbon generation whereas Group II oils values are within the peak oil window. The higher Ts/Tm ratios show possible control by organic facies and depositional conditions (Moldowan et al., 1986; Seifert and Moldowan, 1986). The C_{31} 22S/(22S + 22R) and C_{32} 22S/(22S + 22R) isomer ratios in homohopanes serve as precise indicators for documenting the oil window and equilibrium conditions in source rock and crude oils, as documented by Seifert and Moldowan (1986). The studied PTB oils have C_{31} and C_{32} 22S/(22S + 22R) values within the range of 0.57–0.58 and 0.57–0.60 (Table 2), exhibiting equilibrium zone and specify that the peak stage of oil generation has been reached or surpassed (Peters et al., 2005).

The most reliable and applicable biomarker parameters for thermal maturity evaluation for crude oils and source rocks are C_{29}-ββ/(ββ + αα) and C_{29}–20S/(20S + 20R). The isomerization process of C_{29} sterane progresses with increasing thermal maturity (Seifert and Moldowan, 1986). The average values of C_{29}-ββ/(ββ + αα) and C_{29}–20S/(20S + 20R) in crude oil samples are 0.53 and 0.52, showing the thermally mature stage (Fig. 13a). These parameters show the remarkable consistency in hydrocarbon generation mainly within the early to peak stage. The ratios of Moretane/Hopane are partially dependent on source rock variation and environmental conditions, and decline with increasing of thermal maturity e.g. immature source rocks possess 0.8 whereas

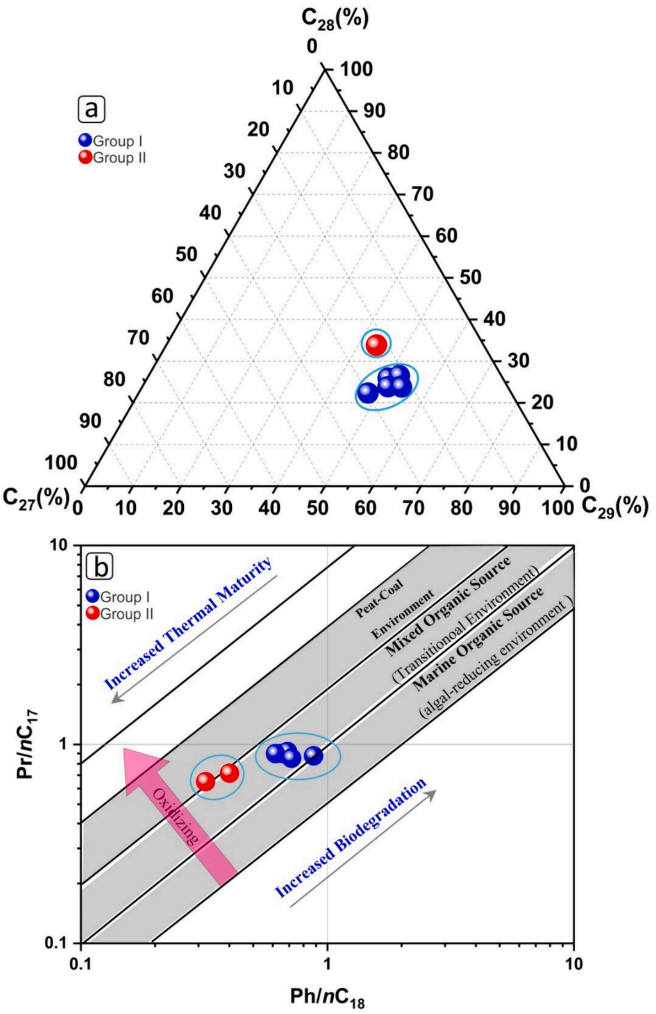

Fig. 10. Ternary diagram showing the relative content of C_{27}, C_{28} and C_{29} regular steranes (a); Cross plot of Pr/nC$_{17}$ vs Ph/nC$_{18}$ showing depositional environment and organic matter source of Potwar crude oils (b).

mature source rocks have less than 0.15 Moretane/Hopane ratios (Mackenzie et al., 1980; Seifert and Moldowan, 1986; Peters et al., 2005). The values of Moretane/Hopane in studied oils range from 0.10 to 0.12, revealing mature stage of hydrocarbon generation for PTB oils (Table 2).

Several aromatic maturity parameters have been assessed for the PTB oils (Table 2). These aromatic maturity parameters are commonly employed in the assessment of thermal maturation in both crude oils and source rocks, offering additional insights over wider maturity ranges compared to saturated hydrocarbons (Radke, 1988). These indicators include the methylphenanthrene index (MPI-1), the methylphenanthrene ratio (MPR), methyl naphthalene ratio (MNR), and the methyldibenzothiophene ratio (MDR). These alkylated aromatic hydrocarbon isomers (MPI, MPR, MNR and MDR) are considered to be thermodynamically stable parameters for the thermal maturity assessment (Radke and Welte, 1983; Alexander et al., 1985; Radke, 1988). The precise descriptions and mathematical expressions for these maturity indices of PTB oils are documented in Table 2. Research has demonstrated that several indicators of biomarker maturity achieve stability as the oil window commences, rendering them less applicable for extensively mature oils and condensates (as described by van Graas, 1990). In such circumstances, criteria relying on aromatic hydrocarbons might prove more efficient for assessing thermal history. The MPI-1; as proposed by Radke et al. (1982) emerges as a valuable tool for approximating vitrinite reflectance (%Rc (MPI-1)) (Radke, 1988; Radke et al., 1982). The thermal maturity of the PTB oil groups can be defined based on the significant difference in their MPI-1 (methylphenanthrene index) values. In Group-I oils, the average MPI-1 and calculated %Rc (MPI-1) values are notably lower at 0.89 and 0.93, indicating comparatively lower thermal maturity. On the other hand, Group II oils exhibit average MPI-1 and %Rc (MPI-1) values of 1.25 and 1.15, signifying higher thermal maturity. Therefore, in this context, thermal maturity can be characterized as the degree of chemical alteration and maturation the hydrocarbons within these oil groups have undergone, with higher MPI-1 values corresponding to more advanced thermal maturity. MPR and its corresponding viternite referlatance (%Rc-MPR) is a geochemical parameter used to assess the thermal maturity of OM, chiefly in oils and source rocks (Radke et al., 1984). It provides insights into the level of thermal alteration the organic material has experienced. In the studied PTB oils, MPR and %Rc (MPR) values in Group II (average 1.99 and 0.46) relatively higher than those in Group I (average 1.36 and 0.36), indicating that Group II has relatively higher maturity (Table 2). These findings are further supported by the high maturity exhibited in Group II oils, as indicated by the cross-plot of %Rc (MPI-1) versus %Rc (MDR) (Radke, 1988) (Fig. 13d). In addition, the MNR ratio also has good agreement with the aromatic parameters (e.g., MPR, MPI and MDR), which further support the Group II oil having higher maturity (Table 2). The F1 and F2 parameters, calculated by the methyl-phenanthrene homologues, have been demonstrated to offer greater efficacy in assessing thermal maturity, and these ratios displaying lesser effects of lithology and kerogen types (Kvalheim et al., 1987; Bao et al., 1992). The examined crude oils in Group II exhibit elevated values of both F1 and F2 (average 0.61 and 0.34) than those in Group I (average 0.51 and 0.29), placing them within the region of higher maturity stages (Fig. 13c). In summary, the saturated hydrocarbon maturity parameters show that both Group I and Group II oils have similar thermal maturity locating into the zone of mature level (Fig. 13a-b). However, aromatic hydrocarbons, which are more sensitive and reliable indicators of thermal maturity (Radke, 1988; Peters et al., 2005), revealed the authentic maturity level of Group II oils, which experienced relatively higher maturity than those of Group I (Fig. 13c-d). This discrepancy in thermal maturity assessments between saturated and aromatic hydrocarbons in other study area's samples is also observed by several published literatures (Asif et al., 2011a; Chanyshev et al., 2017; Liu et al., 2019; Chen et al., 2023).

5.2. *Organic source input of crude oils*

The source of OM for PTB oils was ascribed using n-alkane, terpanes, and sterane hydrocarbons. A short chain with the distribution of n-alkanes $< n\mathrm{C}_{20}$ is associated with algae and other microbes, whereas an extended series of n-alkanes ($>n\mathrm{C}_{25}$) may suggest the presence of terrigenous higher plant material (Eglinton and Hamilton, 1967; Peters et al., 2005). The OEP based on n-alkane distribution characterized by elevated values of CPI or OEP (Scalan and Smith, 1970), exhibits a greater influence of terrigenous plant sources. The n-alkanes distribution in PTB oils shows unimodal with long chain ($>n\mathrm{C}_{25}$) for all the samples (Fig. 4), showing that the oils might have derived from both lacustrine and aquatic organisms. CPI and OEP values in studied oil samples are approximately close to 1 (average), this implies a mixed source of oils.

The ratios associated with acyclic isoprenoids and n-alkanes (specifically Pr/Ph, Pr/nC$_{17}$ and Ph/nC$_{18}$) are generally applied for depositional environmental conditions and origin of source rocks and oils (Peters and Moldowan, 1993; Peters et al., 2005). Lower ratios of Pr/Ph (<1) specify the anoxic sedimentary setting, generally ascribed to an enhanced saline paleoenvironmental conditions (Didyk et al., 1978). Pr/Ph values in PTB crude oils are generally higher than 1 (average 1.43), showing the mixed OM, deposited under a transitional environment (Fig. 10b). The distribution of tricyclic terpanes is thought to originate from marine and terrestrial sources, and their precursor organisms are

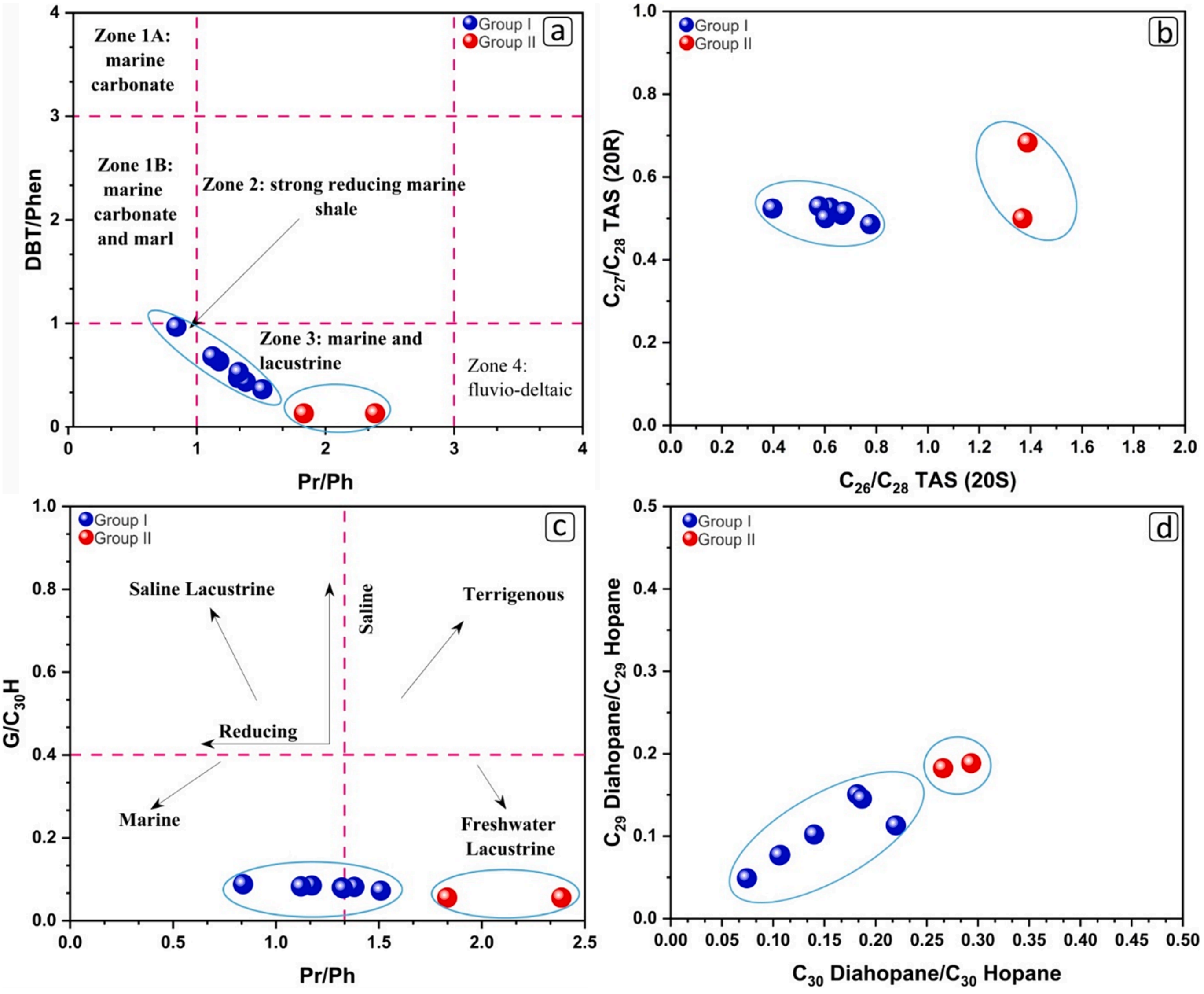

Fig. 11. Cross-plot of DBT/Phen indicate lithology and depositional conditions (a) C_{27}/C_{28} TAS(20R) vs C_{26}/C_{28} TAS (20S) differentiate two groups (b) the plot of $G/C_{30}H$ vs Pr/Ph showing depositonal environment and saline conditions (c); C_{29} Diahopane/ C_{29} Hopane and C_{30} Diahopane/C_{30} Hopane ratios showing variation in crude oils (d).

typically algae, bacteria, and higher plants (Hanson et al., 2000; Preston and Edwards, 2000; George et al., 2004; Peters et al., 2005; Xiao et al., 2024). The elevated ratios of $C_{19}TT/C_{23}TT$ are generally associated with terrigenous organic matter, while lower ratios indicate a marine origin. The $C_{19}TT/C_{23}TT$ ratio in our distinguished Group I oil samples ranges from 0.41 to 0.56. This indicates a predominance of marine algal sources and minimal terrigenous input. In contrast, Group II oils have a relatively higher level of $C_{19}TT/C_{23}TT$, ranging from 0.68 to 0.73, indicating that their source could have more contribution of terrigenous input. Similarly, $C_{25}TT/C_{24}TeT$ ratios in Group I oils range from 0.53 to 0.76, with one sample as an outlier at 0.35, which is significantly lower than the other samples examined (Table 4). Their lower ratios indicate a marine influence with some effect of terrigenous source, while the Group II oils show higher values of $C_{25}TT/C_{24}TeT$ than Group I, ranging from 0.92 to 1.03, indicating a typical lacustrine source. Moreover, $(C_{19} + C_{20})/(C_{23} + C_{24})TT$ ratios in Group I oils ranging from 0.58 to 0.83 indicate a mixed source, while Group II oils with higher $(C_{19} + C_{20})/(C_{23} + C_{24})TT$ ratio ranged from 1.01 and 1.05 also indicate a terrigenous source.

The relative distribution of regular steranes of $C_{27}\%$-$C_{29}\%$ is generally applied for the initial OM source. In general, $C_{27}\%$ is known to be a precursor of algal OM and $C_{28}\%$ is assumed to be sourced from phytoplankton and/or algae. While, $C_{29}\%$ is attributed to land plant organisms (Huang and Meinschein, 1979; Volkman et al., 1999). On the contrary, the C_{29} steranes have also been accredited to marine algal sources especially for Paleozoic source rocks and related oils (Grantham, 1986a; Summons and Walter, 1990; Kelly, 2009). Several studies have observed the abundance of C_{29} steranes from these older rocks and oils, especially from China in Tarim Basin and Sichuan Basin (Cai et al., 2009; Wang et al., 2019; Luemba et al., 2021), Huqf oils of South Oman Salt Basin and Eastern Siberian oils (Grantham, 1986b; Grosjean, 2009; Kelly et al., 2011). Furthermore, the PTB oils exhibit a predominance of C_{29} steranes in contrast to the prevalence of C_{27} and C_{28} steranes (Fig. 10a). Based on the structural configuration of PTB, most of our studied oils belong to the Paleozoic age, thus the C_{29} steranes can be endorsed to a marine algal source. Moreover, it is recommended that C_{27}-C_{29} regular steranes are more appropriate and useful when they are consistent with other parameters (such as Pr/Ph, Pr/nC_{17} and Ph/nC_{18}, and ratios of $G/C_{30}H$ vs. Pr/Ph). These indicators for PTB crude oils suggest that Group I oils are predominantly derived from marine algal sources, while Group

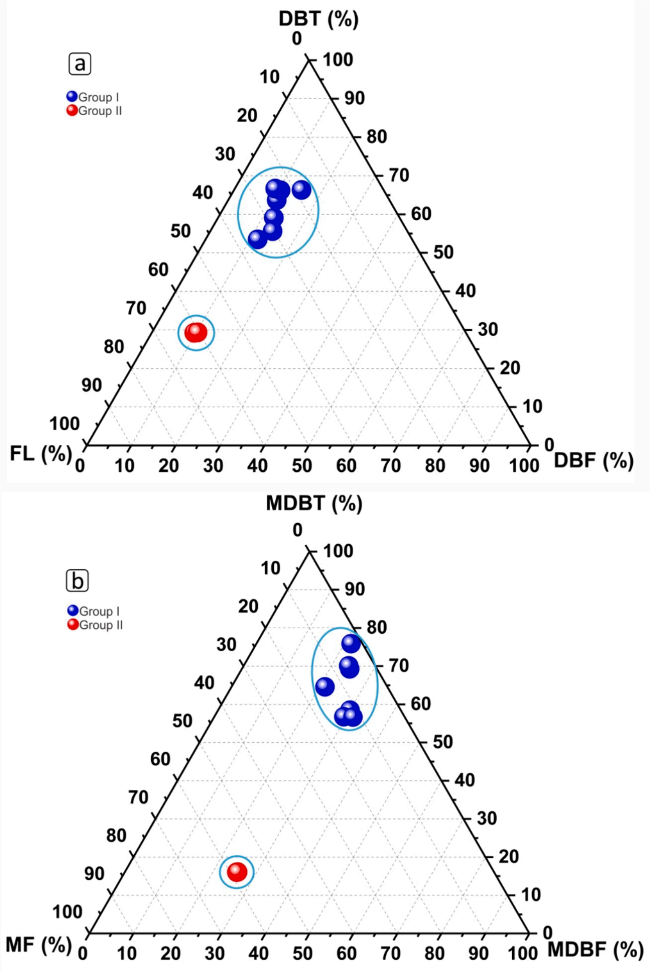

Fig. 12. Ternary diagrams indicating the relative abundance of DBT, FL and DBF (a), relative abundance of MDBT, MDBF and MF for PTB crude oils (b).

II oils indicate the possible origin of lacustrine-derived oils (Fig. 10a and b, Fig. 11c). TAS from steranes' aromatization and remain stable in oils, except in highly biodegraded oils (level 10) (Peters et al., 2005; Yang et al., 2015). TAS are important for oil correlations and thermal maturity assessment when *n*-alkanes and acyclic isoprenoids in crude oils have undergone substantial degradation or complete depletion (Li et al., 2012; Peters et al., 2005). Yang et al. (2015) proposed a ternary plot based on the relative content of C_{26}%, C_{27}%, and C_{28}% TAS for oil to oil and oil to source correlation studies. The analyzed crude oils from Group I show close proximity in ternary plot of C_{26} %, C_{27}%, and C_{28}% TAS, indicating a high degree of molecular similarity, while Group II oils appear distinctly separated, suggesting differences in their sources (Fig. 7b).

5.3. Depositional environment of crude oils

Deciphering the depositional environment and source rock lithology, the DBT/Phen and Pr/Ph ratios offer valuable insights into the composition of both source rocks and crude oils (Hughes et al., 1995). The DBT/Phen ratios reveal the reduced sulfur associated with OM, whereas the Pr/Ph values estimate the redox conditions. DBT/Phen vs. Pr/Ph graph distinguishes: marine carbonate (Zone 1A in Fig. 11a), marine carbonate and marl (Zone 1B), highly reducing marine shale (Zone 2), comprising both marine and lacustrine environments (Zone 3), and fluvial deltaic depositions (Zone 4) (Hughes et al., 1995). This classification scheme relies on the premise that these ratios exhibit sulfur contents in water and variation in Eh-Ph conditions, resulting in substantial chemical and biological transformations during the time of sedimentary deposition (Hughes et al., 1995; Wang et al., 2015; Awan et al., 2022). The measured ratios of DBT/Phen and Pr/Ph for PTB oils ranging from 0.13 to 0.97 and 0.84–2.39, showing that PTB crude oils originated from more marine and lacustrine environment (Zone 3), however, the Eocoil-6 sample appears to be moderately influenced by marine and reducing conditions (Fig. 11a). DBT, FL, and DBF, along with their alkylated derivatives, represent the predominant aromatic hydrocarbon compounds commonly identified in various oils and source rocks, these biomarkers have similar structural characteristics that may have genetic association (Asif et al., 2011b; Sadik et al., 2013). An elevated presence of DBF typically arises in terrigenous crude oil and coal, while carbonate and marine shale-sourced crude oils tend to exhibit a heightened DBT ratio (Hughes et al., 1995; Radke et al., 2000). In this aspect, Li et al (2013) proposed a ternary diagram involving DBT, FL and DBF to distinguish depositional settings, and lithological characteristics, and categorize both the oils and source rocks. The PTB crude oil samples have higher ratios of DBT in Group I (average 61.60 %), while lower ratios are observed in Group II (average 29.76 %). This implies Group I is rich in sulfur compounds compared to Group II. The lower content of FL is observed in Group I (average 26.39 %) than that of Group II (average 61.66 %). The relative concentration of DBF in Groups I and II seems identical (average 11.58 %) (Table 4). The interpretation supports the mixed OM source (marine and lacustrine), potentially from both biogenic and thermogenic processes. The triangular plot of DBT, FL and DBF displays that the data points of Group I have separately appeared from Group II (Fig. 12a). These results advocate that crude oils derived from the mixed environment of OM such as marine and lacustrine predominantly marine. These findings are further supported by the ternary plot of methyldibenzothiophenes (MDBT %), methyldibenzofurans (MDBF %), and methylfluorenes (MF %) (see Fig. 12b). Previous research has observed the prevalence of alkyldibenzothiophenes over alkylfluorenes and alkyldibenzofurans in marine oils and carbonates (Pu et al., 1990; Radke et al., 2000). Notably, Group I oils exhibit significantly higher MDBT (%) compared to MDBF and MF, while Group II oils are characterized by predominant MDBF (%) and MF (%) (Table 4), indicating distinct origins for these two oil groups (Fig. 12b).

The Pr/Ph ratio serves as the distinctive marker for assessing the prevailing redox conditions. The ratio > 3 reflects the oxic environment, while the lower ratio indicates anoxic water bottom (Didyk et al., 1978; Ten Haven et al., 1987). Pr/Ph ratio in Group I crude oil samples is around 1.24 (average) while Group II oils have 2.11 (average), this shows that deposition of Group I oils was mainly under suboxic (marine environment) and Group II oils mainly formed with highly oxic conditions with lacustrine depositional environment. The gammacerane compound is indicative of water salinity or the existence of a freshwater environment (Peters et al., 2005). The PTB oils show very low contents of gammacerane and the ratio of $G/C_{30}H$ in these oils range from 0.06 to 0.09, averaging 0.08, showing a freshwater lacustrine sedimentary environment for Group II and marine environment for group I (Fig. 11c). In addition, the cross plot of gammacerane versus Pr/Ph also supporting this conclusion (Fig. 11c).

The homohopane index (HHI), expressed as $C_{35}/(C_{31}\text{-}C_{35})$, is frequently employed for identifying the redox conditions of source rocks and oils. A higher ratio of HHI generally indicates a more reducing (anoxic) water condition during the deposition, while lower ratios suggest a more oxidizing environment (Peters and Moldowan, 1993). The PTB oils from Group I show moderately higher HHI values, while Group II has lower ratios (Table 4). This indicates that Group I oils were formed under a reducing environment, while Group II oils belong to a potentially more oxidizing environment.

5.4. Oil classification

The geochemical heterogeneity among oils in the PTB was

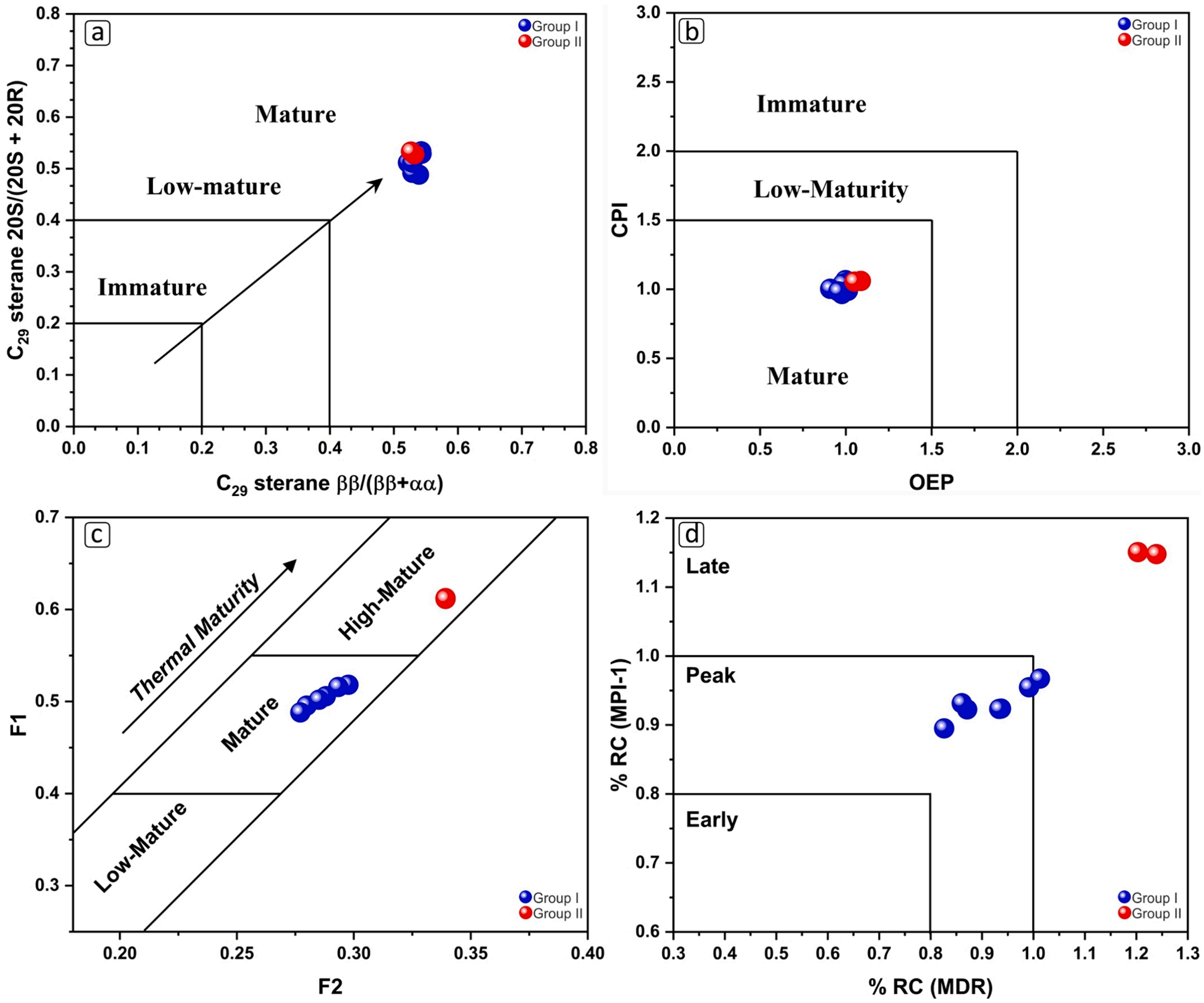

Fig. 13. Cross plots of thermal maturity assessment: C_{29}-20S/(20S + 20R) versus C_{29}-ββ /(ββ + αα) (a) CPI versus OEP (b), F1 versus F2 (c), and %R_C (MPI-1) versus %R_C (MDR) (d).

determined by molecular parameters and hierarchical cluster analysis (HCA) to discriminate the oil families with accuracy. Fig. 14 presents a HC dendrogarm generated from 30 source and depositional environment related parameters employing the SPSS-IBM statistical software (Table 3).

Based on the HC analysis, two distinct families (Family-I and Family-II) have been recognized (Fig. 14). The selected parameters in HC analysis have been assessed by one-way ANOVA that differentiates families by statistical grouping. The cluster distance, ranging from 0 to 25, is determined within an *n*-dimensional space, where the sample number represents the quantity of specified parameters employed (Fig. 14). A comprehensive set of 30 parameters provides robust evidence for the existence of two prominent groups among crude oils within the PTB. The crude oil samples of two different wells (Paleozoil-1 to Paleozoil-8) share a strong affinity in their biomarker characteristics; for example, the relative distribution of C_{27} to C_{29} regular steranes, and ratios of Pr/nC_{17} vs. Ph/nC_{18} ratio and DBT/phen differ in Eocoil-8 and Eocoil-9 oils, thus clearly discriminating two families (Figs. 10 and 11). Besides, the ratios G/C_{30}H with Pr/Ph, C_{29} diahopane/C_{29} hopane versus C_{30} diahopane/C_{30} hopane, C_{27}/C_{28} TAS (20R) and C_{26}/C_{28} TAS (20S), and C_{21}/C_{22} methyltriaromatic steroid and ternary plots of DBT, DBF and FL with their alkylated homologs such as MDBT, MF and MDBF distinguish the two oil families (Figs. 11 and 15). Based on these parameters, Family-I oils are characterized marine depositional environment under suboxic water settings, sourced from algal OM. However, Family-II crude oil samples have different origin of lacustrine OM deposited under a freshwater oxic environment (Table 4). The analysis of crude oils' thermal maturity using parameters related to saturated hydrocarbons indicates that these oils fall within the thermally mature category, spanning from early to peak oil window stages. Conversely, the assessment of aromatic hydrocarbon maturity reveals that Group-II oils have higher maturity.

5.5. *Implications for petroleum exploration and development*

Oil classification is valuable in petroleum exploration and development, facilitating the identification of reservoir connectivity and optimizing production strategies, thereby reducing exploration risks. This is achieved by enabling more precise predictions of reservoir characteristics based on oil geochemistry (Peters et al., 2005). Globally, organic-rich Paleozoic source rocks and their derived oils were extensively studied across regions including Pakistan, China, Australia, India,

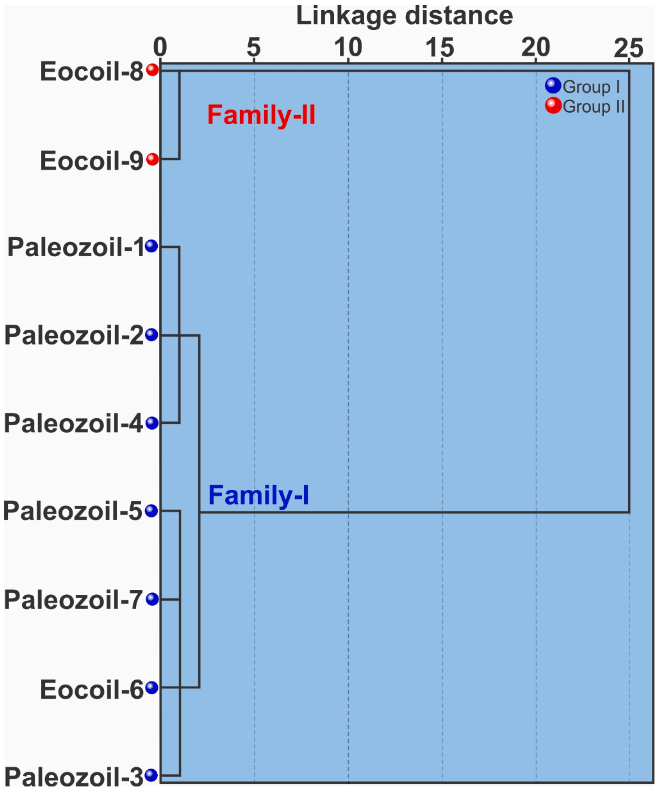

Fig. 14. Dendrogarm indicating the geochemical relationship and established groups among oils based on the selected parameters of (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Source and depositional environment. Red and blue symbol represent samples. Note: the parameters used for distinguish oil familes are illustrated in Table 3.

Oman, and Russia, providing key insights into their geological evolution and source rock properties (Grosjean et al., 2009; Kelly et al., 2011; Bhattacharya et al., 2017; Wang et al., 2019; Awan et al., 2020). The detailed geochemical profiling of studied oils, particularly from the Paleozoic age, reveals distinct oil groups with varied geochemical signatures indicative of different source rocks and burial histories. Such distinctions, notably between marine and lacustrine sources, reflect past marine transgressions, sea level fluctuations, and climatic conditions during sedimentary deposition. The identified complexities highlight the necessity for additional studies on the PTB's source rocks and their genetic links to the basin oils, especially considering the scant existing literature (Ahmed and Alam, 2007; Fazeelat et al., 2010; Irfan & Fazeelat, 2020; Khan et al., 2020). Future efforts should focus on oil-source correlation research using diverse PTB source rocks to enhance exploration strategies and improve hydrocarbon recovery efficiency in the organic-rich regions of the PTB.

6. Conclusions

We systematically analyzed hydrocarbon molecular markers within the crude oils from the PTB, Pakistan, to determine sedimentary environment, OM sources, and oil to oil correlation. Following are the conclusive facts of this study:

(1) The detected biomarker imprints and the hierarchical cluster analysis of the analyzed PTB crude oils have distinctively identified two oil families (Family I and Family II) with varying source origins and environments.
(2) Family-I crude oils were characterized by moderately lower ratios of Pr/Ph, C_{19} TT/C_{23}TT, C_{25}TT/C_{24}TeT, and $C_{(21+22)}/C_{(28+29)}$, C_{30} Diahopane/C_{30} Hopane, and a predominance of C_{29} regular steranes compared to Family-II crude oils. This indicates that Family-I crude oils were primarily derived from marine source rocks deposited under suboxic water stratification with substantial input from algal organic matter.
(3) Family-II crude oils consistently exhibited higher ratios of $(C_{19} + C_{20})/(C_{23} + C_{24})$TT, C_{26}/C_{28} TAS (20S) and C_{27}/C_{28} TAS (20R), and a relative abundance of fluorene and methyl dibenzofuran, suggesting that Family-II crude oils were predominantly originated from lacustrine source rocks deposited under oxic conditions.

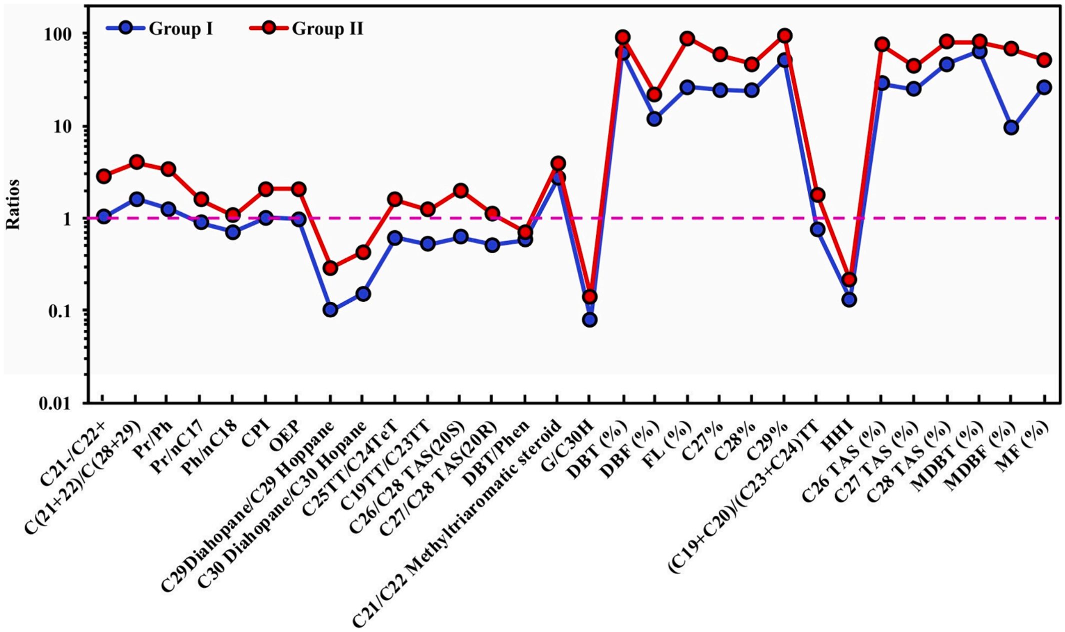

Fig. 15. The average distribution of selected molecular parameters for oil-oil correlation showing variation between two groups. The data is obtained from Table 4; abbreviations of geochemical parameters are explained in Table 4.

(4) The thermal maturation indicators based on saturated hydrocarbons, including $C_{29}\alpha\alpha\alpha20S/(20S+20R)$, $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$, Ts/Tm, and Moretane/Hopane, suggest that all crude oils from the PTB were thermally mature. Nevertheless, the aromatic maturity parameters and the calculated vitrinite reflectance values e.g., %Rc (MPI), %Rc (MDR), and %Rc (MPR), demonstrated that Family-II crude oils were reached to a higher level of thermal evolution.

CRediT authorship contribution statement

Sajjad Ali: Writing – original draft. **Meijun Li:** Supervision, Resources, Funding acquisition. **Jian Fu:** Writing – review & editing. **Asghar A.A.D. Hakro:** Writing – review & editing, Methodology, Data curation. **Hong Xiao:** Validation, Conceptualization. **Xiaolin Lu:** Visualization, Formal analysis. **Rizwan Sarwar Awan:** Writing – review & editing, Conceptualization. **Wang Dongyong:** .

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.

Data availability

Data will be made available on request.

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