



## Article

# Organic Geochemistry of Crude Oils from the Kohat Basin, Pakistan

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**Abstract:** The crude oils from the reservoirs of Mela-01 and Mela-04 wells located in the Kohat Basin, Pakistan, were geochemically analyzed to evaluate the origin, depositional conditions, and thermal maturity of the rock units and possible facies from which these oils were sourced. Gas chromatography-mass spectrometry (GC-MS) was performed on the samples to obtain biomarker and non-biomarker parameters. Analyzed non-biomarker parameters, including carbon preference index (CPI), terrigenous to aquatic ratio (TAR), isoprenoids pristane to phytane (Pr/Ph), and biomarker parameters, including steranes and dibenzothiophene/phenanthrene (DBT/P) of aromatic compounds, were utilized in the present study to achieve the objectives. Most of these parameters suggest a mixed source of organic matter (marine/terrestrial) with sub-oxic conditions in the source rocks for the analyzed oil samples in the studied wells from Mela oilfield, Kohat Basin. Furthermore, the CPI and different biomarker parameters such as steranes  $C_{29}$  S/S + R,  $\beta\beta/\alpha\alpha + \beta\beta$ , moretane to hopane ( $M_{29}/C_{30}H$ ), pentacyclic terpanes  $C_{27}$  (Ts/Ts + Tm),  $H_{32}$  (S/S + R) hopanes, and aromatic methylphenanthrene index (MPI) indicate that the analyzed oils have originated from thermally mature rocks falling in the oil window. As the studied Kohat Basin has multiple source rocks and contributes to the major petroleum production of the country, the present investigations reveal that its oil Mela oils were generated by the strata of mixed organic matter that were deposited in marine sub-oxic conditions. Furthermore, this study suggests that this stratum would also have been produced in unexplored surrounding areas such as Tirah, Orakzai, and the Bannu Depression.

**Keywords:** geochemistry; biomarkers; paleodepositional conditions; thermal maturity; hydrocarbon potential; Mela crude oils; organic matter; source rocks; Kohat Basin



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## 1. Introduction

Reservoir rocks are evaluated for the quantity and quality of petroleum they contain [1]. Source rocks are evaluated for their past, present, or future potential to generate petroleum. Thermally mature, organic-rich strata are required for the entire petroleum system, including source, reservoir, and cover rocks [2–6], while organic-rich strata are likewise important to emergent unconventional resource systems such as gas hydrates [7,8]. The identification of likely hydrocarbon regions in undiscovered sedimentary basins is heavily dependent on organic geochemical data. Organic geochemical data play a crucial role in the identification of prospective hydrocarbon-bearing regions in undeveloped sedimentary basins. Organic geochemistry in the field of hydrocarbon exploitation determines

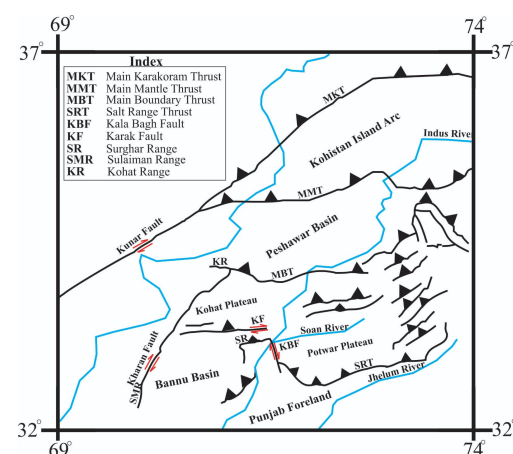
the origin, depositional conditions, burial history, and alteration of organic matter under thermal stress, all of which can lead to the formation of hydrocarbons [1,4,9–14].

Biomarkers are compounds preserved in sediments with little or no alteration to their original structure. Sediments and crude oils contain these complex organic compounds, which are primarily composed of carbon, hydrogen, and other elements and are derived from once-living organisms [15]. They have undergone little structural change from their progenitor organic molecules. The relative abundances and distributions of saturates, aromatic hydrocarbons, and cyclic geochemical relics in sediments and petroleum oils are used to determine the deposition environment of the source rock [15–19]. For basin studies, petroleum geoscientists can use biological markers to learn more about oil's origin and dynamics, such as petroleum formation issues, organic matter characteristics, analysis of thermal maturation, geological age, sedimentary facies, and reconstruction of the depositional environment [3–5,15,20–30].

The objective of this study is to geochemically analyze the crude oils from the Mela oilfield in the Kohat Basin in Pakistan and determine the origin, thermal maturity, and redox conditions of the organic matter in the source rocks that produced these crude oils. By examining the organic geochemical features of the above crude oils within the context of thermal maturity and depositional conditions of organic matter, this study will provide a more holistic understanding of the hydrocarbon potential of the study area, which shares geological similarities with the surrounding regions containing proven reserves and can be considered of crucial economic and strategic importance.

## 2. Geological Setting

The studied Kohat Basin, located on the western edge of the Himalayan Belt in northern Pakistan [31], is one of the most productive basins in Pakistan, containing oil and gas fields such as Chanda, Nashpa, Mela, Manzali, Maramzai, Makori, and Mami Khel, which contribute significantly to the nation's petroleum production. Geologically, the study basin is bounded by the Main Boundary Thrust (MBT), the Surghar Range Thrust (ST), the Kalabagh Fault, the Kurram Fault, and the Bannu Depression (Figure 1). The Kohat Basin is a complex, hybrid terrane with strike-slip and contractile elements [32]. Its structural setup is represented by north-dipping, low-angle imbricate thrust faults underneath a blind passive-roof thrust [33–35]. It is stratigraphically composed of Jurassic-Pleistocene geological units [36], including multiple clastic and carbonate source rocks [37–39] and reservoir rocks [35,40–44]. Most of these rocks crop out in cores of anticlines created as detachment folds and pressure ridges over complicated, positive flower structures that suggest significant, but ambiguous, north-to-south shortening. The uplift of the MBT started in the late Miocene, and this deformation affected the rocks of Kohat Basin as early as the Pleistocene [32,45].



**Figure 1.** Tectonic map illustrating structural elements of the northern Pakistan and showing the location of the study area. The blue lines indicate the river flow, while the black triangles corresponds to thrusting, and red lines to thrust faults, respectively (modified by [46]).

### 3. Materials and Methods

#### 3.1. Samples

The two crude oil samples from Mela-01 and Mela-04 wells in the Kohat Basin, Pakistan, were collected and utilized in the current research. The study area is shown in Figure 1.

#### 3.2. Laboratory Work

Alkane distribution and biomarker parameters were determined using an Agilent 6890 series gas chromatograph equipped with a DB-5 fused silica column (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu$ m) with a data station and integrator, and for GC-MS, a Shimadzu GC-2010 gas chromatograph interfaced with a QP-2010 plus mass spectrometer was used. Prior to gas chromatography analysis, the sample was fractionalized and separated by column chromatography into polar (NSO), aromatics, and saturates. The glass column was prepared by washing it with dichloromethane and then placing it on glass fiber that had been pre-treated. Two-thirds of the glass column was filled with silica slurry in n-hexane, followed by alumina slurry in n-hexane. Briefly, 100–150 mg of sample was loaded at the top, and the saturate fraction of maltenes was eluted with 30 mL of n-hexane; aromatic hydrocarbons were eluted with dichloromethane; and the polar fraction (NSO compounds) was eluted with 30 mL of ethyl acetate. Following the evaporation of a solvent, three fractions were weighed and then analyzed.

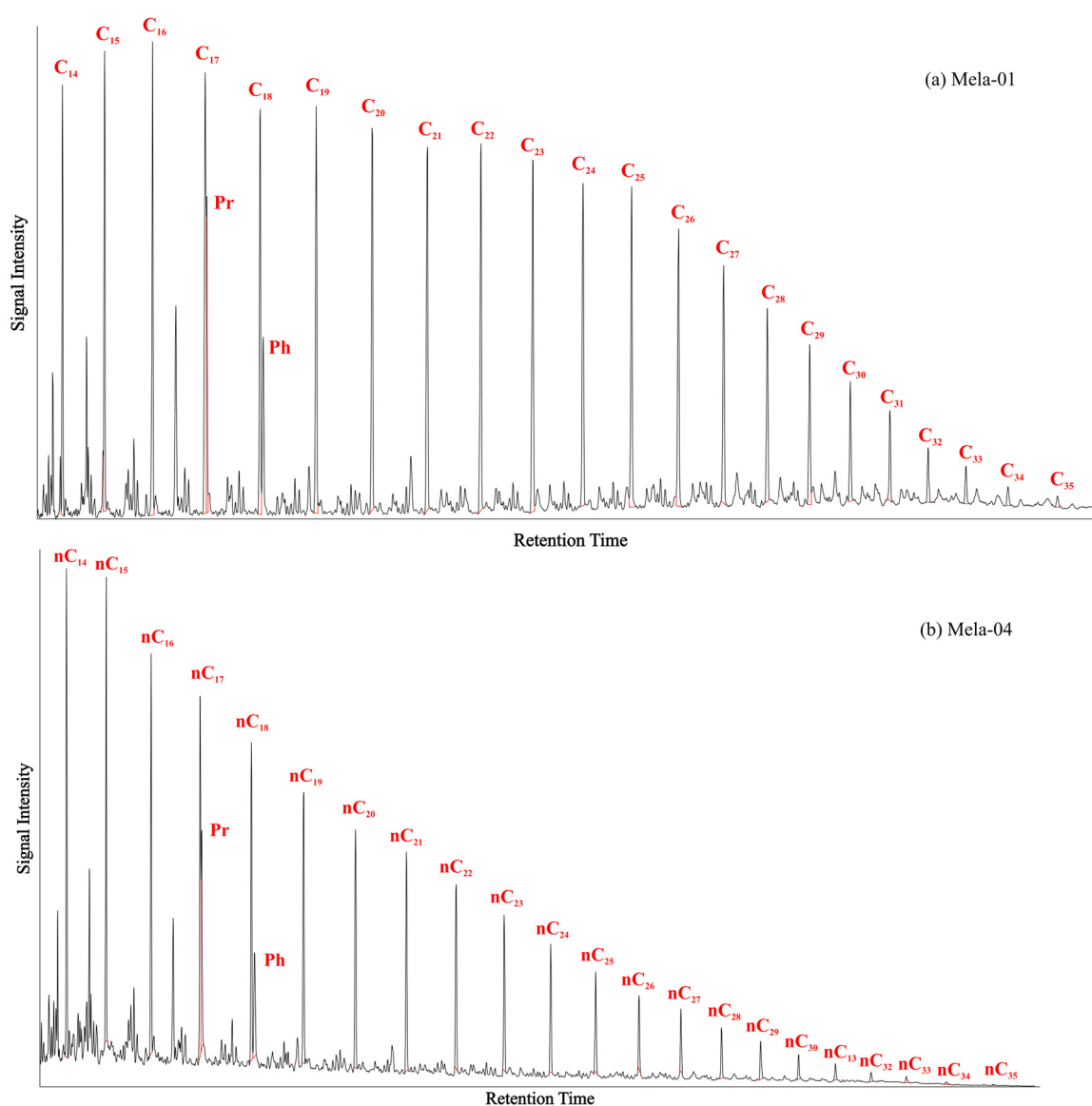
The saturates and aromatic fractions were further subjected to GC apparatus equipped with a data station and integrator using a DB-1 column. One microliter of the sample fraction (saturated and aromatic hydrocarbon) was injected using a split injection mode and capillary column, keeping the oven temperature at 100 °C for a minute before being raised to 320 °C at 5 °C per minute, while the injector and column temperatures were maintained at 320 °C [47]. The carrier gas used was nitrogen, and the performance of gas chromatography was checked by using a validation standard consisting of saturated (nC<sub>17</sub> and pristane) and blank samples after every 10 samples. The saturated and aromatic fractions were prepared by dissolution in DCM (6:1 dilution).

### 4. Results

The different parameters and ratios of n-alkanes and isoprenoids ( $m/z$  57), steranes and diasteranes ( $m/z$  217 and 218), terpanes ( $m/z$  191), and aromatic hydrocarbons ( $m/z$  178, 184, and 192) were measured and calculated here to evaluate the nature, level of thermal maturity, and depositional conditions of organic matter that have sourced these oils. The chromatograms of the analyzed oils have been shown in Figures 2–5.

The n-alkane ( $m/z$  57) distribution pattern of the studied oils from Mela-01 and Mela-04 wells indicates that short-chain alkanes predominate, followed by heavier hydrocarbons, as illustrated in Figure 2a,b. The long-chain n-alkanes are comparatively abundant in Mela-01 relative to Mela-04 (Figure 2a,b).

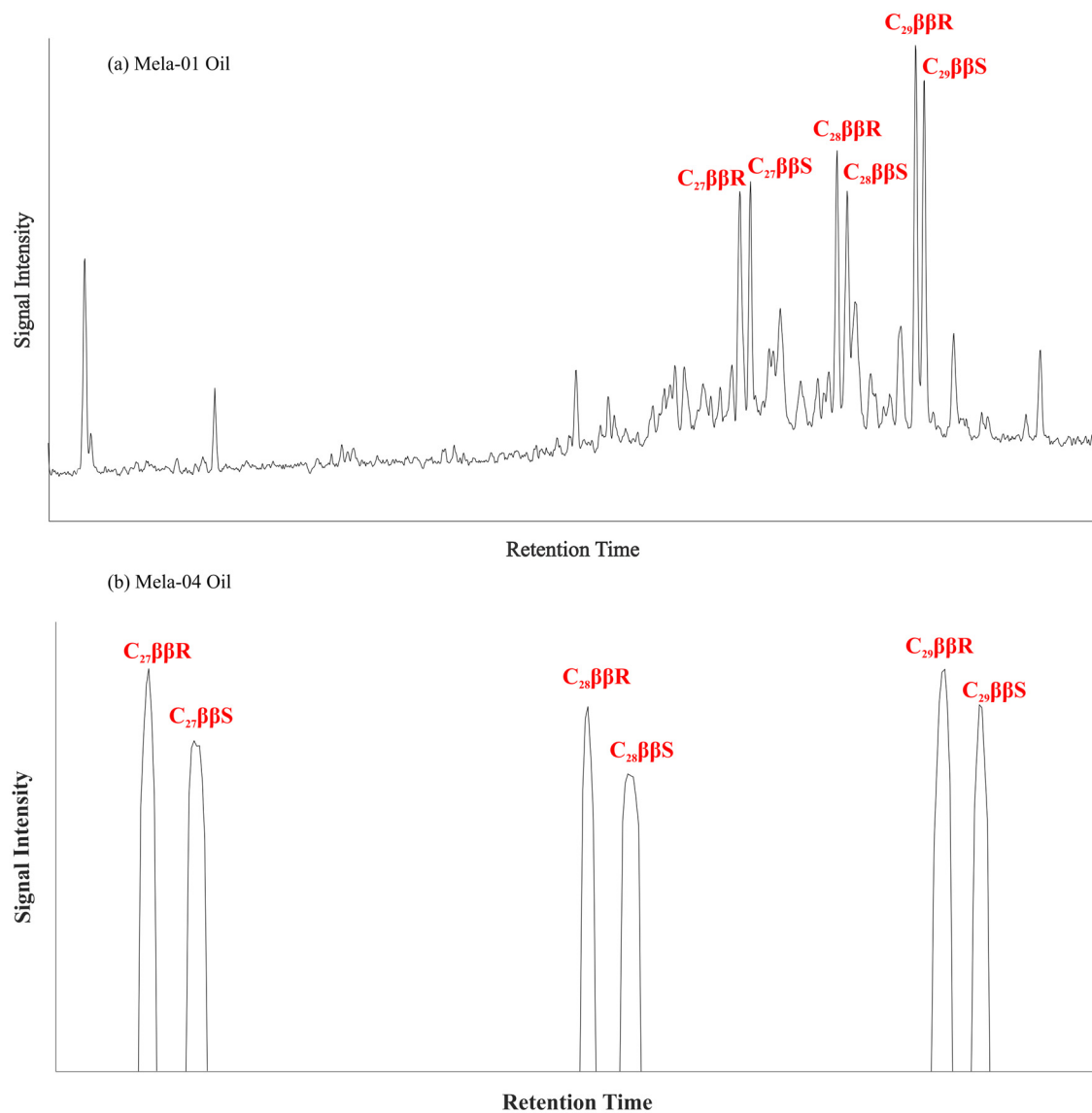
The CPI and terrigenous-aquatic ratio (TAR) of n-alkanes have values of 1.04 and 0.43, respectively, in Mela-01, whereas 1 and 0.13, respectively, in Mela-04 (Table 1), well indicate an almost mixed odd and even n-alkanes distribution [48].



**Figure 2.**  $m/z$  57 chromatograms representing n-alkanes and isoprenoids in Mela oils in the study area. (a) Mela-01, and (b) Mela-04 wells, respectively.

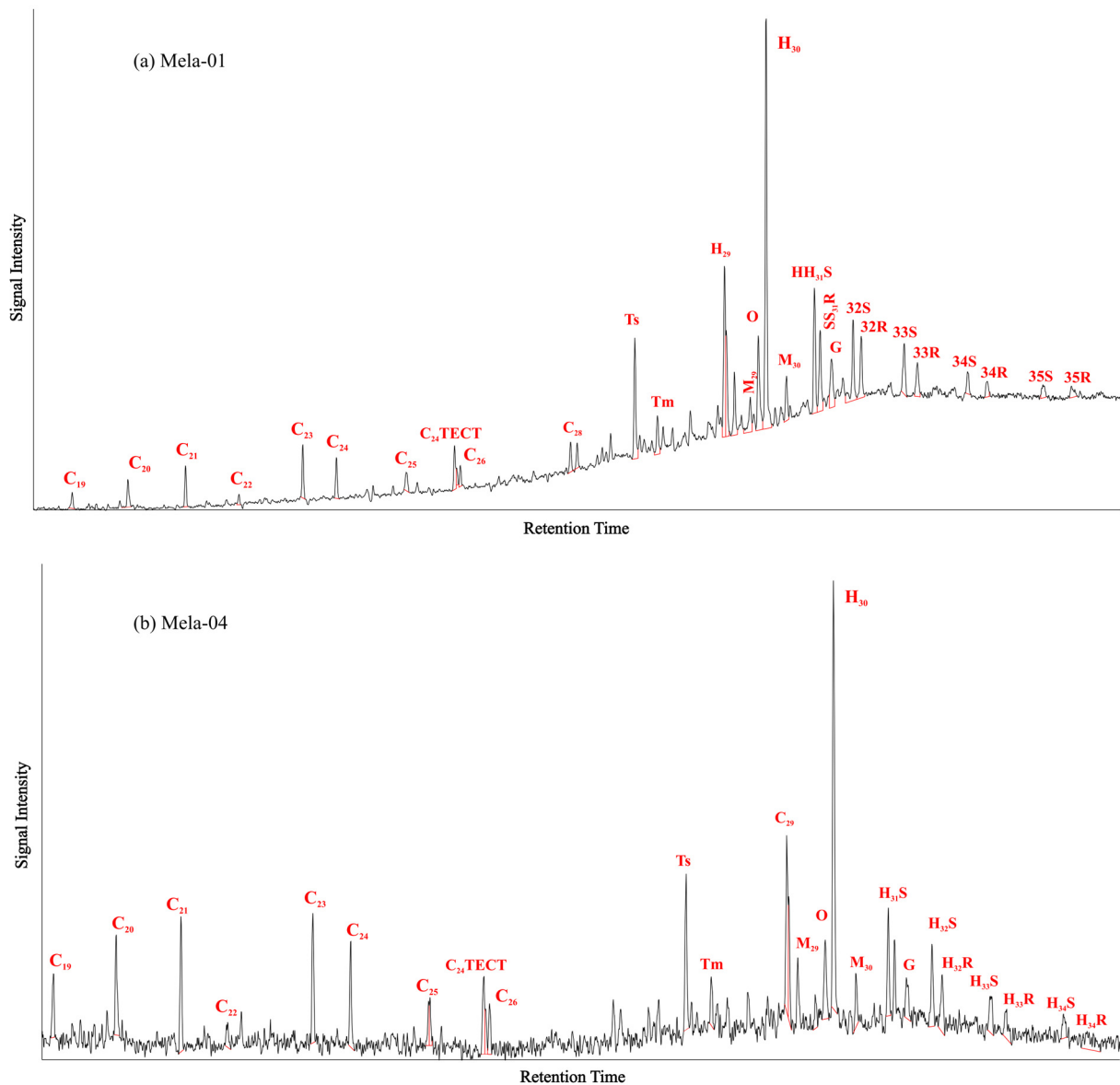
A significant concentration of pristane and phytane isoprenoids is present in both the analyzed oil samples (Figure 2a,b) with the former dominating over the latter, i.e.,  $Pr/Ph = 1.04$  and  $1.52$  for Mela-01 and Mela-04, respectively (Table 1). The calculated  $Pr/nC_{17}$  values are  $0.39$  and  $0.55$ , and phytane/ $nC_{18}$  values are  $0.48$  and  $0.45$  in Mela-01 and Mela-04, respectively (Table 1).

The steranes and diasteranes biomarkers were also observed in the chromatograms ( $m/z$  217 and 218) of the analyzed oil samples (Figure 3a,b). The measured  $C_{27}$  sterane value is  $30.26\%$  and the measured  $C_{29}$  sterane value is  $38.39\%$  in Mela-01, whereas in Mela-04 the  $C_{27}$  is  $34.81\%$  and the  $C_{29}$  is  $35.5\%$ , respectively (Table 1). Comparatively, the  $C_{29}$  land plant-related sterane is higher in Mela-01 relative to Mela-04.



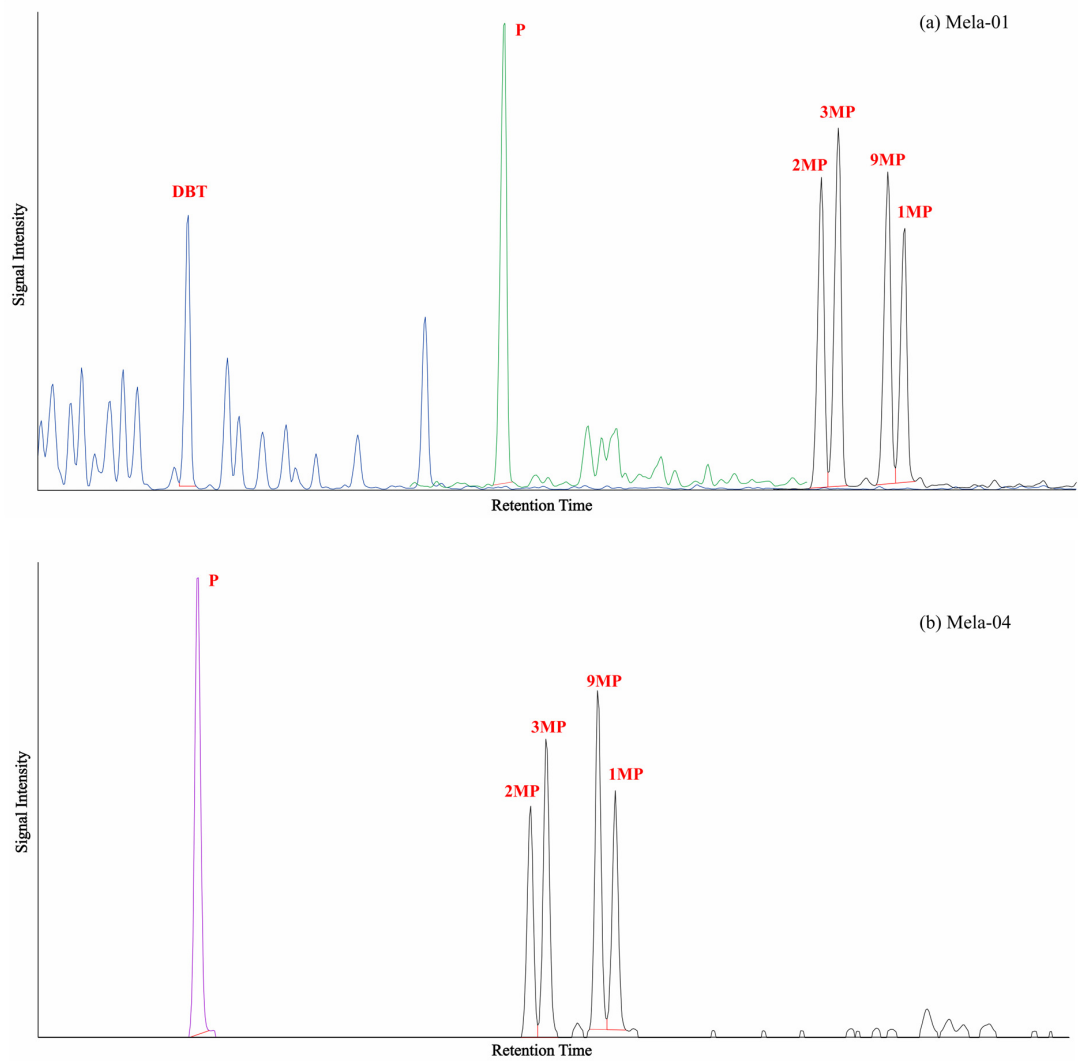
**Figure 3.** (a,b) Chromatograms showing distribution of  $C_{27}$ ,  $C_{28}$ , and  $C_{29}$  steranes in the studied Mela oils from Kohat Basin.

The terpanes chromatograms of the analyzed oils contain tricyclic, tetracyclic, and pentacyclic terpanes biomarkers. The  $C_{19}/C_{23}$  tricyclic values are 0.26 and 0.33, the  $C_{20}/C_{23}$  tricyclic values are 0.68 and 0.81, and the  $C_{23}/C_{24}$  tricyclic values are 0.82 and 0.81 in Mela-01 and Mela-04, respectively (Table 1). The tetracyclic terpanes are also present in significant amounts, indicating relatively higher concentrations than  $C_{23}$  tricyclic terpanes in both wells, with  $C_{24}TeT/C_{23}$  tricyclic being 0.99 and 0.69 and  $C_{24}TeT/C_{30}H$  being 0.11 and 0.2 (Table 1). Figure 4a,b also depicts the presence of hopanes and homohopanes, including Ts, Tm,  $C_{29}$  norhopane,  $C_{30}$  hopane,  $C_{35}$  and  $C_{34}$  HH,  $C_{31}RH$ , oleanane, and gammacerane. The  $C_{35}$  homohopane is higher than the  $C_{34}$  HH in Mela-01, with a  $C_{35}/C_{34}$  HH value of 0.89, and is absent in Mela-04. Oleanane has also significantly contributed to both oils, with  $O/C_{30}H$  values of 0.28 and 0.24 in Mela-01 and Mela-04, respectively. Others include moretane with  $M_{29}/C_{30}H$  at 0.4 in both wells,  $G/C_{30}H$  at 0.18 and 0.14, and  $C_{31}RH/C_{30}H$  at 0.23 and 0.16 in Mela-01 and 04 wells, respectively, as listed in Table 1. These values indicate significant amounts of  $C_{31}RH$ , oleanane, and gammacerane (Figure 4a,b).



**Figure 4.** (a,b) Terpanes ( $m/z$  19) distribution in the analyzed oils from Mela oilfield.

The aromatic compound dibenzothiophene (DBT) is sulfur containing, which is relatively abundant in marine carbonate and marl, while high phenanthrene results from precursors inherited from land plants [49]. Both the analyzed oil samples contain these aromatics in substantial amounts, with DPT/P 0.55 in Mela-01 and 0.31 in Mela-04 (Figure 5).



**Figure 5.** Aromatic hydrocarbon (*m/z* 178, 184 and 192) in the analyzed oils from Mela oilfield in the study area. (a) Mela-01, and (b) Mela-04 wells, respectively.

**Table 1.** n-alkanes, isoprenoids, terpanes, and aromatics ratios in oils from Mela oilfield wells, Kohat Basin.

Short-Chain N-Alkanes								Steranes			Terpanes						
Well	Sample	CPI	TAR	OEP	Pr/nC <sub>17</sub>	Ph/n-C <sub>18</sub>	Pr/Ph	C <sub>27</sub> %	C <sub>28</sub> %	C <sub>29</sub> %	C <sub>19</sub> /C <sub>19</sub> + C <sub>23</sub>	C <sub>20</sub> /C <sub>23</sub>	C <sub>22</sub> /C <sub>21</sub>	C <sub>24</sub> /C <sub>23</sub>	C <sub>26</sub> /C <sub>25</sub>	C <sub>29</sub> /C <sub>30H</sub>	H <sub>31</sub> R/C <sub>30H</sub>
Mela-01	Oil	1.04	0.43	1.09	0.39	0.48	1.04	30.26	31.34	38.39	0.26	0.68	0.26	0.82	0.74	0.42	0.23
	Oil	1	0.13	1.05	0.55	0.45	1.52	34.81	28.69	35.5	0.33	0.81	0.24	0.81	1.48	0.42	0.16



Table 1. Cont.

		Thermal Maturity Parameters						
		Steranes C <sub>29</sub>		Terpanes				Aromatics
		S/S + R	ββ/αα + ββ	M <sub>29</sub> /C <sub>30</sub> H	Ts/Ts + Tm	H <sub>32</sub> (S/S + R)	C <sub>31</sub> H (S/S + R)	MPI
Mela-01	Oil	0.5	0.5	0.12	0.73	0.58	0.58	0.99
	Oil	0.57	0.52	0.08	0.76	0.54	0.6	0.81

## 5. Discussion

### 5.1. Source and Depositional Condition

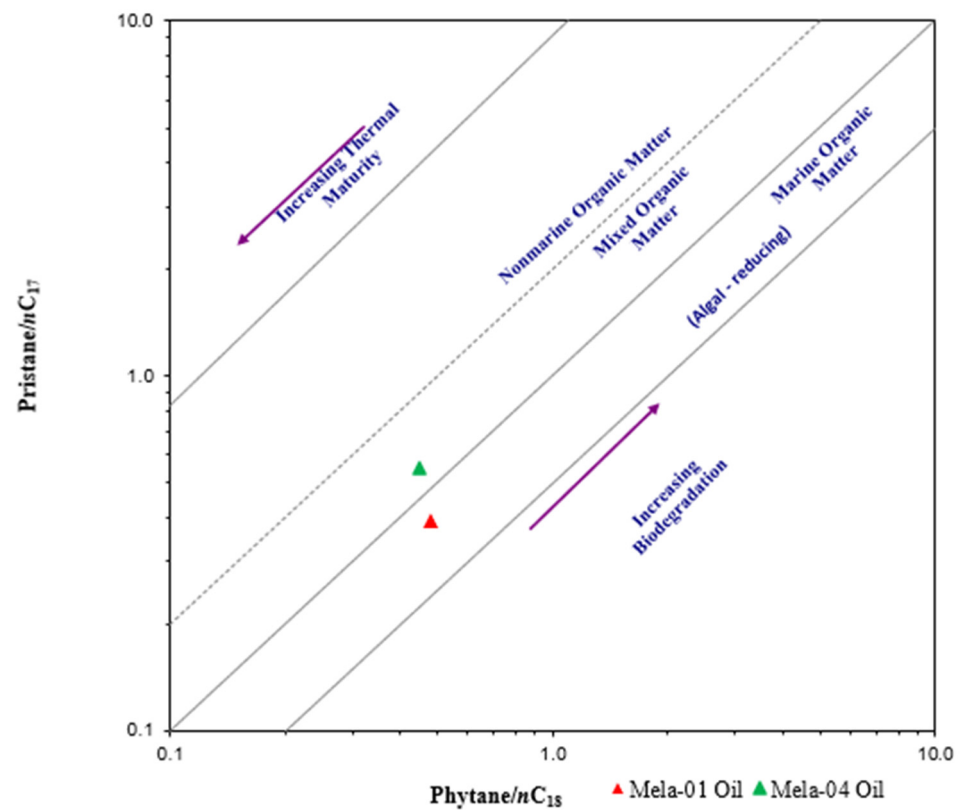
In the present study, several biomarker parameters were utilized for the evaluation of the nature and redox conditions of the organic input at the time of deposition. Details of these biomarkers are discussed below.

#### 5.1.1. Short Chain N-Alkanes and Isoprenoids

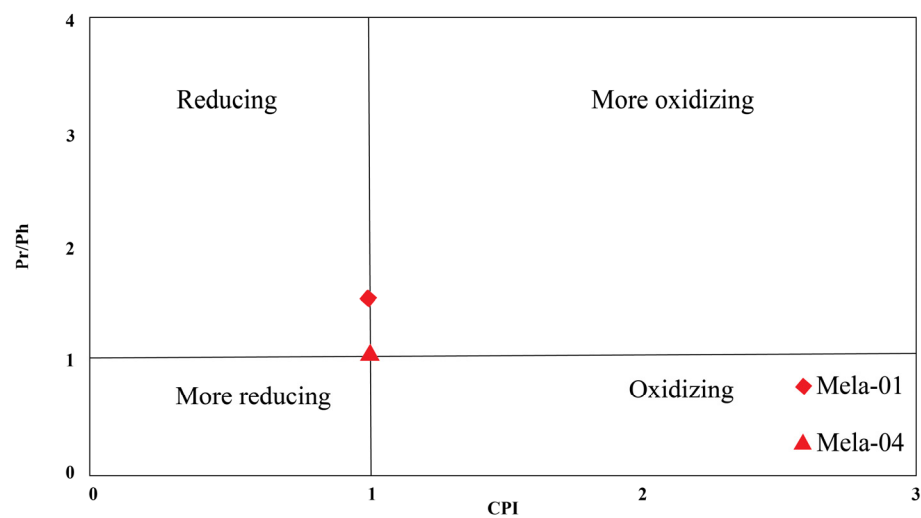
The distribution pattern of n-alkanes on *m/z* 57 chromatograms in the analyzed oils from the studied wells indicates that short-chain alkanes predominate, followed by heavier hydrocarbons, reflecting a mixed source of organic matter received by the source units at the time of deposition. Figure 2a,b clearly shows that heavier and medium n-alkanes are relatively higher in Mela-01 than in Mela-04. Peters et al. [15] suggested that high concentrations of short-chain n-alkanes are either due to marine organic source input or sometimes due to higher thermal maturation. The appreciable concentration of short-chain n-alkanes and their unimodal pattern suggest that the oils have not experienced secondary alterations (biodegradations). The commonly used source-related n-alkane parameters CPI and TAR (1.04, 0.43), respectively, in Mela-01 and 1 and 0.13 values in Mela-04 wells (Table 1) indicate mixed organic matter, which is comparatively higher in the case of Mela-01 oil. High terrestrial input results in high TAR values; however, the CPI may also be influenced by thermal maturity, where sometimes high thermal stress results in a CPI~1 [15,50].

Pristane and phytane isoprenoids are the sources and best indicators of oxicity [15,51]. The calculated values of the isoprenoids Pr/Ph are 1.04 and 1.54 for Mela-01 and Mela-04, respectively, which indicate mixed sources of organic materials and sub-oxic conditions, as their values >3.0 represent oxic terrestrial organic matter, <0.6 anoxic, and the values in the range from 1–3 indicate sub-oxic conditions during deposition of sediments. However, Pr and Ph can also be influenced by thermal maturity [52–56]. The high concentration of phytane represents either marine input and/or reducing conditions or thermal maturity because phytane is generated more rapidly than pristane during maturation [15,53]. Both pristane/n-C<sub>17</sub> versus phytane/n-C<sub>18</sub> and Pr/Ph vs. CPI plots proposed by Shanmugam [57] and Peters and Moldowan [52], respectively, indicate a mixed source of organic input in Mela-04 but comparatively more algal input in Mela-01 deposited in sub-oxic conditions (Figure 6a,b).





(a)



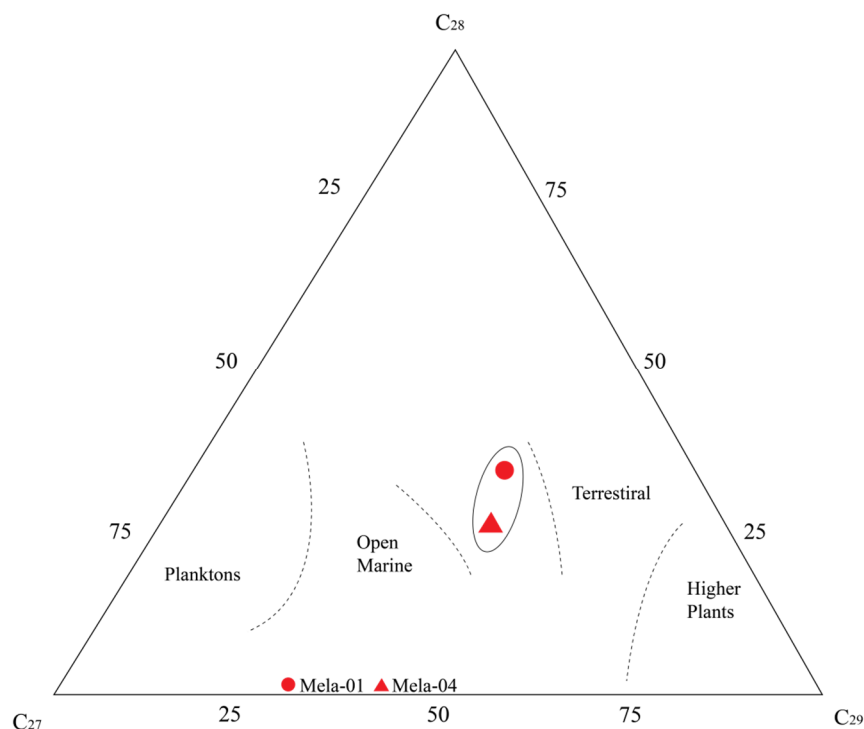
(b)

**Figure 6.** Organic source and redox conditions of the examined oils in the studied wells through the (a)  $\text{Pr}/\text{nC}_{17}$  vs.  $\text{Ph}/\text{nC}_{18}$  and (b)  $\text{Pr}/\text{Ph}$  vs. CPI cross plots.

### 5.1.2. Steranes and Diasteranes

Among sterane biomarkers, the  $\text{C}_{27}$  steranes are mainly linked with algae, and the  $\text{C}_{29}$  steranes are associated with terrestrial organic materials [58,59]. The chromatograms of normal steranes and rearranged diasteranes of the analyzed oils (Figure 3) depict that mixed organic matter (marine/terrestrial) was deposited in the rocks from which the analyzed oils were sourced [15,52]. This interpretation is consistent with the distribution pattern of n-alkanes and isoprenoids in the present study. Furthermore, a comparatively high terrestrial input has been observed in the case of Mela-04 relative to Mela-01 based on

the relative abundance of  $C_{29}$  steranes, as indicated by the plot between  $C_{27}$ ,  $C_{28}$ , and  $C_{29}$  regular steranes (Figure 7).

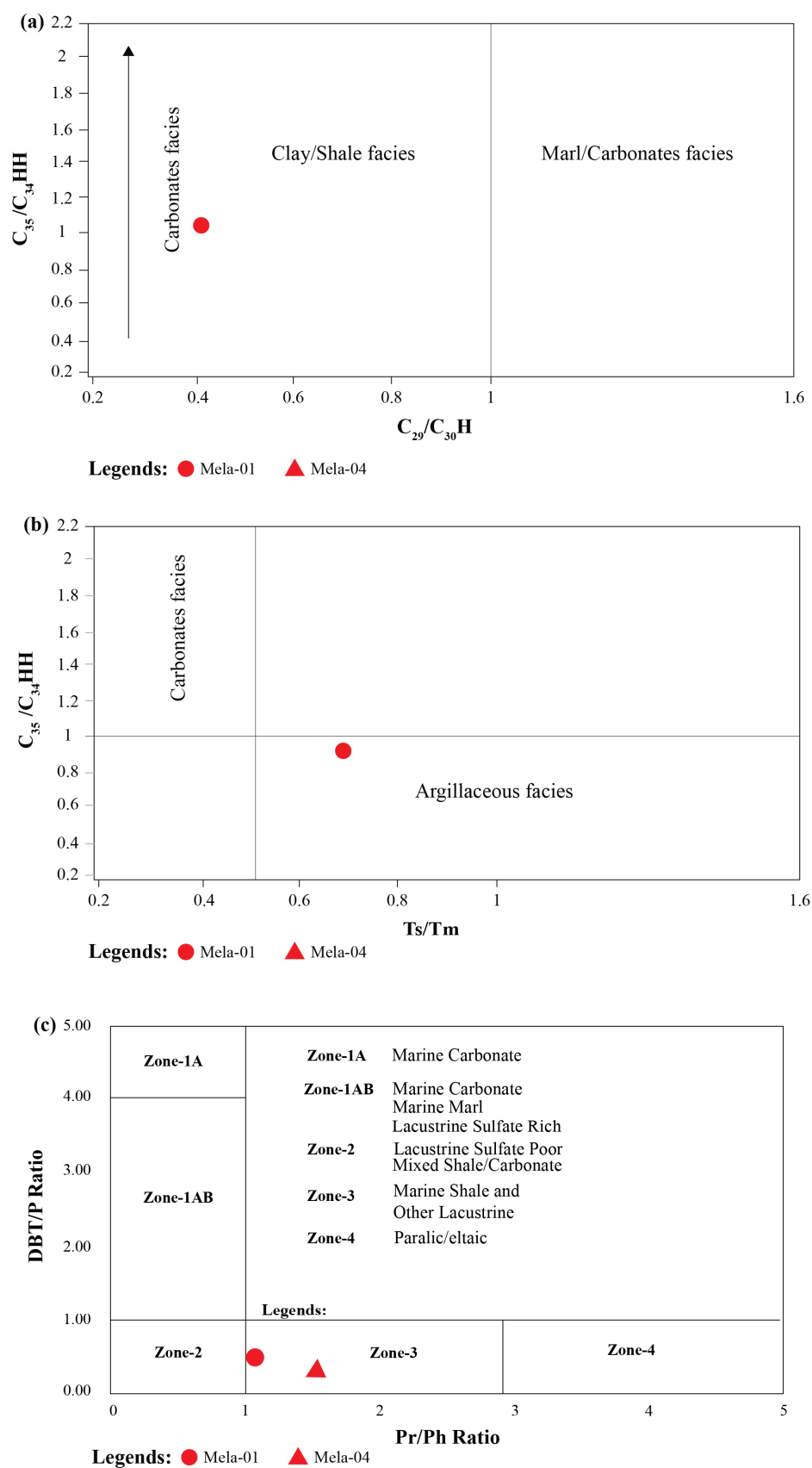


**Figure 7.** Ternary plot of regular steranes ( $C_{27}$ – $C_{29}$ ) of the analyzed oils from Mela oilfield indicating source of organic matter in the study area.

### 5.1.3. Terpanes

The terpene biomarkers of the examined oils contain tricyclic, tetracyclic, and pentacyclic biomarkers. The chromatograms of the examined oils also revealed the presence of homohopanes ( $C_{31}$ – $C_{35}$ ),  $C_{30}$ -hopanes,  $C_{29}$ -norhopanes, 17a (H)-trisnorhopanes (Tm), and 18 (H)-trisnorhopanes (Ts). Different ratios were calculated from biomarker peaks and were used in the present investigations to assess the source and depositional setting of the analyzed oil samples. The tricyclic terpene ratios  $C_{19}/C_{23}$  and  $C_{20}/C_{23}$  further suggest that the source units have received significant terrestrial input from marine organic matter, as reported in Table 1, because the  $C_{23}$  tricyclic terpanes are dominant in marine organic materials, while the  $C_{19}$  and  $C_{20}$  tricyclic terpanes originate from terrestrial materials [15]. As seen in Figure 4a,b and Table 1 with  $C_{24}Tet/C_{23}TCT$ , the oil samples in both of the examined wells also have a considerable quantity of  $C_{24}$  tetracyclic, which further indicates a substantial quantity of continental organic matter combined with marine organic materials [60–62].

The relative lower concentration of  $C_{29}$ -norhopane than  $C_{30}$ -hopane ( $C_{29}/C_{30}$  17a H) with values of 0.48 and 0.78 (Table 1 and Figure 5a,b) reflects the shale facies of the source rocks from which the oils originated, as clay-rich source rocks contain relatively high concentrations of  $C_{30}$ -hopane ( $C_{29}/C_{30}$  H < 1) [14]. Furthermore, the  $C_{25}$  tricyclic terpanes are marine-related, and the  $C_{26}$  tricyclics are associated with lacustrine clay/carbonate facies [15], so these clay-rich facies were deposited in marine environments, as indicated by the low values of this ratio (0.74 and 1.48) (Figure 8a and Table 1). As a result, the  $C_{26}/C_{25}$  tricyclic vs.  $C_{29}/C_{30}$  H confirms clay-rich facies deposited in marine settings for the investigated oils (Figure 8a).



**Figure 8.** Facies analysis for the analyzed crude oils in Mela oilfield using (a)  $C_{35}/C_{34}$  hopane vs.  $C_{29}/C_{30}$  H plot, (b) Ts/Tm vs.  $C_{35}/C_{34}$  H plot, and (c) DBT/P and Pr/Ph cross plot.

In addition to thermal maturity and depositional environmental assessment, the  $Ts/Ts + Tm$  and  $C_{35}/C_{34}$  HH also provide information about the lithology of the source units [15]. The ratios of  $Ts/Ts + Tm$  ( $>0.5$ ) and  $C_{35}/C_{34}$  HH ( $<1$ ) also support the shale lithology of the source rocks for the oils, as shown in Figure 8b.

Marine carbonate source rocks can be differentiated from other lithologies by containing high  $C_{22}/C_{21}$  and low  $C_{24}/C_{23}$  tricyclic terpane values, so the calculated values of  $C_{22}/C_{21}$  (0.24–0.26) and  $C_{24}/C_{23}$  (0.81–0.82) indicate that the analyzed oils have not originated from other than carbonate lithologies, as suggested by Peters et al. [15]. The  $C_{35}$  HH is associated with a reducing environment, so the 0.89 value of  $C_{35}/C_{34}$  HH for Mela-01 indicates a reducing depositional environment at the time of organic matter accumulation in the sediments, while its absence in Mela-04 may reflect oxidizing conditions [54].

In paleoenvironmental studies, the  $C_{31}R/C_{30}$  hopane ratio distinguishes marine and lacustrine depositional environments. The value of this ratio in a marine environment is generally  $>0.25$  and lower for lacustrine depositional settings [15]. In addition, the  $C_{31}R$  homohopane/ $C_{30}H$  (Table 1), accompanied by  $C_{35}/C_{34}$  HH and  $C_{31}R/C_{30}H$  vs.  $Pr/Ph$  plots, also suggest a marine depositional environment for Mela oils.

The pentacyclic homohopane oleanane is usually associated with extracts and oils originating from terrigenous Cretaceous and younger rocks [63–65]. The oleanane index ( $O/C_{30}H$ )  $>30\%$  indicates high terrigenous organic material, and  $<10\%$  indicates insignificant terrigenous input [66]. The oleanane index calculated from terpane chromatograms for the analyzed oils ranged from 0.24–0.28, as listed in Table 1, indicating a substantial contribution by terrestrial organic matter (intermediate between marine and terrestrial) [15]. The presence of gammacerane, a salinity (redox conditions) indicator, in quantities ranging from 0.14–0.18 in the examined oils (Table 1; Figure 4a,b) indicates that deposition of organic matter and facies was not in freshwater conditions [52,67,68]. The sub-oxic conditions were also supported by calculated values of  $Pr/Ph$  (1.04–1.52) for these oils.

#### 5.1.4. Aromatics

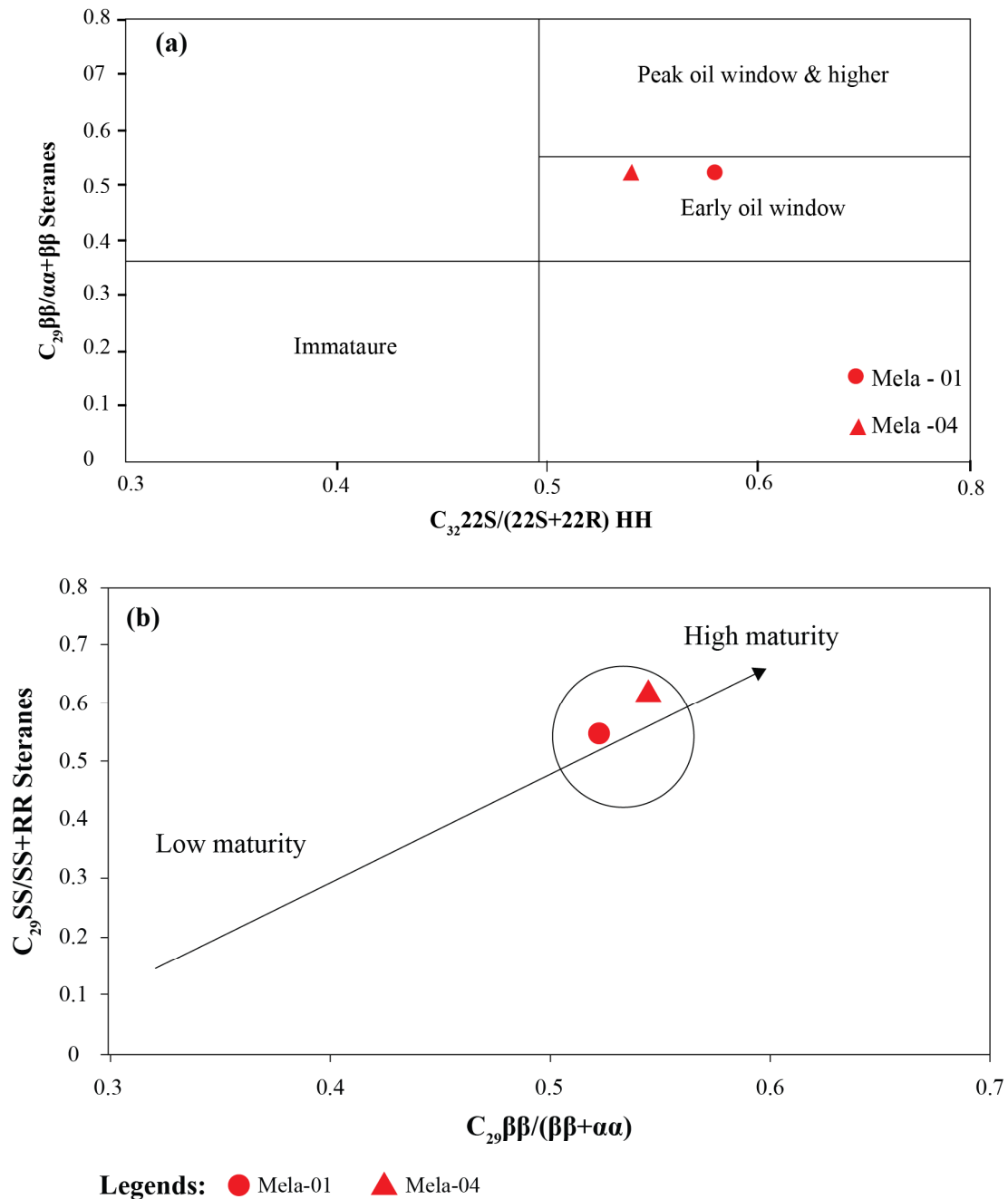
The aromatic compound dibenzothiophene (DBTs) is a sulfur-containing aromatic compound that is relatively abundant in marine carbonate and marl, while high phenanthrene results from precursors inherited from land plants [49]. A relatively high concentration of phenanthrene (P) in crude oils and source sediments compared to dibenzofuran (DBF) and dibenzothiophene (DBT) is related to a high concentration of type III kerogen [69–71]. In the present study, the dibenzothiophene/phenanthrene ratios (0.5 and 0.31) in oil samples in Mela-01 and Mela-04 wells, respectively, indicate a significant contribution of both aromatic compounds, and by using the plot of  $DBT/P$  versus  $Pr/Ph$  proposed by Hughes et al. [49], the oil samples fall within the mixed shale/carbonates zone (Figure 8c).

#### 5.2. Thermal Maturity

In the present study, the thermal maturity of the analyzed oil samples from selected wells in the Mela oilfield, Kohat Basin, was assessed using parameters of n-alkanes and ratios of terpanes and steranes as biomarkers. The relative abundance of short-chain alkanes in the analyzed oil samples followed by CPI values indicates an oil window, as  $CPI \sim 1$  is sometimes also due to thermal maturity, and  $>1.5$  shows immaturity. Similarly, the abundance of short-chain alkanes is either contributed by marine organic matter or may be caused by thermal maturity, where higher molecules crack into lower molecules [15,21,52].

The  $C_{29} 20S/(20S + 20R)$  sterane value increases from 0 to 0.5 with increasing thermal maturation of organic matter and attains equilibrium from 0.52–0.55, while at a 0.4 value, the onset of petroleum generation occurs, but Seifert et al. [72] have noted lower values ranging from 0.23–0.29 in low-maturity oils. The present oils yield a value of this ratio ranging from 0.5–0.57, reflecting the oil stage of the source rocks (Figure 9b). This parameter is affected by the mineral contents of the source rocks too [52,73]. The  $C_{29} \beta\beta/\alpha\alpha + \beta\beta$  in another index of thermal maturity that is valid up to the peak oil window [74] increases from 0–0.7 and equilibrium is established at 0.67–0.7 and is not affected by the nature of

organic matter as suggested by Seifert and Moldowan [74], Welte and Tissot [21], and Peters et al. [15]. This ratio found in the analyzed oils in the study area ranged from 0.5–0.52, indicating an early mature stage (Figure 9a,b).



**Figure 9.** Biomarker's parameters showing maturity of the analyzed oil samples from the study area using (a)  $C_{29} \beta\beta / \alpha\alpha + \beta\beta$  vs.  $C_{32} 22S / (22S + 22R)$  plot, and (b)  $C_{29} \beta\beta / \alpha\alpha + \beta\beta$  vs.  $C_{29} (S/S + R)$  plot. The circle indicates the area of the marine shale lithology of the analyzed oils.

In addition to n-alkanes and steranes, terpanes parameters, including  $C_{32} 22S / (22S + 22R)$ , were also utilized in the thermal maturity analysis of the investigated oils. This value increases from 0–0.6 with thermal maturation and reaches equilibrium at 0.57–0.62. The values of this ratio of 0.58 and 0.54 for Mela-01 and Mela-04, respectively, indicate the oil generation stages, whereas in Mela-04, the thermal maturity of the source unit is relatively higher (Figure 9a).

The Tm/Ts (stereoisomers of C<sub>27</sub> hopanes) are also used to determine the level of thermal maturity, which is applicable up to the postmature level but dependent on the depositional environment and source of organic materials. Oils from carbonate lithologies will have a low value compared to those from shale facies [75–77]. During the maturation process, the stability of Tm is less than that of Ts [78]. So, Ts/Tm increases with thermal maturity as well as with reducing depositional environments [52]. This value has been calculated for the analyzed oils and ranges between 0.73–0.76 for Mela-01 and Mela-04, respectively, also indicating a mature stage for hydrocarbon generation. The same status of thermal maturity is also supported by M<sub>29</sub>/C<sub>30</sub>H having values of 0.12 and 0.08 for the analyzed oils, respectively. Moreover, moretanes are thermally less stable than hopanes and range from about 0.8 in immature to 0.15–0.05 in mature organic matter [15,74,79]. The methylphenanthrene index values range from 0.81 to 0.99 and indicate the oil window of the source rocks for oils (Table 1).

## 6. Conclusions

Detailed geochemical analyses were conducted on two oil samples from two wells in the Mela oilfield in the Kohat Basin to determine the redox conditions and nature of organic matter that have generated these oils. By applying GC and GC-MS techniques, various biomarker parameters were obtained and used.

- The short-chain alkane distribution patterns along with their standard ratios, including CPI, TAR, and isoprenoids (Pr/Ph), indicate a mixed source of organic matter deposition in sub-oxic conditions in marine depositional environments. The CPI and OEP further indicate that source units that have generated the analyzed oils fall into the oil window.
- The steranes parameters such as C<sub>29</sub> and C<sub>27</sub>, which are commonly used source indicators, also support the mixed source of organic matter, while maturity-related parameters from the steranes group also indicate maturity for the oil of the source units.
- The organic input and facies of the source units were also determined by terpanes (C<sub>20</sub>/C<sub>23</sub>, C<sub>19</sub>/C<sub>23</sub>), oleanane index, C<sub>29</sub>/C<sub>30</sub>H, Ts/Tm, C<sub>35</sub>/C<sub>34</sub> HH, C<sub>26</sub>/C<sub>25</sub> tri-cyclic, and C<sub>31</sub> R H/C<sub>30</sub> H, and DBT/P, where most of the parameters indicate shale lithologies containing mixed organic matter deposited in sub-oxic marine conditions.
- Most of the maturity-related biomarkers and non-biomarker parameters, such as CPI, C<sub>29</sub> S/S + R, ββ/αα + ββ, moretane to hopane (M<sub>29</sub>/C<sub>30</sub>H), pentacyclic terpanes C<sub>27</sub> (Ts/Ts + Tm), H<sub>32</sub> (S/S + R) hopanes, and aromatic methylphenanthrene index (MPI), agree that the analyzed oils from the selected wells in the Mela oilfield have originated from thermally mature rocks falling in the oil window.
- As in the study basin, proven source rocks are Paleocene and Cretaceous shales, which are shallow marine deposits having marine organic matter, but this study reveals that the oils in the Mela wells have been generated by the strata of mixed organic matter, which may be deltaic, so these strata can increase the hydrocarbon potentiality in the area and can be expected in the surrounding non-explored areas of the basin too.

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