

## Article

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

Syed Mamoon Siyar <sup>1,2,\*</sup>, Fayaz Ali <sup>1</sup>, Sajjad Ahmad <sup>1</sup>, George Kontakiotis <sup>3,\*</sup> , Hammad Tariq Janjuhah <sup>4</sup> , Samina Jahandad <sup>5</sup> and Waqas Naseem <sup>6</sup>

<sup>1</sup> Department of Geology, University of Peshawar, Peshawar 25130, Pakistan; fayaz.ali@uop.edu.pk (F.A.); dr.s\_ahmed@uop.edu.pk (S.A.)

<sup>2</sup> Department of Geology, University of Malakand, Chakdara 18800, Pakistan

<sup>3</sup> Department of Historical Geology-Paleontology, Faculty of Geology and Geoenvironment, School of Earth Sciences, National and Kapodistrian University of Athens, Panepistimiopolis, Zografou, 15784 Athens, Greece

<sup>4</sup> Department of Geology, Shaheed Benazir Bhutto University, Sheringal 18050, Pakistan; hammad@sbbu.edu.pk

<sup>5</sup> Hydrocarbon Development Institute of Pakistan, Islamabad 45700, Pakistan; samojahandad@gmail.com

<sup>6</sup> Department of Geology, The University of Poonch, Rawalakot 10250, Pakistan; waqasnaseem@upr.edu.pk

\* Correspondence: mamoon280@yahoo.com (S.M.S.); gkontak@geol.uoa.gr (G.K.)

**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 okthe 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



**Citation:** Siyar, S.M.; Ali, F.; Ahmad, S.; Kontakiotis, G.; Janjuhah, H.T.; Jahandad, S.; Naseem, W. Organic Geochemistry of Crude Oils from the Kohat Basin, Pakistan. *Geosciences* **2023**, *13*, 199. <https://doi.org/10.3390/geosciences13070199>

Academic Editors: Jesus

Martinez-Frias, Sebastian Lüning and Tomislav Malvić

Received: 3 June 2023

Revised: 26 June 2023

Accepted: 27 June 2023

Published: 29 June 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 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

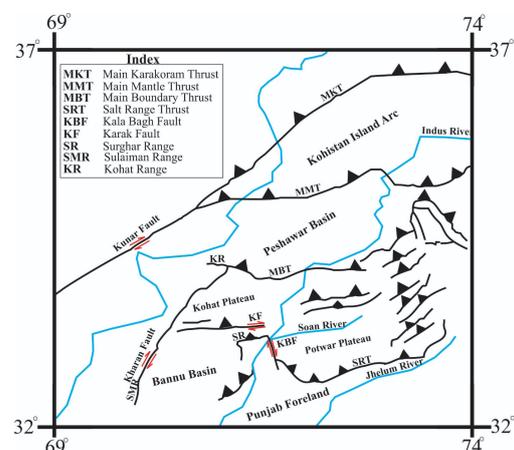
the origin, depositional conditions, burial history, and alteration of organic matter under thermal stress, all of which can lead to the formation of hydrocarbons [1,4,9–14].

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 × 0.32 mm × 0.25 μm) 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.

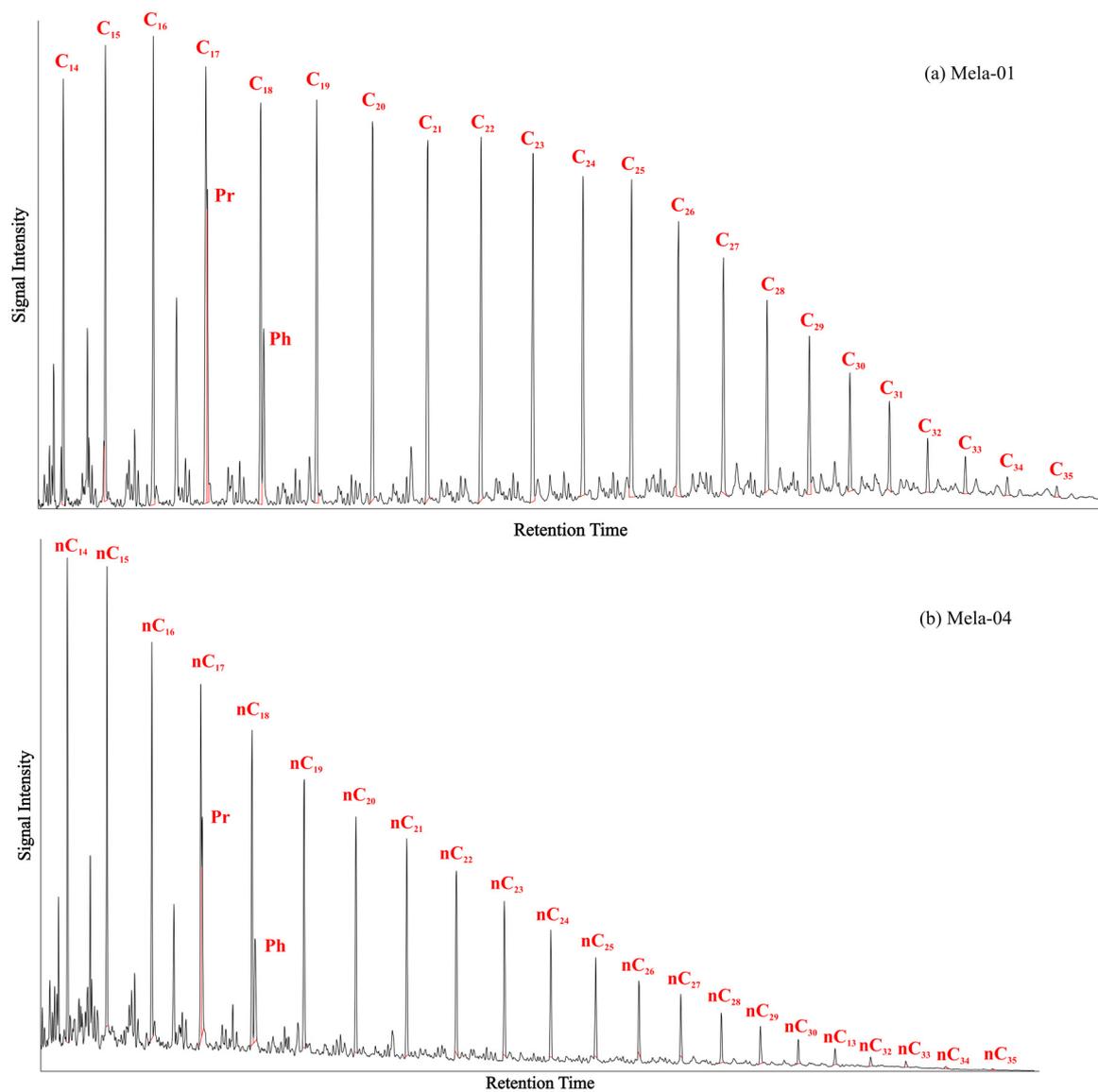
The saturates and aromatic fractions were further subjected to GC apparatus equipped with a data station and integrator using a DB-1 column. One microliter of the sample fraction (saturated and aromatic hydrocarbon) was injected using a split injection mode and capillary column, keeping the oven temperature 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).

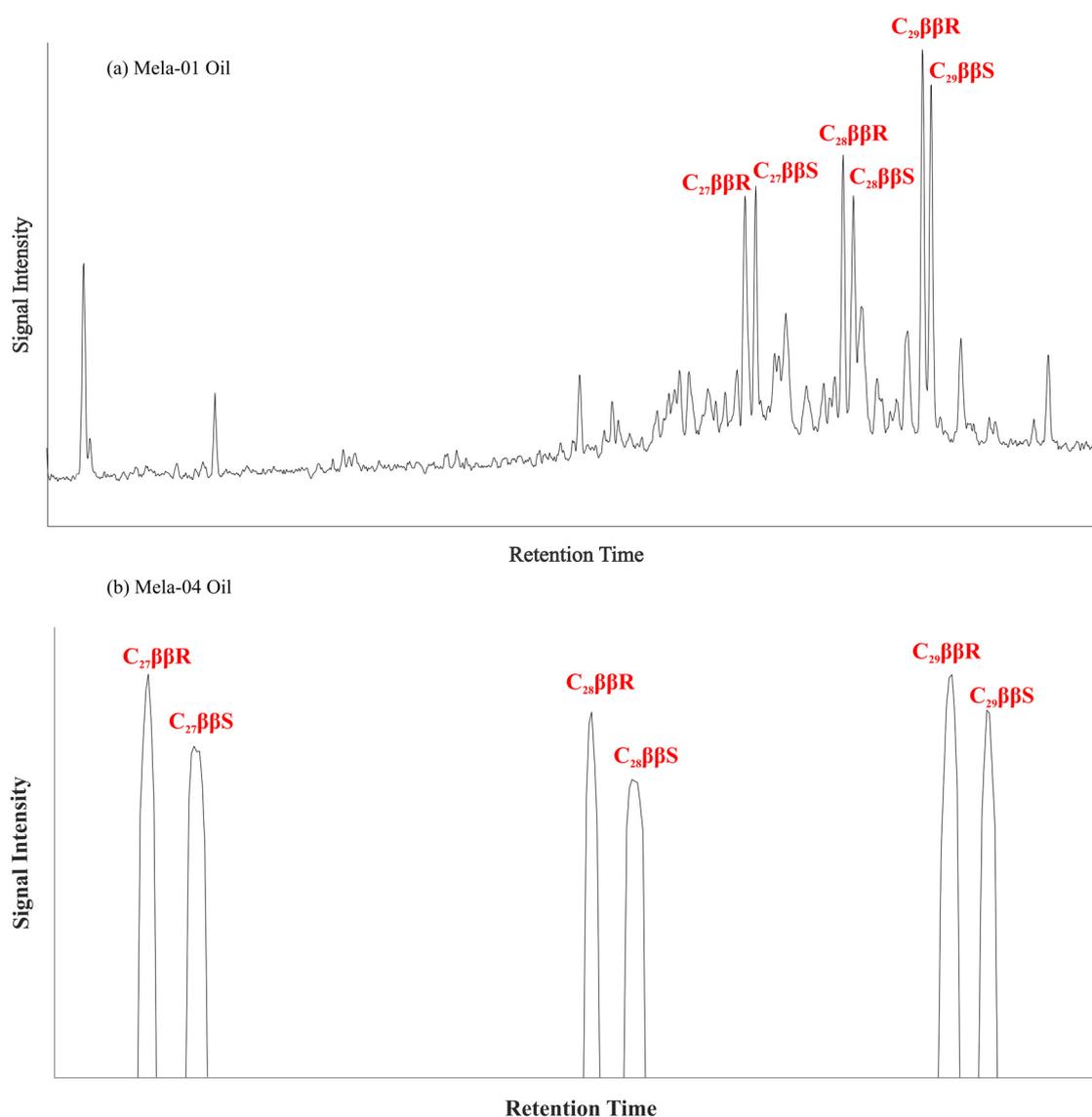
The CPI and terrigenous-aquatic ratio (TAR) of n-alkanes have values of 1.04 and 0.43, respectively, in Mela-01, whereas 1 and 0.13, respectively, in Mela-04 (Table 1), well indicate an almost mixed odd and even n-alkanes distribution [48].



**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.

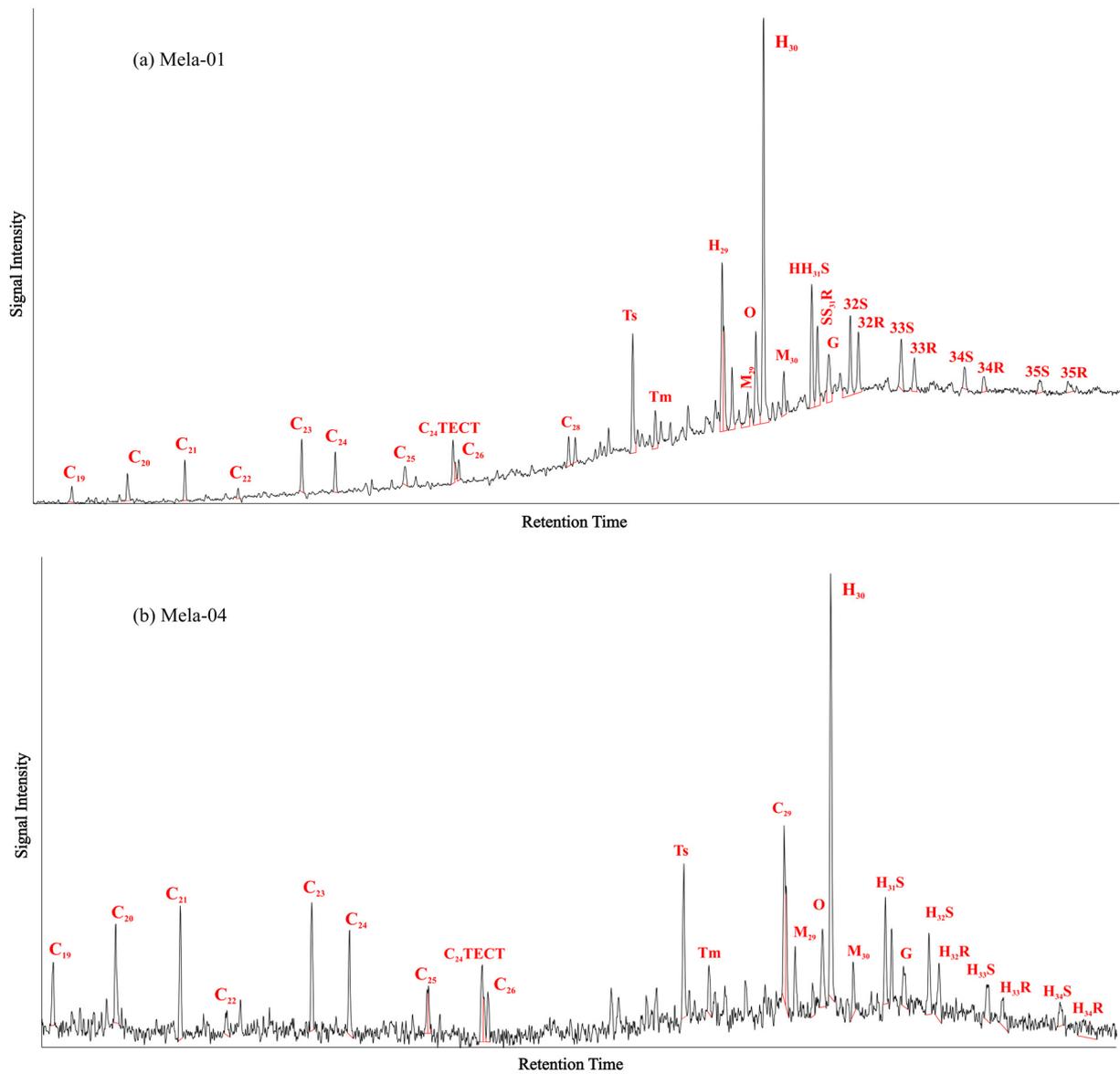
A significant concentration of pristane and phytane isoprenoids is present in both the analyzed oil samples (Figure 2a,b) with the former dominating over the latter, i.e.,  $Pr/Ph = 1.04$  and  $1.52$  for Mela-01 and Mela-04, respectively (Table 1). The calculated  $Pr/n-C_{17}$  values are  $0.39$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



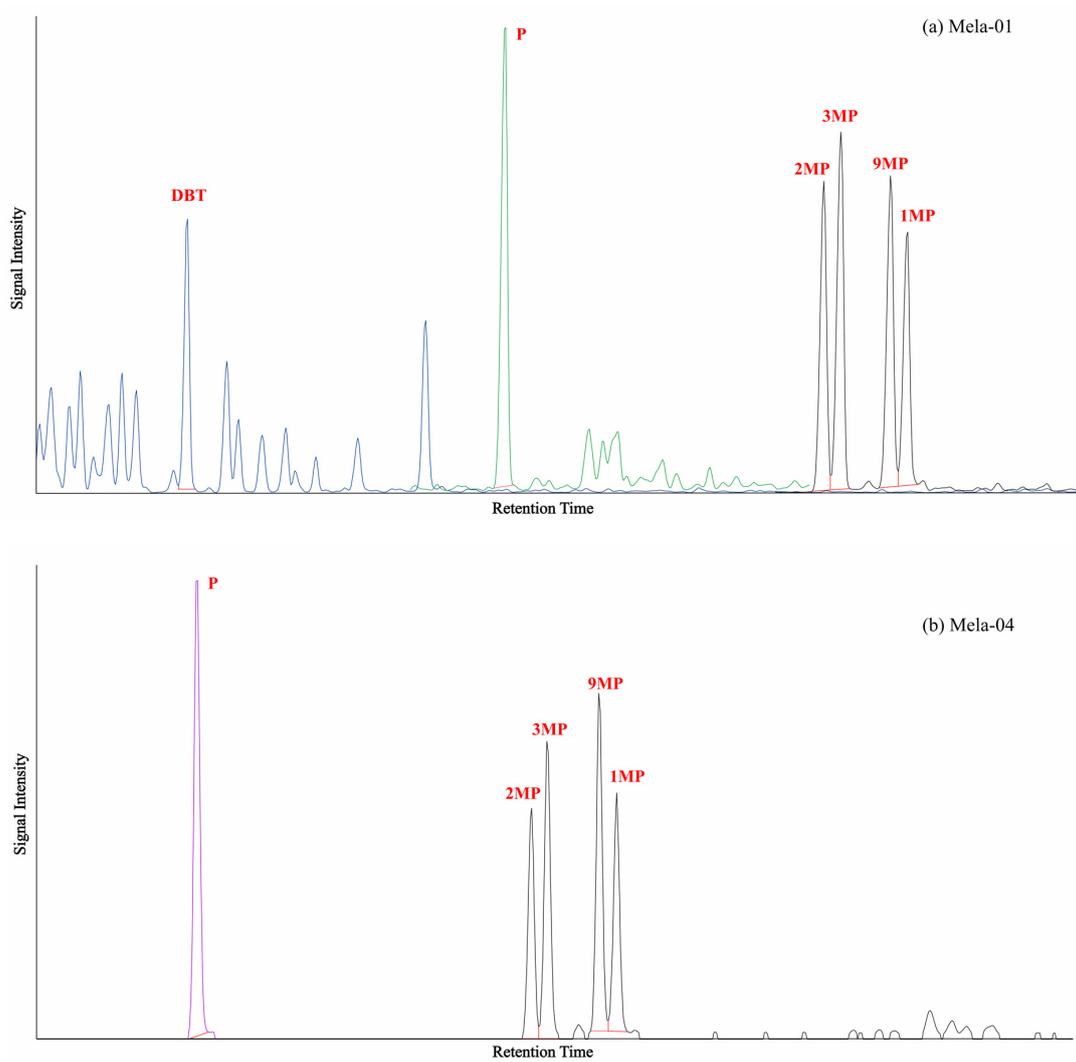
**Figure 3.** (a,b) Chromatograms showing distribution of  $C_{27}$ ,  $C_{28}$ , and  $C_{29}$  steranes in the studied Mela oils from Kohat Basin.

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.

Well	Sample	Short-Chain N-Alkanes						Steranes				Terpanes					
		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
Mela-04	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	$\beta\beta/\alpha\alpha + \beta\beta$	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
Mela-04	Oil	0.57	0.52	0.08	0.76	0.54	0.6	0.81

## 5. Discussion

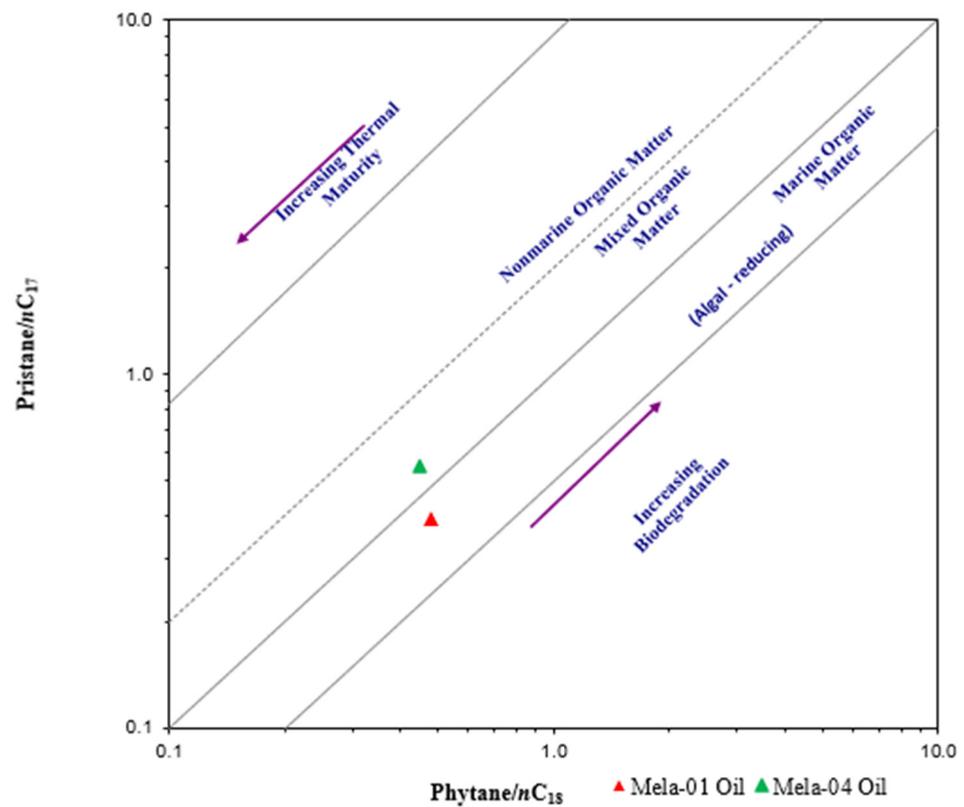
### 5.1. Source and Depositional Condition

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.

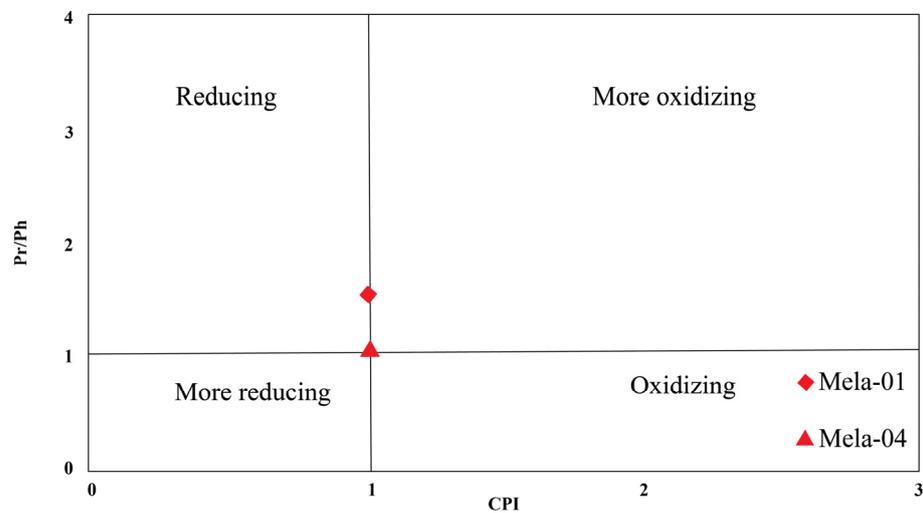
#### 5.1.1. Short Chain N-Alkanes and Isoprenoids

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)



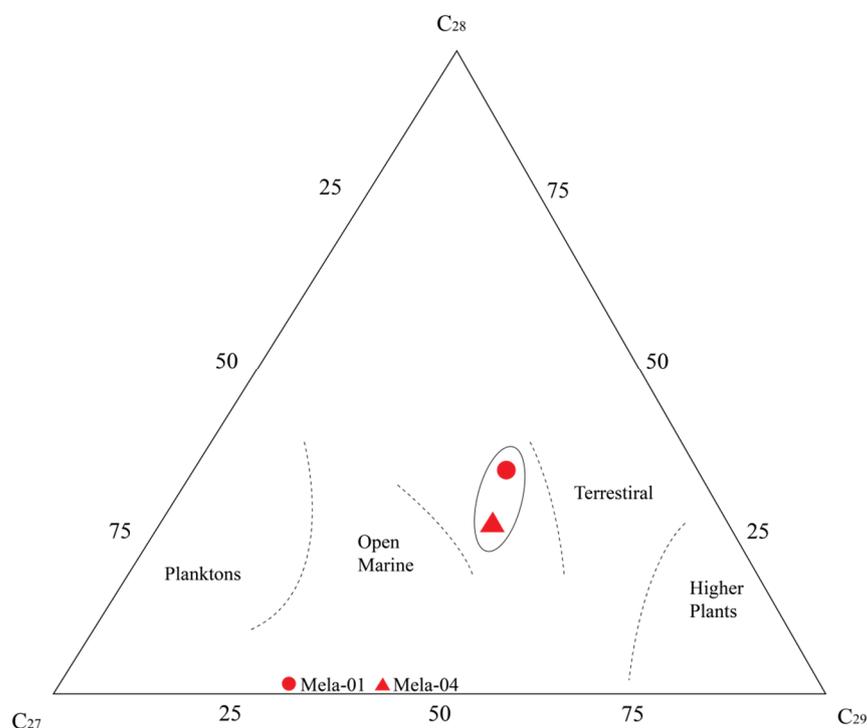
(b)

**Figure 6.** Organic source and redox conditions of the examined oils in the studied wells through the (a) Pr/n-C<sub>17</sub> vs. Ph/nC<sub>18</sub> and (b) Pr/Ph vs. CPI cross plots.

### 5.1.2. Steranes and Diasteranes

Among sterane biomarkers, the C<sub>27</sub> steranes are mainly linked with algae, and the C<sub>29</sub> 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).

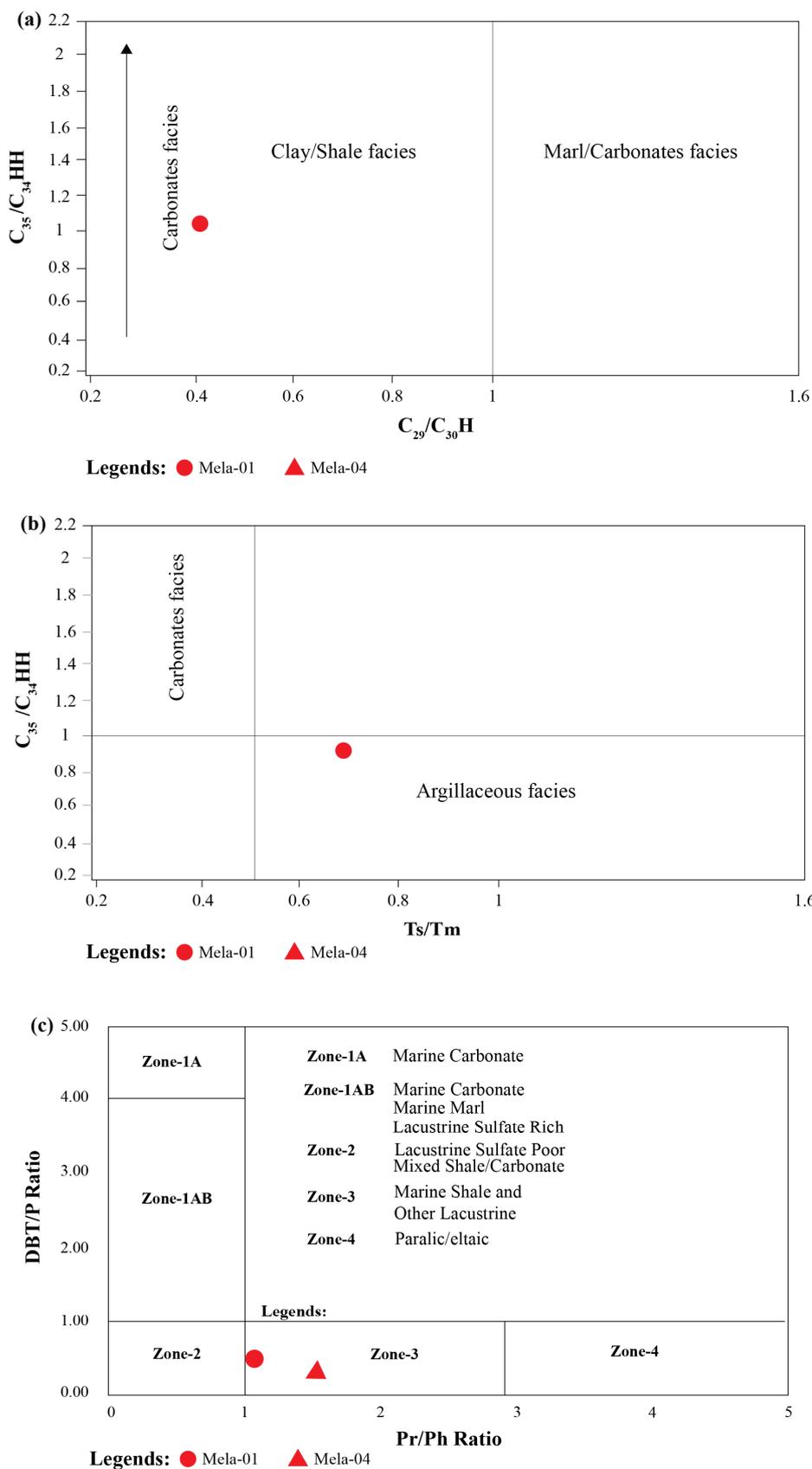


**Figure 7.** Ternary plot of regular steranes ( $C_{27}$ – $C_{29}$ ) of the analyzed oils from Mela oilfield indicating source of organic matter in the study area.

### 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)-trisorhopanes (Tm), and 18 (H)-trisorneohopanes (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  $T_s/T_s + T_m$  and  $C_{35}/C_{34}$  HH also provide information about the lithology of the source units [15]. The ratios of  $T_s/T_s + T_m$  ( $>0.5$ ) 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  $C_{31}R H/C_{30}H$  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

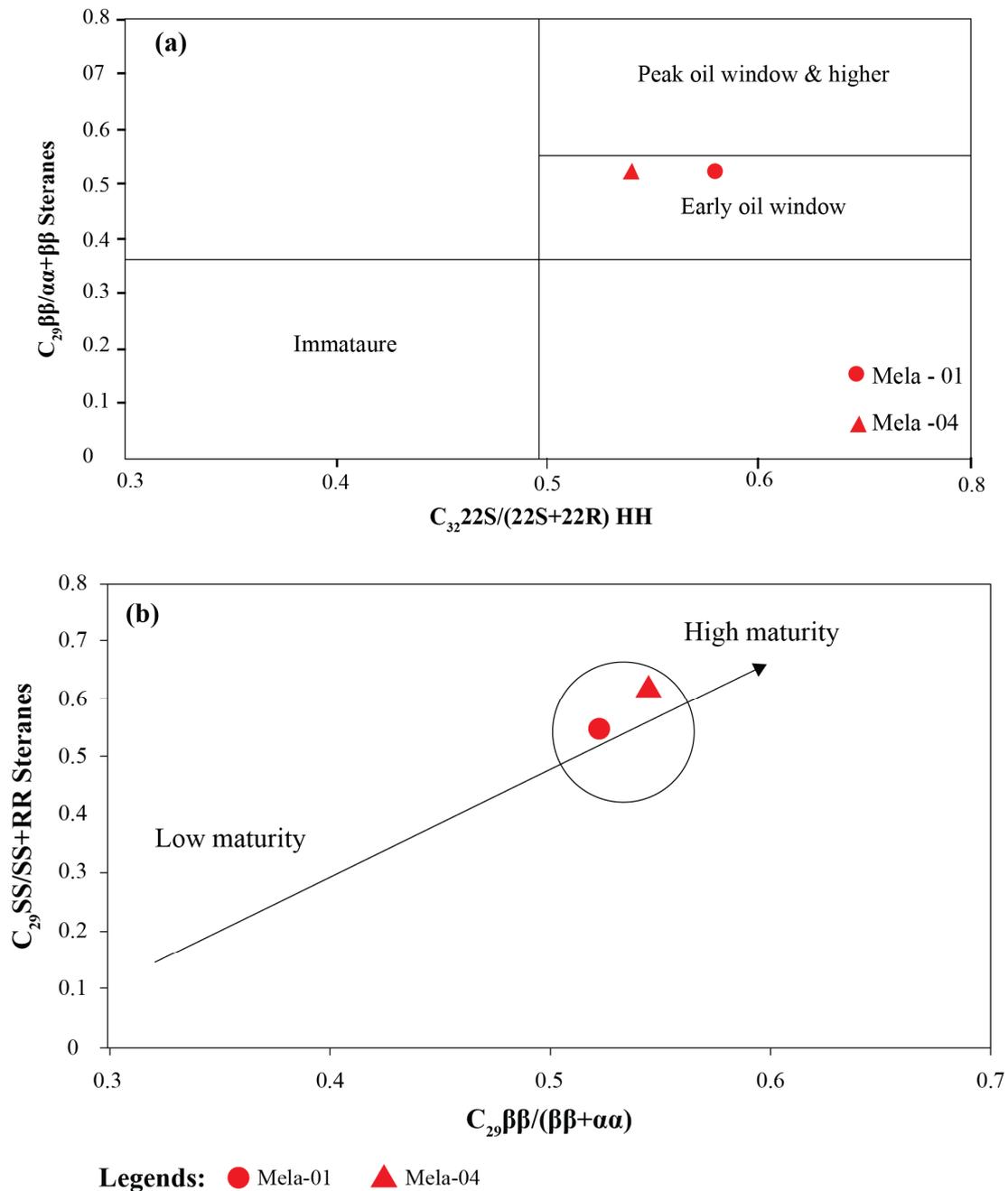
The aromatic compound dibenzothiophene (DBTs) is a sulfur-containing aromatic compound that is relatively abundant in marine carbonate and marl, while high phenanthrene results from precursors inherited from land plants [49]. A relatively high concentration of phenanthrene (P) in crude oils and source 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> tricyclic, 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.

**Author Contributions:** Conceptualization, S.M.S. and F.A.; methodology, S.M.S., F.A., S.A., S.J. and G.K.; software, S.M.S., F.A., S.A. and H.T.J.; validation, F.A., S.A., H.T.J. and G.K.; formal analysis, S.M.S., F.A., S.A. and S.J.; investigation, S.M.S., F.A., S.A., S.J. and G.K.; resources, F.A., S.A. and S.J.; data curation, F.A., S.A. and S.J.; writing—original draft preparation, F.A., S.A. and W.N.; writing—review and editing, H.T.J. and G.K.; visualization, F.A., S.A., H.T.J. and G.K.; supervision, F.A. and S.A.; project administration, F.A.; funding acquisition, G.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** The data used in this work are available on request to the corresponding author(s).

**Acknowledgments:** The senior author would like to thank Oil and Gas Development Company Limited (OGDCL) for providing the data for this research.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Maslen, E. Evaluating the Source, Age, Thermal History and Palaeoenvironments of Deposition of Australian and Western Canadian Petroleum Systems: Compound Specific Stable Isotopes Coupled with Inorganic Trace Elements. Ph.D. Thesis, Curtin University, Singapore, 2010.
2. Magoon, L.B.; Dow, W.G. The Petroleum System. *Pet. Syst.—Source Trap*. **1994**, *60*, 3–24. [\[CrossRef\]](#)
3. Kontakiotis, G.; Karakitsios, V.; Cornée, J.-J.; Moissette, P.; Zarkogiannis, S.D.; Pasadakis, N.; Koskeridou, E.; Manoutsoglou, E.; Drinia, H.; Antonarakou, A. Preliminary results based on geochemical sedimentary constraints on the hydrocarbon potential and depositional environment of a Messinian sub-salt mixed siliciclastic-carbonate succession onshore Crete (Plouti section, eastern Mediterranean). *Mediterr. Geosci. Rev.* **2020**, *2*, 247–265. [\[CrossRef\]](#)
4. Kontakiotis, G.; Karakitsios, V.; Maravelis, A.G.; Zarkogiannis, S.D.; Agiadi, K.; Antonarakou, A.; Pasadakis, N.; Zelilidis, A. Integrated isotopic and organic geochemical constraints on the depositional controls and source rock quality of the Neogene Kalamaki sedimentary successions (Zakynthos Island, Ionian Sea). *Mediterr. Geosci. Rev.* **2021**, *3*, 193–217. [\[CrossRef\]](#)
5. Maravelis, A.G.; Kontakiotis, G.; Bellas, S.; Antonarakou, A.; Botziolis, C.; Janjuhah, H.T.; Makri, P.; Moissette, P.; Cornée, J.-J.; Pasadakis, N. Organic Geochemical Signatures of the Upper Miocene (Tortonian—Messinian) Sedimentary Succession Onshore Crete Island, Greece: Implications for Hydrocarbon Prospectivity. *J. Mar. Sci. Eng.* **2022**, *10*, 1323. [\[CrossRef\]](#)
6. Avramidis, P.; Zelilidis, A. Potential source rocks, organic geochemistry and thermal maturation in the southern depocenter (Kipourio–Grevena) of the Mesohellenic Basin, central Greece. *Int. J. Coal Geol.* **2007**, *71*, 554–567. [\[CrossRef\]](#)
7. Johnson, J.E.; Phillips, S.C.; Torres, M.E.; Piñero, E.; Rose, K.K.; Giosan, L. Influence of total organic carbon deposition on the inventory of gas hydrate in the Indian continental margins. *Mar. Pet. Geol.* **2014**, *58*, 406–424. [\[CrossRef\]](#)
8. Burton, Z.F.M.; Dáfov, L.N. Testing the Sediment Organic Contents Required for Biogenic Gas Hydrate Formation: Insights from Synthetic 3-D Basin and Hydrocarbon System Modelling. *Fuels* **2022**, *3*, 555–562. [\[CrossRef\]](#)
9. Tserolas, P.; Maravelis, A.; Pasadakis, N.; Zelilidis, A. Organic geochemical features of the Upper Miocene successions of Lefkas and Cephalonia islands, Ionian Sea, Greece: An integrated geochemical and statistical approach. *Arab. J. Geosci.* **2018**, *11*, 105. [\[CrossRef\]](#)
10. Maravelis, A.G.; Koukounya, A.; Tserolas, P.; Pasadakis, N.; Zelilidis, A. Geochemistry of Upper Miocene–Lower Pliocene source rocks in the Hellenic Fold and Thrust Belt, Zakynthos Island, Ionian Sea, western Greece. *Mar. Pet. Geol.* **2015**, *66*, 217–230. [\[CrossRef\]](#)
11. Dembicki, H., Jr. Three common source rock evaluation errors made by geologists during prospect or play appraisals. *AAPG Bull.* **2009**, *93*, 341–356. [\[CrossRef\]](#)
12. Grohmann, S.; Romero-Sarmiento, M.-F.; Nader, F.H.; Baudin, F.; Littke, R. Geochemical and petrographic investigation of Triassic and Late Miocene organic-rich intervals from onshore Cyprus, Eastern Mediterranean. *Int. J. Coal Geol.* **2019**, *209*, 94–116. [\[CrossRef\]](#)
13. Bou Daher, S.; Nader, F.H.; Müller, C.; Littke, R. Geochemical and petrographic characterization of Campanian–Lower Maastriichtian calcareous petroleum source rocks of Hasbayya, South Lebanon. *Mar. Pet. Geol.* **2015**, *64*, 304–323. [\[CrossRef\]](#)
14. Gürgey, K. Geochemical characteristics and thermal maturity of oils from the Thrace Basin (Western Turkey) and Western Turkmenistan. *J. Pet. Geol.* **1999**, *22*, 167–189. [\[CrossRef\]](#)
15. Peters, K.E.; Peters, K.E.; Walters, C.C.; Moldowan, J. *The Biomarker Guide*; Cambridge University Press: Cambridge, UK, 2005; Volume 1.
16. Rezaee, R. *Petroleum Geology*; Alavi Publication: Tehran, Iran, 2002; p. 479.
17. Vandenbroucke, M.; Largeau, C. Kerogen origin, evolution and structure. *Org. Geochem.* **2007**, *38*, 719–833. [\[CrossRef\]](#)
18. Maravelis, A.G.; Chamilaki, E.; Pasadakis, N.; Vassiliou, A.; Zelilidis, A. Organic geochemical characteristics and paleodepositional conditions of an Upper Carboniferous mud-rich succession (Yagon Siltstone): Myall Trough, southeast Australia. *J. Pet. Sci. Eng.* **2017**, *158*, 322–335. [\[CrossRef\]](#)
19. Pasadakis, N.; Dagounaki, V.; Chamilaki, E.; Vafidis, A.; Zelilidis, A.; Piliotis, I.; Panagopoulos, G.; Manoutsoglou, E. Organic geochemical evaluation of Neogene formations in Messara (Heraklion, Crete) basin as source rocks of biogenetic methane. *Miner. Wealth* **2012**, *166*, 8–26.
20. Idris, H.; Salihu, A.; Abdulkadir, I.; Almustapha, M. Application of geochemical parameters for characterization of oil samples using GC-MS technique. *Int. J. Phys. Sci.* **2008**, *3*, 152–155.
21. Welte, D.; Tissot, P. *Petroleum Formation and Occurrence*; Springer: Berlin/Heidelberg, Germany, 1984.
22. Burton, Z.F.M.; Moldowan, J.M.; Sykes, R.; Graham, S.A. Unraveling Petroleum Degradation, Maturity, and Mixing and Addressing Impact on Petroleum Prospectivity: Insights from Frontier Exploration Regions in New Zealand. *Energy Fuels* **2018**, *32*, 1287–1296. [\[CrossRef\]](#)
23. Burton, Z.F.M.; Moldowan, J.M.; Magoon, L.B.; Sykes, R.; Graham, S.A. Interpretation of source rock depositional environment and age from seep oil, east coast of New Zealand. *Int. J. Earth Sci.* **2019**, *108*, 1079–1091. [\[CrossRef\]](#)

24. Thompson-Butler, W.; Peters, K.E.; Magoon, L.B.; Scheirer, A.H.; Moldowan, J.M.; Blanco, V.O.; Gonzalez, R.E.; Graham, S.A.; Zumberge, J.E.; Wavrek, D.A. Identification of genetically distinct petroleum tribes in the Middle Magdalena Valley, Colombia. *AAPG Bull.* **2019**, *103*, 3003–3034. [[CrossRef](#)]
25. Yurchenko, I.A.; Moldowan, J.M.; Peters, K.E.; Magoon, L.B.; Graham, S.A. Source rock heterogeneity and migrated hydrocarbons in the Triassic Shublik Formation and their implication for unconventional resource evaluation in Arctic Alaska. *Mar. Pet. Geol.* **2018**, *92*, 932–952. [[CrossRef](#)]
26. Ali, S.K.; Janjuhah, H.T.; Shahzad, S.M.; Kontakiotis, G.; Saleem, M.H.; Khan, U.; Zarkogiannis, S.D.; Makri, P.; Antonarakou, A. Depositional Sedimentary Facies, Stratigraphic Control, Paleoecological Constraints, and Paleogeographic Reconstruction of Late Permian Chhidru Formation (Western Salt Range, Pakistan). *J. Mar. Sci. Eng.* **2021**, *9*, 1372. [[CrossRef](#)]
27. Kontakiotis, G.; Moforis, L.; Karakitsios, V.; Antonarakou, A. Sedimentary Facies Analysis, Reservoir Characteristics and Paleogeography Significance of the Early Jurassic to Eocene Carbonates in Epirus (Ionian Zone, Western Greece). *J. Mar. Sci. Eng.* **2020**, *8*, 706. [[CrossRef](#)]
28. Gharib, A.F.; Özkan, A.M.; Hakimi, M.H.; Zainal Abidin, N.S.; Lashin, A.A. Integrated geochemical characterization and geological modeling of organic matter-rich limestones and oils from Ajeel Oilfield in Mesopotamian Basin, Northern Iraq. *Mar. Pet. Geol.* **2021**, *126*, 104930. [[CrossRef](#)]
29. Ahmed, A.; Jahandad, S.; Hakimi, M.H.; Gharib, A.F.; Mehmood, S.; Kahal, A.Y.; Khan, M.A.; Munir, M.N.; Lashin, A. Organic matter characteristics and conventional oil potentials of shales from the Early Jurassic Datta Formation in the Upper Indus Basin, Northern Pakistan. *J. Asian Earth Sci.* **2022**, *224*, 104975. [[CrossRef](#)]
30. Makri, V.I.; Bellas, S.; Moschou, G.; Pasadakis, N. An Integrated Approach for the Thermal Maturity Modeling Re-Assessment of an Exploration Well in the Hellenides Fold and Thrust Belt. *Geosciences* **2023**, *13*, 76. [[CrossRef](#)]
31. Yasir, M.; Ahmed, W.; Islam, I.; Sajid, M.; Janjuhah, H.T.; Kontakiotis, G. Composition, Texture, and Weathering Controls on the Physical and Strength Properties of Selected Intrusive Igneous Rocks from Northern Pakistan. *Geosciences* **2022**, *12*, 273. [[CrossRef](#)]
32. Pivnik David, A.; Sercombe William, J. Compression- and transpression-related deformation in the Kohat Plateau, NW Pakistan. *Geol. Soc. Lond. Spec. Publ.* **1993**, *74*, 559–580. [[CrossRef](#)]
33. Abbasi, I.A.; McElroy, R. Thrust kinematics in the Kohat Plateau, Trans Indus Range, Pakistan. *J. Struct. Geol.* **1991**, *13*, 319–327. [[CrossRef](#)]
34. McDougall, J.W.; Hussain, A. Fold and Thrust Propagation in the Western Himalaya Based on a Balanced Cross Section of the Surghar Range and Kohat Plateau, Pakistan. *AAPG Bull.* **1991**, *75*, 463–478. [[CrossRef](#)]
35. Ahmed, B.; Bakht, S.; Wahid, S.; Hanif, M. Structural analysis and reservoir characterisation of Cretaceous sequence in Kohala Bala, Khyber Pakhtunkhwa, Pakistan. *Rud.-Geološko-Naft. Zb.* **2022**, *37*, 65–81. [[CrossRef](#)]
36. Meissner, C.R., Jr.; Master, J.; Rashid, M.; Hussain, M. *Stratigraphy of the Kohat Quadrangle, Pakistan*; 2330–7102; Geological Survey Professional Publisher; U.S. Government Publishing Office: Washington, DC, USA, 1974.
37. Siyar, S.M.; Zafar, M.; Jahandad, S.; Khan, T.; Ali, F.; Ahmad, S.; Fnais, M.S.; Abdelrahman, K.; Ansari, M.J. Hydrocarbon generation potential of Chichali Formation, Kohat Basin, Pakistan: A case study. *J. King Saud Univ.-Sci.* **2021**, *33*, 101235. [[CrossRef](#)]
38. Wandrey, C.J.; Law, B.; Shah, H.A. *Patala-Nammal Composite Total Petroleum System, Kohat-Potwar Geologic Province, Pakistan*; US Department of the Interior, US Geological Survey: Reston, VA, USA, 2004.
39. Bilal, A.; Yang, R.; Mughal, M.S.; Janjuhah, H.T.; Zaheer, M.; Kontakiotis, G. Sedimentology and Diagenesis of the Middle-Late Eocene Carbonate Deposits of the Ceno-Tethys Ocean. *J. Mar. Sci. Eng.* **2022**, *10*, 1794. [[CrossRef](#)]
40. Zaheer, M.; Khan, M.R.; Mughal, M.S.; Janjuhah, H.T.; Makri, P.; Kontakiotis, G. Petrography and Lithofacies of the Siwalik Group in the Core of Hazara-Kashmir Syntaxis: Implications for Middle Stage Himalayan Orogeny and Paleoclimatic Conditions. *Minerals* **2022**, *12*, 1055. [[CrossRef](#)]
41. Rahim, H.-U.; Qamar, S.; Shah, M.M.; Corbella, M.; Martín-Martín, J.D.; Janjuhah, H.T.; Navarro-Ciurana, D.; Lianou, V.; Kontakiotis, G. Processes Associated with Multiphase Dolomitization and Other Related Diagenetic Events in the Jurassic Samana Suk Formation, Himalayan Foreland Basin, NW Pakistan. *Minerals* **2022**, *12*, 1320. [[CrossRef](#)]
42. Fazal, A.G.; Umar, M.; Shah, F.; Miraj, M.A.; Janjuhah, H.T.; Kontakiotis, G.; Jan, A.K. Geochemical Analysis of Cretaceous Shales from the Hazara Basin, Pakistan: Provenance Signatures and Paleo-Weathering Conditions. *J. Mar. Sci. Eng.* **2022**, *10*, 800, Correction in *J. Mar. Sci. Eng.* **2022**, *10*, 1654. [[CrossRef](#)]
43. Ahmad, I.; Shah, M.M.; Janjuhah, H.T.; Trave, A.; Antonarakou, A.; Kontakiotis, G. Multiphase Diagenetic Processes and Their Impact on Reservoir Character of the Late Triassic (Rhaetian) Kingriali Formation, Upper Indus Basin, Pakistan. *Minerals* **2022**, *12*, 1049. [[CrossRef](#)]
44. Wadood, B.; Khan, S.; Li, H.; Liu, Y.; Ahmad, S.; Jiao, X. Sequence stratigraphic framework of the Jurassic Samana Suk carbonate formation, North Pakistan: Implications for reservoir potential. *Arab. J. Sci. Eng.* **2021**, *46*, 525–542. [[CrossRef](#)]
45. Meigs, A.J.; Burbank, D.W.; Beck, R.A. Middle-late Miocene (>10 Ma) formation of the Main Boundary thrust in the western Himalaya. *Geology* **1995**, *23*, 423–426. [[CrossRef](#)]
46. Kazmi, A.H.; Jan, M.Q. *Tectonic Map of Pakistan*; Geological Survey of Pakistan: Quetta, Pakistan, 1982.
47. Fowler, M.; Hamblin, A.; Hawkins, D.; Stasiuk, L.; Knight, I. Petroleum geochemistry and hydrocarbon potential of Cambrian and Ordovician rocks of western Newfoundland. *Bull. Can. Pet. Geol.* **1995**, *43*, 187–213.

48. Bourbonniere, R.A.; Meyers, P.A. Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. *Limnol. Oceanogr.* **1996**, *41*, 352–359. [[CrossRef](#)]
49. Hughes, W.B.; Holba, A.G.; Dzou, L.I. The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. *Geochim. Cosmochim. Acta* **1995**, *59*, 3581–3598. [[CrossRef](#)]
50. Tserolas, P.; Maravelis, A.G.; Tsochandarīs, N.; Pasadakis, N.; Zelilidis, A. Organic geochemistry of the Upper Miocene-Lower Pliocene sedimentary rocks in the Hellenic Fold and Thrust Belt, NW Corfu island, Ionian sea, NW Greece. *Mar. Pet. Geol.* **2019**, *106*, 17–29. [[CrossRef](#)]
51. Didyk, B.; Simoneit, B.; Brassell, S.T.; Eglinton, G. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature* **1978**, *272*, 216–222. [[CrossRef](#)]
52. Peters, K.E.; Moldowan, J.M. *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments*; Prentice Hall: Hoboken, NJ, USA, 1993.
53. Waples, D. *Geochemistry in Petroleum Exploration*; International Human Resources Development Co.: Boston, MA, USA, 2016; pp. 33–94.
54. Peters, K.E.; Moldowan, J.M. Effects of source, thermal maturity, and biodegradation on the distribution and isomerization of homohopanes in petroleum. *Org. Geochem.* **1991**, *17*, 47–61. [[CrossRef](#)]
55. ten Haven, H.L.; de Leeuw, J.W.; Sinninghe Damsté, J.S.; Schenck, P.A.; Palmer, S.E.; Zumberge, J.E. Application of biological markers in the recognition of palaeohypersaline environments. *Geol. Soc. Lond. Spec. Publ.* **1988**, *40*, 123–130. [[CrossRef](#)]
56. Ten Haven, H.L.; Rullkötter, J.; De Leeuw, J.W.; Damsté, J.S.S. Pristane/phytane ratio as environmental indicator. *Nature* **1988**, *333*, 604. [[CrossRef](#)]
57. Shanmugam, G. Significance of Coniferous Rain Forests and Related Organic Matter in Generating Commercial Quantities of Oil, Gippsland Basin, Australia. *AAPG Bull.* **1985**, *69*, 1241–1254. [[CrossRef](#)]
58. Huang, W.-Y.; Meinschein, W. Sterols as ecological indicators. *Geochim. Cosmochim. Acta* **1979**, *43*, 739–745. [[CrossRef](#)]
59. Groune, K.; Halim, M.; Lemée, L.; Benmakhlouf, M.; Amblès, A. Chromatographic study of the organic matter from Moroccan Rif bituminous rocks. *Arab. J. Chem.* **2019**, *12*, 1552–1562. [[CrossRef](#)]
60. Tao, S.; Wang, C.; Du, J.; Liu, L.; Chen, Z. Geochemical application of tricyclic and tetracyclic terpanes biomarkers in crude oils of NW China. *Mar. Pet. Geol.* **2015**, *67*, 460–467. [[CrossRef](#)]
61. Aquino, N.F. Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleum. *Adv. Org. Geochem.* **1981**, *1983*, 659–667.
62. Ogbesejana, A.B.; Bello, O.M.; Ali, T.; Uduma, U.A.; Kabo, K.S.; Akintade, O.O. Geochemical significance of tricyclic and tetracyclic terpanes in source rock extracts from the Offshore Niger Delta Basin, Nigeria. *Acta Geochim.* **2021**, *40*, 184–198. [[CrossRef](#)]
63. Murray, A.P.; Sosrowidjojo, I.B.; Alexander, R.; Kagi, R.I.; Norgate, C.M.; Summons, R.E. Oleananes in oils and sediments: Evidence of marine influence during early diagenesis? *Geochim. Cosmochim. Acta* **1997**, *61*, 1261–1276. [[CrossRef](#)]
64. El-Sabagh, S.M.; El-Naggar, A.Y.; El Nady, M.M.; Ebiad, M.A.; Rashad, A.M.; Abdullah, E.S. Distribution of triterpanes and steranes biomarkers as indication of organic matters input and depositional environments of crude oils of oilfields in Gulf of Suez, Egypt. *Egypt. J. Pet.* **2018**, *27*, 969–977. [[CrossRef](#)]
65. Rullkötter, J.; Peakman, T.M.; Lo Ten Haven, H. Early diagenesis of terrigenous triterpenoids and its implications for petroleum geochemistry. *Org. Geochem.* **1994**, *21*, 215–233. [[CrossRef](#)]
66. Kara-Gülbay, R.; Ziya Kırmaç, M.; Korkmaz, S. Organic geochemistry and depositional environment of the Aptian bituminous limestone in the Kale Gümüşhane area (NE-Turkey): An example of lacustrine deposits on the platform carbonate sequence. *Org. Geochem.* **2012**, *49*, 6–17. [[CrossRef](#)]
67. Chen, J.; Summons, R.E. Complex patterns of steroidal biomarkers in Tertiary lacustrine sediments of the Biyang Basin, China. *Org. Geochem.* **2001**, *32*, 115–126. [[CrossRef](#)]
68. Zhongquan, L.; Xiangchun, C.; Youde, X.; Bingbing, S.; Zhiping, Z.; Pengfei, Z. Depositional environment, age determination and source diagnose of oils from the western Chepaizi Uplift (Junggar Basin) constrained by molecular biomarkers. *J. Pet. Sci. Eng.* **2022**, *214*, 110495. [[CrossRef](#)]
69. Radke, M. Application of aromatic compounds as maturity indicators in source rocks and crude oils. *Mar. Pet. Geol.* **1988**, *5*, 224–236. [[CrossRef](#)]
70. Ogbesejana, A.B.; Bello, O.M. Distribution and geochemical significance of dibenzofurans, phenyldibenzofurans and benzo[b]naphthofurans in source rock extracts from Niger Delta basin, Nigeria. *Acta Geochim.* **2020**, *39*, 973–987. [[CrossRef](#)]
71. Radke, M.; Vriend, S.; Ramanampisoa, L. Alkyldibenzofurans in terrestrial rocks: Influence of organic facies and maturation. *Geochim. Cosmochim. Acta* **2000**, *64*, 275–286. [[CrossRef](#)]
72. Seifert, W.K.; Moldowan, J.M.; Jones, R. Application of biologic markers in combination with stable carbon isotopes to source rock/oil correlations, Prudhoe Bay, Alaska. *AAPG Bull.* **1981**, *65*, 990–991.
73. Mackenzie, A.S.; McKenzie, D. Isomerization and aromatization of hydrocarbons in sedimentary basins formed by extension. *Geol. Mag.* **2009**, *120*, 417–470. [[CrossRef](#)]
74. Seifert, W.K.; Moldowan, J.M. Use of biological markers in petroleum exploration. *Methods Geochem. Geophys.* **1986**, *24*, 261–290.

75. Price, P.; O'Sullivan, T.; Alexander, R. *The Nature and Occurrence of Oil in Seram, Indonesia*; 1987; Volume 12, pp. 12–98. Available online: <https://www.semanticscholar.org/paper/The-Nature-and-Occurrence-of-Oil-in-Seram%2C-Price-O%27sullivan/7a84396760793c6d1aca019c939f2d73da499750> (accessed on 3 June 2023).
76. McKirdy, D. A geochemical comparison of some crude oils from pre-Ordovician carbonate rocks. In *Advances in Organic Geochemistry*; Wiley: Hoboken, NJ, USA, 1983; pp. 99–107.
77. Rullkötter, J.; Spiro, B.; Nissenbaum, A. Biological marker characteristics of oils and asphalts from carbonate source rocks in a rapidly subsiding graben, Dead Sea, Israel. *Geochim. Cosmochim. Acta* **1985**, *49*, 1357–1370. [[CrossRef](#)]
78. Seifert, W.K.; Moldowan, J.M. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. *Geochim. Cosmochim. Acta* **1978**, *42*, 77–95. [[CrossRef](#)]
79. Mackenzie, A.; Patience, R.; Maxwell, J.; Vandenbroucke, M.; Durand, B. Molecular parameters of maturation in the Toarcian shales, Paris Basin, France—I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochim. Cosmochim. Acta* **1980**, *44*, 1709–1721. [[CrossRef](#)]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.