Biomarker insights into the Chichali Formation and Petroleum Systems of the Kohat Basin, Western Himalayas

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Abstract

An extensive biomarker investigation was undertaken to appraise the contribution of the Chichali Formation to the petroleum system within the Kohat Sub-Basin, yielding profound insights into the organic matter category, source, thermal maturity, and depositional environment of the Chichali Formation and oil samples extracted from the Mela-01 and Mela-05 wells. Through a comparison of the biomarker parameters of the Chichali Formation with those of the oil samples, a robust oil-to-source correlation was established. The study found that the Chichali Formation rocks, obtained from well cuttings and outcrop, were marked by an algal organic source and a marine anoxic depositional environment, while the oil samples exhibited a terrestrial organic source and a sub-oxic and deltaic depositional environment. Distinctive biomarker parameters, including n-alkanes, isoprenoids, terpanes, steranes, and methyl-phenanthrene (MP), offered an insight into the organic matter maturity differences between the oils and the Chichali Formation. Furthermore, the oils revealed the presence of the oleanane biomarker, implying the Cretaceous or younger age of the source rock. Notably, the study uncovered that there is no correlation between the Chichali Formation and oils in the studied wells of the Mela oilfield in the Kohat Sub-Basin, concerning maturity, depositional environment, and organic matter type. A distinctive source rock of Cretaceous or younger than Cretaceous age was postulated for the Mela oils.

Keywords: Biomarker Analysis; Cretaceous Shale & Crude Oil, Kohat Basin

1. Introduction

Biomarkers are complex chemical compounds derived from living organisms that are found in both source rocks and crude oils. Their structure remains relatively unchanged during diagenesis and catagenesis. Biomarkers can provide valuable information on the type, organic matter input, thermal maturity, age, and depositional environment of source rocks and crude oils. The petroleum industry frequently uses biomarkers for the genetic correlation of oils to their sources (Seifert and Moldowan, 1981; Peters et al., 2005). Source rock geochemistry plays a vital role in hydrocarbon exploration. Source rocks are primary elements of the petroleum system, where those organic rich rocks produce commercial hydrocarbons upon thermal maturation (Rezaee, 2002). Reservoir rocks are tested for hydrocarbons they contain, and geochemical data helps to identify hydrocarbon bearing zones and their present and future potential (Tissot & Welte, 1984; Siyar et al., 2023). Nature of organic matter, status of thermal maturity, alteration to petroleum and organic matter are all characterized in petroleum geochemistry (Maslen, 2010).

The Kohat sub-basin is a prominent hydrocarbon-producing region in northern Pakistan. Several exploratory wells were initially drilled in this basin, and their status was dry, followed by major successful discoveries such as the Chanda, Nashpa, Mela, Manzalai, Makori, Mami Khel, Tolanj, Maramzai, and Makori East oil-condensate-gas fields. For successful petroleum exploration in a basin, knowledge of the petroleum source rocks is crucial, as is knowledge of the reservoir rocks. Previous studies have suggested that the Late Proterozoic-Lower Cambrian Salt Range Formation, Permian Wargal, Sardhai, and Chhidru formations, Jurassic Datta Formation, Cretaceous Chichali and Lumshiwal formations, Paleocene Lockhart Formation, and Eocene Patala Formation are the most probable source rocks in the Kohat and adjacent Potwar sub-basins (Wandrey et al., 2004; Craig et al., 2018). Siyar et al. (2021) studied the source rock potential of the Cretaceous rock unit in the Kohat Basin. Siyar et al. (2023) have pointed out a mixed source of organic matter in the analyzed crude oil. The crude oil in Chanda-01 well has been analyzed and correlated with Jurassic rock units in the same area. However, the understanding primarily relied on organic petrography and pyrolysis data, with limited contribution from biomarker investigations, and no publicly accessible studies on the source-to-oil correlation in the Kohat sub-basin. To tackle the research gap in this area, the present research focuses on biomarker studies of the Chichali Formation and crude oils in the Kohat sub-basin, which provide insights for future petroleum exploration strategies in the region. The study has used a comprehensive biomarker investigation to appraise the contribution of the Chichali Formation to the petroleum system within the Kohat Sub-Basin, yielding profound insights into the organic matter category, source, thermal maturity, and depositional environment of the Chichali Formation and oil samples extracted from two studied wells.

2. Geological setting

The Kohat sub-basin in northern Pakistan is a complex tectonic region with a unique passive roof duplex geometry. This area is characterized by thrust sheets of pre-Tertiary stratigraphy, and a hybrid terrain with compressional features and strike-slip faults (McDougall, 1988; Pivnik, 1992; Pivnik and Sercombe, 1993). The basin is bounded by the Main Boundary Thrust (MBT) to the north and the Surghar Range thrusts to the south, while the River Indus and Kurram-Parachinar Range mark the eastern and western margins, respectively (Figures 1a, 1b). Along MBT, Mesozoic-Paleocene sedimentary rocks are thrusted over the Miocene molasses, whereas the Surghar Range thrust caused the Mesozoic sediments to thrust southward over the alluvium of the Punjab Foreland. The Kalabagh right-lateral strike-slip fault separates the Surghar Range thrust from the Salt Range Thrust (SRT) (Searle et al., 1996; Noor et al., 2013; Ahmad et al., 2016).

The Kohat sub-basin preserves the sedimentary record of Himalayan convergence sediments in northwest Pakistan (Pivnik and Wells, 1996). The known stratigraphic succession in the sub-basin is composed of a complex succession of sedimentary rocks, including limestones, evaporites, sandstones, shales, and conglomerates, ranging in age from Triassic to Quaternary. At deeper levels, it is possible that the Paleozoic sequence is also present (Figure

2) (Sercombe et al., 1998; Craig et al., 2018; Ghani, 2019). This sub-basin was an isolated basin in the Tethys Sea, located at the northwestern boundary of the Indian Tectonic Plate (Pivnik and Wells, 1996). The Early Eocene evaporites in the Kohat sub-basin are thicker than those in the adjacent Potwar sub-basin, representing the local limits of the basins in this area (Paracha et al., 2004a).

In petroleum exploration, knowledge of the petroleum source rocks is crucial for success, like the knowledge of reservoir rocks. The Kohat Basin is a prolific basin with source rocks of different ages and hydrocarbon generation in the area. However, limited literature is available on source rocks in the study area. Siyar et al. (2021) recently conducted TOC and Rock-Eval pyrolysis on Cretaceous sediments to evaluate their hydrocarbon potential. They concluded that the organic matter in these rocks is gas-prone, in the early stage of oil generation but immature to produce gaseous hydrocarbons. Paleocene rocks like the Hangu, Lockhart, and Patala formations may also be present in the studied basin (Siyar et al., 2021). These rock units contain sufficient organic content and oil/gas and gas-prone maceral/kerogen in the Kala Chitta Ranges (Khan et al., 2020; Latif, 2021).

The Kohat sub-basin is a complex tectonic region with a diverse stratigraphic succession. It represents a prolific hydrocarbon basin with different source rocks of varying ages. However, further investigation of the source rocks in this area is necessary to enhance the understanding of the petroleum system in the Kohat sub-basin.

3. Materials and methods

Overall, this study examined a total of twenty-four rock samples and two crude oil samples. Specifically, seventeen well cuttings (ten from Mela-05 and seven from Mela-01) and seven outcrop samples were collected from the Chichali Formation. TOC measurements were taken for all rock samples, and based on high TOC values, six samples (three each from Mela-05 and outcrop) were selected for biomarker analysis along with the Mela crude oil samples (one from Mela-01 and one from Mela-05). Prior to analysis, the rock samples were cleaned using distilled water to eliminate potential contaminants and inorganic carbon, and then the dehydrated samples were pulverized using an agate mortar and dried over night at 40 °C weighted on balance and utilized at 100 mg for TOC measurements (Peters, 1986)..

TOC levels in the rock samples were determined using the CS-580A (Carbon Sulfur analyzer, Helios). Bitumen, or extractable organic matter, was obtained from the rocks via a Soxhlet apparatus using a dichloromethane (97%) and methanol (3%) solvent mixture with copper chips. The whole set up was subjected to water circulation during an extraction period of 72 hours. The soluble part of the extracts, called maltenes, was then then separated into saturates, aromatics, and NSO (polar) compounds using column chromatography techniques. For obtaining these fractions, a glass column of 30 cm length and 1 cm diameter was filled (two thirds) with a slurry of silica in the solvent of n-hexane and also with alumina slurry as an absorbent in n-hexane (one-thirds). A 100 mg extract was used, which was eluted into saturated solutions using n-hexane (30 ml), aromatics by using dichloromethane (DCM, 30 ml) and ethyl acetate (30 ml) for the polar fraction (Peters & Moldowan, 1993). Gas chromatography-mass spectrometry was utilized to identify and analyze n-alkanes and biomarker compounds. Further, identification and interpretation of the analyzed biomarkers were achieved using published literature (McLafferty, 1980; Philp, 1985).

All the analyses were carried out at Hydrocarbon Development Institute of Pakistan (HDIP), and geochemistry lab of Oil and Gas Development Company Limited (OGDCL) of Pakistan.

4. Results and

4.1. Organic richness

The organic richness and abundance can be evaluated using indicators such as TOC, S2 and S1+S2 of Rock-Eval pyrolysis (Tissot and Welte, 1984; Hakimi and Ahmed, 2016). The assessment of kerogen types generally involves the HI vs. Tmax and HI vs. OI diagrams, the HI and OI are represented as $HI=100\times S2/TOC$ and $OI=100\times S3/TOC$, respectively (Van Krevelen, 1961; Peters, 1986; Hunt, 1991). The Mela-05 well cuttings from the Chichali Formation Exhibit Total Organic Carbon (TOC) values ranging from 0.90 to 1.40%, which suggests that it is a good source rock for petroleum. In contrast, the TOC values for the Mela-01 well and outcrop samples range from 0.29 to 0.59%, indicating a poor to fair source rock for petroleum (Peters and Cassa, 1994; Table 1). The source rocks experience significant terrestrial input and oxidation, leading to poorer OM preservation conditions in Mela-01 well and outcrop samples compared to Mela-05 well cuttings (Table 1).

4.2. Extracts and biomarkers

The column chromatography resulted in fractions of saturates ranging from 45% to 50%, 20% to 30% aromatics, and 26% to30% polar for the outcrops. The saturates are ranged from 51% to 56%, aromatics from 24 to 30%, and polar from 18 to 20% in the cutting's samples. In case of analyzed two crude oil samples, the polar (44%, 39%) and aromatic fractions (28% & 31%) are higher than saturates (27% & 31%) as listed in Table 2. The terrigenous-aquatic (TAR) values for the Mela-05 well cuttings range from 0.077 to 0.18 and for the Mela-01 and Mela-05 crude oil samples, they are 0.51 and 0.60, respectively. The Chichali Formation rock samples have pristane to phytane ratios less than one ($Pr/Ph <1$), and greater than one ($Pr/Ph>1$), i.e., 1.47 and 1.55 in Mela oil (Table. 2). The values of Pr/nC_{17} are <0.5 for cuttings and outcrop samples of the Chichali Formation, whereas, Mela oils have $Pr/nC_{17} > 0.6$. The Chichali Formation samples have lower values of C_{19}/C_{23} and C_{20}/C_{23}TT ratios compared to the Mela oil samples. The tricyclic terpanes C_{26}/C_{25} TT ratio has lower values (<1) for outcrop samples of the analyzed formation and is higher (>1) in case of oil samples (Table. 3). The tricyclic terpane to hopane ratio (TT/H) is higher in the outcrop samples of the Chichali Formation, where in contrast, Mela oil has lower values (Table 3). Pentacyclic terpane gammacerane is present in substantial amount both in rock samples and crude oil. C_{29}/C_{30} hopane is higher in rock samples (>1) and is lower compare in crude oil (<1), as listed in Table 3. The Chichali Formation's samples have C_{29} 20S/(20S+20R) sterane ratios ranging from 0.46-0.51, while Mela oil has values ranging from 0.58 to 0.60 (Table 4). Similarly, C_{31} homohopane ratio in the Chichali Formation ranged from 0.47 to 0.58, and from 0.62 to 0.63 in the Mela oil (Table 4). The 18α-trisnorhopanes (Ts) and 17α-trisnorhopanes (Tm) Ts/Ts+Tm ratios range from 0.37 to 0.46, in the analyzed sediments, and for Mela oil, Ts/Ts+Tm ratios range from 0.73 to 0.77. The calculated vitrinite reflectance (VRc %) values based on the methylphenanthrene index (MPI-1) for the Chichali Formation range from 0.77-0.94, while for Mela's oils they range from 0.96-0.99 (Table 4). Similarly, the methyldibenzothiophenes ratio (MDR) is a commonly used maturity parameter, and vitrinite reflectance derived from MDR is represented as calculated vitrinite reflectance (Rcs). Based on MDR, the calculated vitrinite reflectance (Rcs) values for the Chichali Formation ranged from 0.64 to 0.91, while for Mela's oil, they ranged from 1.06 to 1.21 as shown in Table 4.

5. Discussion

5.1. Organic richness

The analysis showed that the source rocks in Mela-05 possess significantly better OM abundance parameters (TOC, S1+S2, and S2) as compared to the source rocks in Mela-01 and well and outcrop samples. The Mela-05 well cuttings from the Chichali Formation exhibit Total Organic Carbon (TOC) values ranging from 0.90 to 1.40%, which suggests that it is a good source rock for petroleum. In contrast, the TOC values for the Mela-01 well and outcrop samples range from 0.29 to 0.59%, indicating a poor to fair source rock for petroleum (Peters and Cassa, 1994; Table 1). The source rocks experience significant terrestrial input and oxidation, leading to poorer OM preservation conditions in Mela-01 well and outcrop samples compared to Mela-05 well cuttings (Table 1).

5.2. Column chromatography

Chemical compounds present in crude oils and extracts can be categorized as saturate, aromatic, and polar compounds. The abundance of these compounds depends on the type of kerogen and the maturity level of organic matter, which can be useful for correlation between oils and source rocks (Tissot and Welte, 1984). Based on the composition of these compounds (Table 2), the Mela oils are classified as aromatic–asphaltic, while the Chichali Formation rock extracts (outcrop and Mela-05 well cutting samples) are classified as paraffinic–naphthenic. The variation in the composition of oils and rock extracts indicates different organic matter inputs. According to these compounds (saturated HC, aromatic HC, and polar compounds), the Chichali Formation rock samples and Mela oils show no genetic-link (Fig. 3).

5.3. Source, redox conditions and facies analysis

5.3.1. n-alkanes and isoprenoids

Short-chain n-alkanes (nC_{15}, nC_{17}, and nC_{19}) are primarily derived from photosynthetic bacteria and aquatic marine algae, whereas long-chain n-alkanes (nC_{27}, nC_{29}, and nC_{31}) are related to higher plants (Tissot and Welte, 1984; Tenzer et al., 1999). The "terrigenous/aquatic" ratio (TAR), a ratio representing the relative contribution of terrestrial higher plants and marine algae and bacteria, is used to determine the origin of the n-alkanes (Peter et al., 2005). The TAR values for the Mela-05 well cuttings range from 0.077 to 0.18, indicating a greater input of aquatic algal sources than land plants. Similarly, outcrop samples exhibit an abundance of short-chain n-alkanes (n-C_{15} to n-C_{20}), suggesting a marine organic matter biomass contribution from algae or plankton (Figure 7 and Table 2).

The TAR values for the Mela-01 and Mela-05 crude oil samples are 0.51 and 0.60, respectively, indicating a source rock with more terrestrial organic matter input. The TAR ratios in the Mela crude oils and the Chichali Formation samples are significantly different, indicating extracts and oils were generated from different source rocks. Additionally, significant amounts of pristane (Pr) and phytane (Ph) were identified in each sample, which can be used to identify paleoenvironmental conditions. In oxic environmental conditions, the decarboxylation of the phytyl side chain produces pristanes with Pr to Ph ratio greater than unity, while phytanes are produced in anoxic conditions due to dehydration plus reduction reactions of the phytyl side-chain ($Pr/Ph<1$) (Peters et al., 2005). The Chichali Formation rock samples have pristane to phytane ratios less than one ($Pr/Ph<1$), suggesting an anoxic marine depositional environment, while pristane to phytane ratios greater than one ($Pr/Ph>1$), i.e., 1.47 and 1.55 in Mela oils, indicating an oxic depositional environment for the source rock of Mela oils. The nature of organic matter in the extracts and crude oils can be determined through the ratio of Pr/n-C_{17} (Peters and Moldowan, 1993; Peters et al., 2005). A marine organic input is suggested for the Chichali Formation's well cuttings and outcrop samples as Pr/nC_{17} <0.5, while Mela oils have a terrigenous source as the Pr/nC_{17} >0.6. The cross-plot of Pr/ n-C_{17} against Ph/ n-C_{18} also indicates a marine anoxic environment for the rock samples of the Chichali Formation and mixed source input with a transitional environment for the Mela oils' source rock (Figure 4) (Shanmugam, 1985).

5.3.2. Terpanes

The concentration of C_{23} tricyclic terpanes (C_{23}TT) is higher in crude oils or extracts generated from marine organic matter, while oils or extracts generated from terrestrial organic matter are rich in C_{19} tricyclic terpanes (C_{19}TT) and C_{20} tricyclic terpanes (C_{20}TT) (Barnes and Barnes, 1983; Peters and Moldowan, 1993). The C_{19}/C_{23}TT and C_{20}/C_{23}TT ratios are used to determine the origin of the organic matter in oils and source rock extracts (Hao et al., 2010). The Chichali Formation samples have lower values of C_{19}/C_{23} and C_{20}/C_{23}TT ratios compared to the Mela oil samples, indicating a different source for the oils (Table 3). The low values of both ratios for the Chichali Formation suggest a significant marine organic matter contribution, while the higher values of both ratios for the Mela oils reflect a source stratum with a higher terrestrial organic matter contribution. Similarly, the C_{26}/C_{25} tricyclic terpanes ratio (C_{26}/C_{25}TT) is higher for lacustrine source rocks, while marine-associated source rocks have lower values (Zumberge, 1987a). The Chichali Formation's outcrop samples show a low value of the C_{26}/C_{25} TT ratio, indicating a marine depositional environment, while higher values of the C_{26}/C_{25} TT ratio in the Mela oil samples reflect the lacustrine environment of deposition (Table 3).

The tricyclic terpanes are mainly sourced from marine algae, whereas hopanes (terpane compounds) are considered to be the product of bacterial organic matter (Simoneit et al., 1993; Greenwood et al., 2000; Peters et al., 2005). The tricyclic terpane to hopane ratio (TT/H) is higher in the outcrop samples of the Chichali Formation, indicating marine organic matter with an algal origin. In contrast, Mela oils have lower values and reflect more terrestrial organic matter input (Table 3). The presence of gammacerane (terpane biomarker) in oils indicates a hypersaline marine or non-marine environment with a stratified water column (Sinninghe-Damste et al., 1995; Peters et al., 2005). The gammacerane index (GI) value for the Mela oil samples suggests a low-saline environment for the source rock deposition (Figure 7 and Table 3). The absence of oleanane, a higher plant biomarker, in the extracts of the Chichali Formation suggests a marine depositional environment with no input from terrestrial organic matter (Moldowan et al., 1994; Peters et al., 2005). On the other hand, the presence of oleanane in Mela oils indicates input from terrestrial-sourced organic matter (Table 3).

Extracts or oils derived from carbonate lithology typically have a C_{29}/C_{30} hopane ratio greater than one, while those derived from shale lithology have a C_{29}/C_{30} hopane ratio less than one (Clark and Philp, 1989; Subroto et al., 1991; Peters et al., 2005). Although the composition of the Chichali Formation is mostly shale, the C_{29}/C_{30} hopane ratio suggests carbonate characteristics, as it is greater than one. In contrast, the Mela oil source rock is of shale composition, as indicated by a C_{29}/C_{30} hopane ratio is <1 (Table 3). The greater value of the C_{29}/C_{30} hopane ratio for the Chichali Formation may be attributed to the presence of belemnites and ammonite fossils in the formation. However, additional geochemical analysis of the Chichali Formation belemnites and ammonites is necessary to verify this statement. It is worth noting that terpanes were not identified in the Chichali Formation cutting extracts, possibly due to the high thermal maturity of the well cuttings (Figure 7).

5.3.3. Steranes

The C_{27} steranes are typically derived from aquatic algae, whereas C_{28} steranes mostly originate from bacterial plankton or fungi. Terrestrial plants mostly produce C_{29} steranes (Peters et al., 2005). The distribution of steranes also reveals the different sources of organic matter for the Chichali Formation extracts and the Mela oils. The Chichali Formation outcrop samples have higher levels of C_{27} steranes than C_{29} steranes, indicating an anoxic environment with algal organic input (Figure 5; Table 3). In contrast, the Mela oils have high levels of C_{29} steranes, indicating an oxic depositional environment of their source rock with terrestrial organic input (Figure 6; Table 3) (Huang and Meinschein, 1979). No steranes were identified in the well cuttings, which may be due to the high cracking of hydrocarbons (Figure 7). The ternary plot of steranes (Figure 6) after Huang and Meinschein (1979) indicates a marine environment with algal organic input for the Chichali Formation, while the Mela oils' source rock was deposited in an estuarine environment with terrestrial organic matter input. This is also reflected in the cross plot of Ph/nC_{18} vs. Pr/nC_{17} (Figure 4).

5.3.4. Aromatics hydrocarbons

The environment of deposition and the lithology of the source rock can be predicted through the relative proportion of dibenzothiophene (DBT) and phenanthrene (P) (DBT/P). Dibenzothiophenes are abundant in marine carbonate and marl and represent the sulfur-rich anoxic environment of deposition (Hughes et al., 1995). Compounds derived from land plants have a high concentration of phenanthrene. A modified plot (Figure 8), after Hughes et al. (1995) shows that the rock samples of the Chichali Formation fall in Zone-2, depicting a lacustrine sulfate-poor depositional environment with mixed shale-carbonate lithology. The Chichali Formation's shales also show carbonate characteristics, as indicated by the C_{29}/C_{30} hopane ratio >1. In contrast, the modified plot (Figure 8) after Hughes et al. (1995) shows that Mela oils fall in Zone-3, depicting the marine shale lithology of their source rock deposited in the suboxic lacustrine environment (Figure 8).

5.4. Thermal maturity analysis

The thermal maturity level of organic matter is a standard tool in the exploration industry. During burial, the composition of organic matter in sediments changes with thermal heat and time (Tissot and Welte, 1984). Source rocks can be considered effective once reaching the appropriate levels of maturity and some minimum generation potential to facilitate expulsion. In addition to conventional methods, biomarkers are widely utilized in determining maturity level of oil or source rocks (Peters et al., 2005). The thermal maturity levels of the Chichali Formation and Mela oils' source rock were evaluated by studying the n-alkanes, hopanes, steranes, and aromatic compounds (Peters and Moldowan, 1993). The Carbon Preference Index (CPI) values of the Chichali Formation well cuttings are almost equal to one, indicating mature organic matter (Table 4). Similarly, the CPI values of the Mela oils samples are almost equal to one, signifying the maturity of their source rock. The ratio between the isomers of C_{31} Homohopane, i.e., 22S/ (22S+22R), is a widely used parameter to determine thermal maturity levels. This ratio achieves equilibrium in the range of 0.57-0.62 (Seifert and Moldowan, 1980; Peters et al., 2005). The C_{31} homohopane ratio in the Chichali Formation ranges from 0.47 to 0.58, indicating marginal maturity of the organic matter, while the ratio ranges from 0.62 to

0.63 in the Mela oils, reflecting the maturity of their source in the peak oil window phase (Table 4).

The sterane isomers ratio (C_{29} 20S/(20S+20R)) is also used as a maturity indicator for oils' source rock and rock extracts (Seifert and Moldowan, 1986; Requejo, 1992). This ratio reaches equilibrium between 0.52-0.55 and indicates the stage of oil generation (Seifert and Moldowan, 1986). The Chichali Formation's samples have C_{29} 20S/(20S+20R) sterane ratios ranging from 0.46-0.51, indicating the oil generation phase, while Mela oils have ratios ranging from 0.58-0.60, indicating the peak oil generation phase of their source rock (Table 4).

The stereoisomers of C_{27} hopanes, 18α-trisnorhopanes (Ts) and 17α-trisnorhopanes (Tm), are utilized to determine the thermal maturity of organic compounds in source rocks and oils, as indicated by Ts/Ts+Tm ratios (Seifert and Moldowan, 1978; Kolaczkowska et al., 1990). In the Chichali Formation, Ts/Ts+Tm ratios range from 0.37-0.46, signifying less mature organic matter. In contrast, for Mela oils, Ts/Ts+Tm ratios range from 0.73-0.77, indicating varying levels of organic matter maturation (Table 4). Standard parameters used to evaluate the maturity stage of organic matter in source rocks are the ratios of substituted naphthalene and phenanthrenes (Tissot and Welte, 1984). As temperature increases, 1, 2-methyl shifts to create more stable naphthalene isomers (van Aarssen et al., 1999). Likewise, the abundance of methylated phenanthrene isomers changes with an increase in thermal maturity, making it comparable to the vitrinite reflectance of organic substances (Radke et al., 1982a). Hughes (1984) observed a similar trend for dibenzothiophenes with thermal maturation. Radke et al. (1982a; 1984) established a correlation between the aromatic compounds and mean vitrinite reflectance (VRo) for thermal maturity. The methyl-phenanthrene index (MPI-1) is a thermal maturity indicator used to derive calculated vitrinite reflectance (VRc %) (Radke and Welte 1983). The calculated vitrinite reflectance (VRc %) values based on the MPI-1 for the Chichali Formation range from 0.77-0.94, while for Mela's oils they range from 0.96-0.99 (Figure 9 and Table 4). This indicates less thermal maturity of the organic matter in the Chichali Formation compared to the source rock's organic matter in Mela oils (Figure 10).

Similarly, the methyldibenzothiophenes ratio (MDR) is a commonly used maturity parameter (Radke, 1988; Chakhmakhchev and Suzuki, 1995). Vitrinite reflectance derived from MDR is represented as calculated vitrinite reflectance (Rcs). Based on MDR, the calculated vitrinite reflectance (Rcs) values for the Chichali Formation range from 0.64-0.91, while for Mela's oils they range from 1.06-1.21, reflecting the higher maturity of the source rock of Mela oils (Figs. 9-10 and Table 4).

5.5. Age related biomarkers

About 90% of the world's discoverable oil-gas reserves are generated from the six stratigraphic intervals of Phanerozoic source rocks. Among them 9% from Silurian, 8% from Upper Devonian, 8% from Pennsylvanian, 25% from Upper Jurassic, 29% from middle Cretaceous and 12.5% from Oligocene-Miocene (Klemme and Ulmishek, 1991).

The organic geochemistry provides a pivotal tool in the petroleum industry which enable to corelate the hydrocarbon reserves to their specific source rocks. By examining the organic matter within these rocks, scholars can discover the timing as well as the conditions oil and gas generation.

Oleanane is a biomarker of flowering plants of angiosperms. Presence of oleanane in the source rock extracts or oils indicates Early Cretaceous or post Cretaceous and terrestrial dominated environment (Peters et al., 2005). Organic matter in marine carbonate or evaporitic settings have no contribution from terrestrial sources, specified by the lack of oleanane (Peters and Moldowan, 1993; Moldowan et al., 1994; Peters et al., 2005). The Chichali Formation extracts have no oleanane, indicating either an environment with no terrestrial organic input or organic matter older than the Early Cretaceous (Table 3). In contrast, the oils samples have a sufficient amount of oleanane as the Oleanane index (OI) values for the Mela oils ranges from 20.63 to 21.45, pointing to a possible source rock of Cretaceous or younger age (Table 3).

5.6. Implication for hydrocarbon exploration and development and future studies

According to the study, the oil samples showed a terrestrial organic source and a sub-oxic and deltaic depositional habitat, but the rocks from the Chichali Formation, which were taken from well cuttings and outcrop, were characterized by an algal organic source and a marine anoxic depositional environment. Unique biomarker characteristics, such as methyl-phenanthrene (MP), terpanes, isoprenoids, n-alkanes, and steranes, provided a clear picture of the variations in organic matter maturity between the oils and the Chichali Formation. Moreover, the oils demonstrated the presence of the oleanane biomarker, suggesting that the source rock is Cretaceous or younger in age. For the Mela oils, a unique source rock that was either Cretaceous or younger than Cretaceous was proposed. The studied Kohat Basin contains multiple source rocks but has not yet confirmed the exact kitchen of the produced free hydrocarbons. The study found that, in terms of age, depositional environment, and organic matter type, there is no genetic relationships with the crude oil in the studied wells of the Mela oilfield in the Kohat Sub-Basin and the Chichali Formation. For the Mela oils, a distinctive source rock that was either Cretaceous or younger than Cretaceous was proposed. Furthermore, organic geochemical data helps to identify unexplored virgin sedimentary basin for hydrocarbons. The study found that the Chichali Formation rocks, obtained from well cuttings and outcrop, were marked by an algal organic source and a marine anoxic depositional environment, while the oil samples exhibited a terrestrial organic source and a sub-oxic and deltaic depositional environment. Distinctive biomarker parameters, including n-alkanes, isoprenoids, terpanes, steranes, and methyl-phenanthrene (MP), offered a vivid glimpse into the organic matter maturity differences between the oils and the Chichali Formation.

Future studies could focus on investigating the depositional environments and geological history of the Chichali Formation and the Mela oil reservoirs using a combination of geochemical, sedimentological, and petrographic techniques. Additionally, the use of advanced analytical techniques such as high-resolution mass spectrometry and nuclear magnetic resonance spectroscopy could help to identify and quantify specific organic compounds and shed light on the processes involved in their formation and preservation. Further studies could also investigate the potential for hydrocarbon exploration and development in the region, taking into account the geological and geochemical characteristics of the samples analyzed in this study.

6. Conclusions

This study employed geochemical techniques to analyze the Cretaceous Chichali Formation and Mela oil samples, yielding the following conclusions.

- The total organic carbon (TOC) values indicated fair to good hydrocarbon potential for the well cuttings and poor to fair potential for the outcrop samples.
- The presence of marine organic matter deposited under anoxic conditions in the Chichali Formation was suggested by the high concentration of saturated compounds, short-chain n-alkanes, C_{27} steranes, and the absence of oleanane and gammacerane, as well as high values of TT/H ratios and low values of Pr/Ph, $C_{19}TT/C_{23}TT$, and $C_{20}TT/C_{23}TT$ ratios.
- In contrast, the Mela oils were found to have a source rock deposited under a suboxic environment with a dominant terrestrial organic input, as indicated by a high concentration of aromatic compounds, long-chain n-alkanes, oleanane, gammacerane,

and C29 steranes, high values of Pr/Ph, C_{19} $TT/C_{23}TT$, and $C_{20}TT/C_{23}TT$ ratios, and low TT/H ratios.

- Additionally, the ratios of n-alkanes, isoprenoids, terpanes, steranes, methyl-phenanthrene, and methyl-dibenzothiophene in the Chichali Formation extracts and the Mela oils indicated a different source rock maturity for the Mela oils. The high Oleanane Index (>20%) for the Mela oils suggested a Cretaceous or younger source rock.
- Finally, the results indicated that there is no genetic relationship between the Mela oils and the Chichali Formation rock extracts.

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References

Ahmad Jr, S., Kroon, D., Rigby, S., Hanif, M., Khan, S., Ali, F., Hussain, H. S., 2016. Endemic vs cosmopolitan tethyan benthic foraminifera from the lower Eocene Panoba Formation, Kohat sub basin, Pakistan: implications for early Eocene warming. Journal of Himalayan Earth Sciences, 49(1), 131.

Ahsan, N., & Chaudhry, M. N., 2008. Geology of Hettangian to middle Eocene rocks of Hazara and Kashmir basins, Northwest lesser Himalayas, Pakistan. Geological Bulletin of Panjab University, 43, 131-152.

Barnes, M., & Barnes, W., 1983. Oxic and anoxic diagenesis of diterpenes in lacustrine sediments. Advances in organic geochemistry 1981, 289-298.

Chakhmakhchev, A., Suzuki, N., 1995. Saturate biomarkers and aromatic sulfur compounds in oils and condensates from different source rock lithologies of Kazakhstan, Japan and Russia. Organic Geochemistry, 23(4), 289-299.

Clark, J., Philp, R., 1989. Geochemical characterization of evaporite and carbonate depositional environments and correlation of associated crude oils in the Black Creek Basin, Alberta. Bulletin of Canadian Petroleum Geology, 37(4), 401-416.

Craig, J., Hakhoo, N., Bhat, G., Hafiz, M., Khan, M., Misra, R., Thusu, B., 2018. Petroleum systems and hydrocarbon potential of the North-West Himalaya of India and Pakistan. Earth-science reviews, 187, 109-185.

Damsté, J. S. S., Kenig, F., Koopmans, M. P., Köster, J., Schouten, S., Hayes, J., de Leeuw, J. W. ,1995. Evidence for gammacerane as an indicator of water column stratification. Geochimica et Cosmochimica Acta, 59(9), 1895-1900.

Damsté, J. S. S., Kenig, F., Koopmans, M. P., Köster, J., Schouten, S., Hayes, J., & de Leeuw, J. W., 1995. Evidence for gammacerane as an indicator of water column stratification. Geochimica et Cosmochimica Acta, 59(9), 1895-1900.

Ghani, H., 2019. Structural evolution of the Kohat and Potwar fold and thrust belts of Pakistan. Universität Potsdam.

Greenwood, P. F., Arouri, K. R., & George, S. C., 2000. Tricyclic terpenoid composition of Tasmanites kerogen as determined by pyrolysis GC-MS. Geochimica et Cosmochimica Acta, 64(7), 1249-1263.

Hakimi, M.H., Ahmed, A.F., 2016. Organic geochemistry characterization of the Paleogene to Neogene source rocks in the Sayhut subbasin, Gulf of Aden Basin with emphasis on organic

Hao, F., Zhou, X., Zhu, Y., Zou, H., Yang, Y., 2010. Charging of oil fields surrounding the Shaleitian uplift from multiple source rock intervals and generative kitchens, Bohai Bay basin, China. Marine and Petroleum Geology, 27(9), 1910-1926.

Huang, W., Meinschein, W., 1979. Sterols as ecological indicators: Geochemica et Cosmochimica Acta, v. 43.

Hughes, W. B., 1984. Use of thiophenic organosulfur compounds in characterizing crude oils derived from carbonate versus siliciclastic sources.

Hughes, W. B., Holba, A. G., Dzou, L. I., 1995. The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. Geochimica et Cosmochimica Acta, 59(17), 3581-3598.

Khan, N; Wasif; Siyar, M, S; Wadood, B; Tariq, A; Tariq., 2022. Hydrocarbon source rock assessment of the shale and coal bearing horizons of the Early Paleocene Hangu Formation in Kala Chitta Range, Northwest Pakistan. Journal of Petroleum Exploration and Production Technology, 1-18

Klemme, H. D. and Ulmishek, G. F. (1991) Effective petroleum source rocks of the world: stratigraphic distribution and controlling depositional factors. American Association of Petroleum Geologists Bulletin, 75, 1809–51.

Kolaczkowska, E., Slougui, N.-E., Watt, D. S., Maruca, R. E., & Moldowan, J. M., 1990. Thermodynamic stability of various alkylated, dealkylated and rearranged 17α-and 17β-hopane isomers using molecular mechanics calculations. Organic Geochemistry, 16(4-6), 1033-1038.

Latif, K., Hanif, M., Shah, S, A., Jan, I, U., Khan, M, Y., Iqbal, Hamid., Khan, A., Siyar, M, S., M, Mohibullah., 2021. Source rock potential assessment of the Paleocene coal and coaly shale in the Attock-Cherat Range of Pakistan. Journal of Petroleum Exploration and Production Technology, 2299-2313, 11

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.

McDougall, J., 1988. Geology and geophysics of the foreland fold-thrust belt of northwestern Pakistan. Corvallis, Oregon State University. Ph. D. dissertation.

McLafferty, F. W. "Interpretation of Mass Spectra;" Third Edition, University Science Books: Mill Valley, CA, 1980.

Moldowan, J. M., Dahl, J., Huizinga, B. J., Fago, F. J., Hickey, L. J., Peakman, T. M., & Taylor, D. W., 1994. The molecular fossil record of oleanane and its relation to angiosperms. Science, 265(5173), 768-771.

Noor I, Ahmad S, Ahsan N, Saif-Ur-Rehman., 2013. Structural geology of Panoba and Chorlakki area, Northeastern Kohat plateau, Khyber Pakhtunkhwa, Pakistan. Int. J. Agric. Appl. Sci. Vol. 5, No.1, 2013.

Paracha, W., 2004. Kohat plateau with reference to Himalayan tectonic general study. CSEG recorder, 29(4), 126-134.

Peter, K. E., Walter, C., & Moldowan, M., 2005. The biomarker guide, volume 2–Biomarkers and isotopes in petroleum exploration and earth history: Cambridge University Press, UK.

Peters, K. E., & Cassa, M. R., 1994. Applied source rock geochemistry: Chapter 5: Part II. Essential elements.

Peters, K. E., & Moldowan, J. M., 1993. The biomarker guide: interpreting molecular fossils in petroleum and ancient sediments.

Philp R. P. (1985) Fossil Fuel Biomarkers. Meth. Geochem. Geophys. 23. Elsevier, New York.

Pivnik, D. A., 1992. Depositional response to encroachment of Himalayan compressional and transpressional deformation on the northern Pakistan foreland: Dartmouth College.

Pivnik, D. A., Sercombe, W. J., 1993. Compression-and transpression-related deformation in the Kohat Plateau, NW Pakistan. Geological Society, London, Special Publications, 74(1), 559-580.

Pivnik, D. A., & Wells, N. A., 1996. The transition from Tethys to the Himalaya as recorded in northwest Pakistan. Geological Society of America Bulletin, 108(10), 1295-1313.

Radke, M., 1988. Application of aromatic compounds as maturity indicators in source rocks and crude oils. Marine and Petroleum Geology, 5(3), 224-236.

Radke, M., Leythaeuser, D., Teichmüller, M., 1984. Relationship between rank and composition of aromatic hydrocarbons for coals of different origins. Organic Geochemistry, 6, 423-430.

Radke, M., Welte, D., 1983. The MP Index (MPI): a maturity parameter based on aromatic hydrocarbons. In 'Advances in Organic Geochemistry 1981' (Eds. Bjøroy, M.) pp. 504–512: John Wiley and Sons Limited: Chichester, UK.

Radke, M., Welte, D. H., Willsch, H., 1982. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. Geochimica et Cosmochimica Acta, 46(1), 1-10.

Requejo, A., 1992. Quantitative analysis of triterpane and sterane biomarkers: methodology and applications in molecular maturity studies. Biological Markers in Sediments and Petroleum, 222-240.

Rezaee, R., 2002. Petroleum Geology, Alavi Publication, 479p.

Searle, M., Kahn, M., 1996. Geological Map of North Pakistan and Adjacent Areas of Northern Ladakh and Western Tibet. (Western Himalaya, Salt Ranges, Kohistan, Karakoram, Hindu Kush), 1: 650 000.

Seifert, W., Moldowan, J., 1986. Use of biological markers in petroleum exploration. Methods in geochemistry and geophysics, 24, 261-290.

Seifert, W. K., Moldowan, J. M., 1978. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. Geochimica et Cosmochimica Acta, 42(1), 77-95.

Seifert, W. K., Moldowan, J. M., 1978. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. Geochimica et Cosmochimica Acta, 42(1), 77-95.

Seifert, W. K., Moldowan, J. M., 1980. Paleoreconstruction by biological markers.

Sercombe, W. J., Pivnik, D. A., Wilson, W. P., Albertin, M. L., Beck, R. A., Stratton, M. A., 1998. Wrench faulting in the northern Pakistan foreland. AAPG bulletin, 82(11), 2003-2030.

Shanmugam, G., 1985. Significance of coniferous rain forests and related organic matter in generating commercial quantities of oil, Gippsland Basin, Australia1. AAPG bulletin, 69(8), 1241-1254.

Siyar, M. S., Zafar, M., Jahandad, S., Khan, T., Ali, F., Ahmad, S., Fnais, M, S., Abdelrahman, K., Ansari, M, J., 2021. Hydrocarbon generation potential of Chichali Formation, Kohat Basin, Pakistan: A case study. Journal of King Saud University-Science, 33 (101235).

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.

Simoneit, B. R., Schoell, M., Dias, R. F., de Aquino Neto, F. R., 1993. Unusual carbon isotope compositions of biomarker hydrocarbons in a Permian tasmanite. Geochimica et Cosmochimica Acta, 57(17), 4205-4211.

Tenzer, G. E., Meyers, P. A., Robbins, J. A., Eadie, B. J., Morehead, N. R., Lansing, M. B., 1999. Sedimentary organic matter record of recent environmental changes in the St. Marys River ecosystem, Michigan–Ontario border. Organic Geochemistry, 30(2-3), 133-146.

Tissot, B., Welte, D., 1984. Petroleum formation and occurrence, Springer. Berlin, Germany. [Google Scholar].

Van Aarssen, B. G., Bastow, T. P., Alexander, R., Kagi, R. I., 1999. Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. Organic Geochemistry, 30(10), 1213-1227.

Van Krevelen, D.W., 1961. Coal Typology Chemistry Physics Constitution, Elsevier Publishing Company.

Wandrey, C. J., Law, B., Shah, H. A., 2004. Patala-Nammal composite total petroleum system, Kohat-Potwar geologic province, Pakistan: US Department of the Interior, US Geological Survey Reston.

Zumberge, J. E., 1987. Prediction of source rock characteristics based on terpane biomarkers in crude oils: A multivariate statistical approach. Geochimica et Cosmochimica Acta, 51(6), 1625-1637.

FIGURE CAPTIONS

Figure 1 a) Map presenting the geological features of the Kohat sub-basin (after Ahsan and Chaudhry 2008), **b**) balanced cross-section (AB) suggesting the extensive thrusting of different rock strata in the Kohat sub-basin (after McDougall 1988)

Figure 2 General stratigraphy of the Kohat sub-basin, Pakistan (modified after Sercombe et al. 1998).

Figure 3 Ternary diagram displaying the gross composition of Chichali Formation extracts (outcrop and well cuttings) and Mela oils in terms of saturated, aromatic hydrocarbons and polar compounds (after Tissot and Welte, 1984).

Figure 4 Ph/nC_{18} vs Pr/nC_{17} cross plot indicates the depositional environment and source input into the Chichali extracts and Mela oil samples, Kohat sub-basin, Pakistan (after Shanmugam 1985).

Figure 5 The cross plot of C_{29}/C_{27} sterane vs Pr/Ph ratios showing the type of organic matter and depositional environment of the samples (after Peters et al. 2005).

Figure 6 Ternary plot showing distribution of C_{27}, C_{28}, and C_{29} steranes for oil-source correlation in Kohat sub-basin, Pakistan (Huang and Meinschein 1979).

Figure 7 Chromatograms displaying the n-alkanes, iso-alkanes, terpane and sterane distribution in the Chichali Formation extracts and Mela oils, Kohat sub-basin, Pakistan.

Figure 8 The Pr/Ph vs DBT/P cross plot of the Chichali Formation extracts and the Mela oils (after Hughes et al. 1995).

Figure 9 Chromatograms showing the distribution of P and MP compounds at the top and the DBT and MDBT compounds at the bottom, the Kohat sub-basin, Pakistan.

Figure 10 The Cross plot of VRc% vs VRm% shows the maturity difference of the Chichali Formation and Mela oil samples in the Kohat sub-basin.

TABLE CAPTIONS

Table: 1 List of TOC values of the analyzed outcrop samples and well cuttings from the studied formation, Kohat sub-basin, Pakistan.

Table: 2 Molecular composition of the Mela oils and the Chichali Formation extracts (outcrop and well cutting samples), in the Kohat sub basin, Pakistan.

Table: 3 Source dependent terpane and sterane parameters for the Chichali Formation outcrop extracts and the Mela oils, the Kohat sub-basin, Pakistan.

Table: 4 Thermal maturity dependent terpane, sterane, and aromatic hydrocarbons in the Chichali Formation extracts and the Mela oils, Kohat sub-basin, Pakistan

Figure 1

Click here to access/download;Figure;Fig. 1.jpg

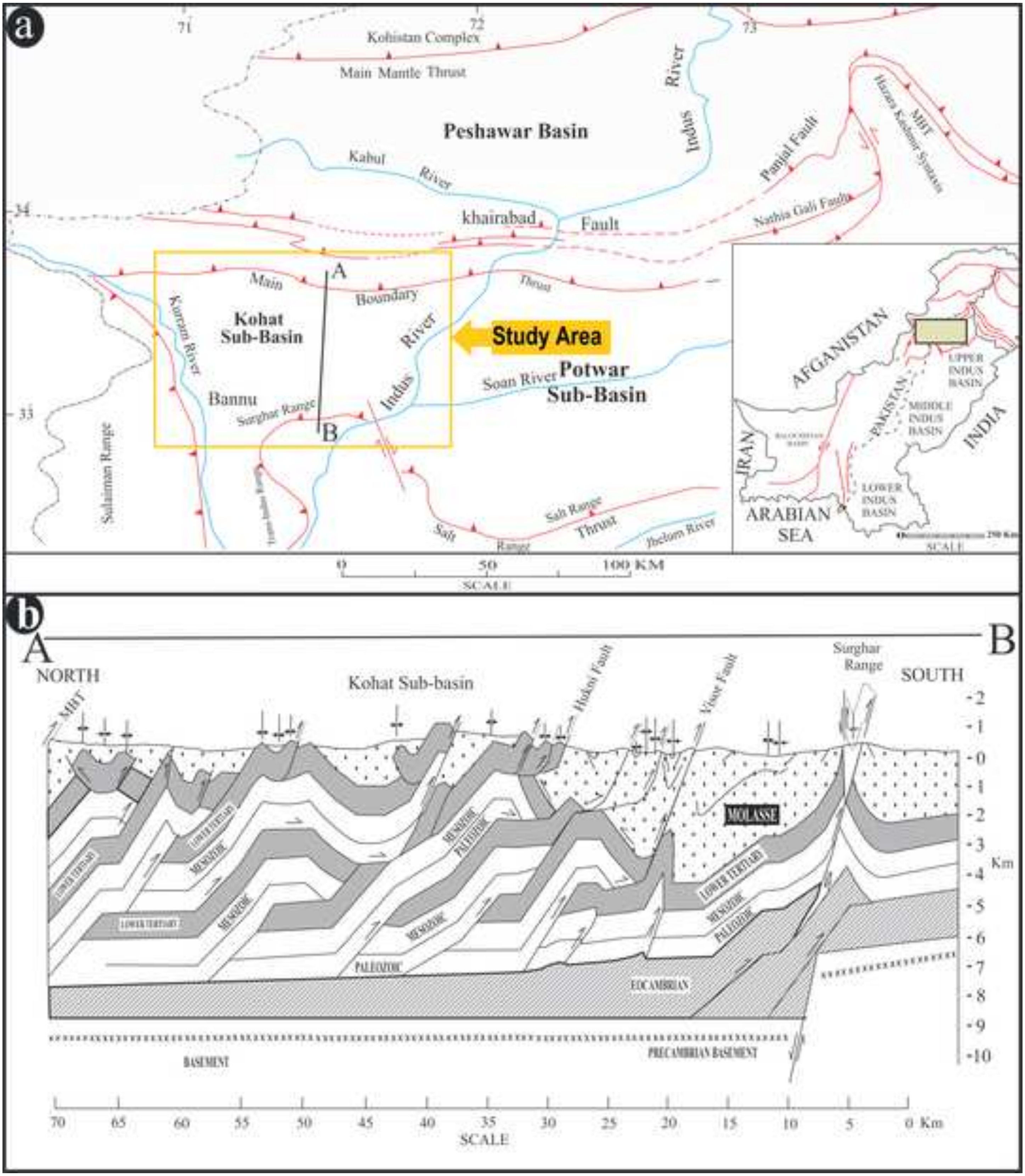

Figure 2

Click here to access/download;Figure;Fig. 2.jpg

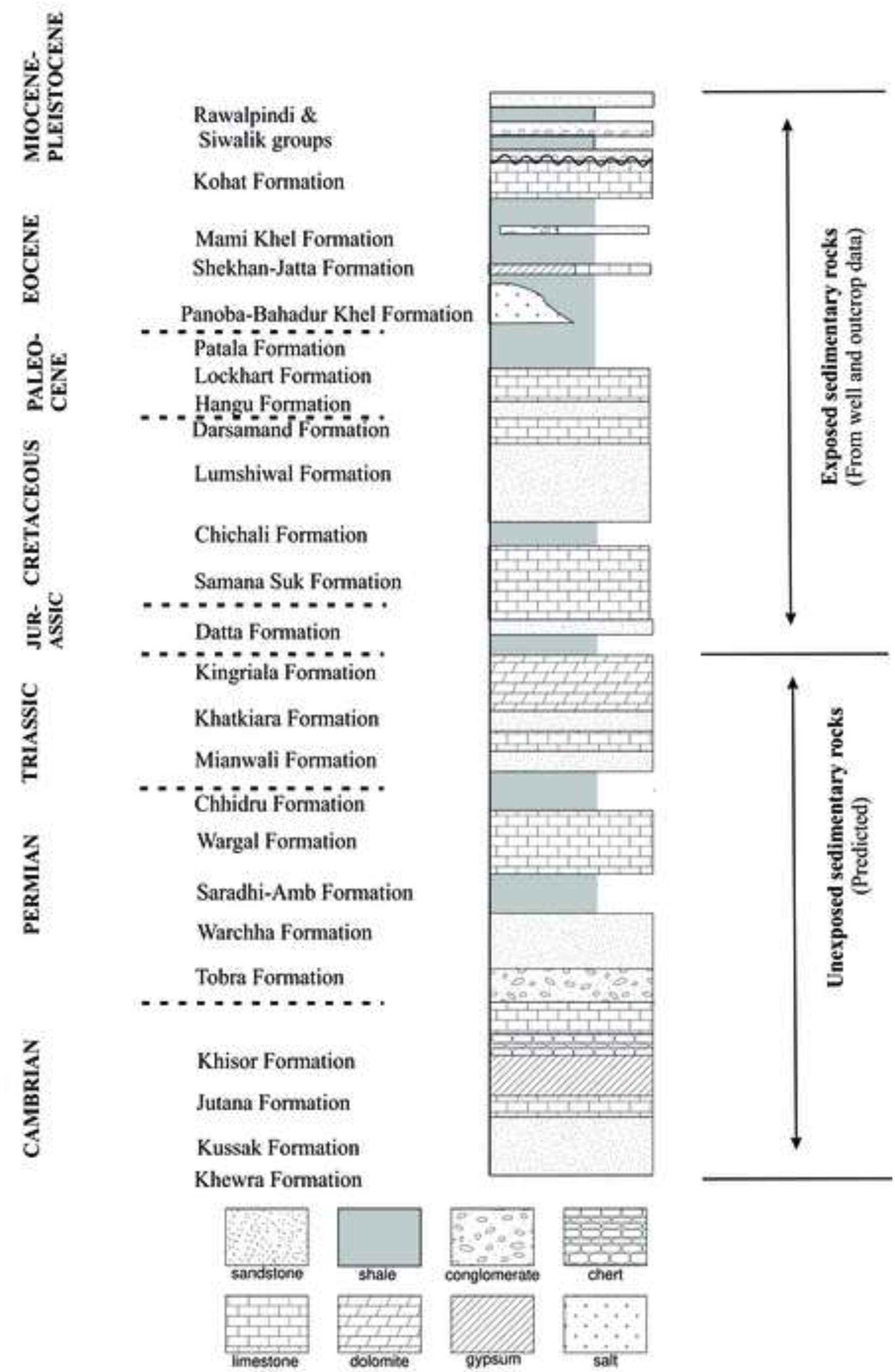

Figure 3

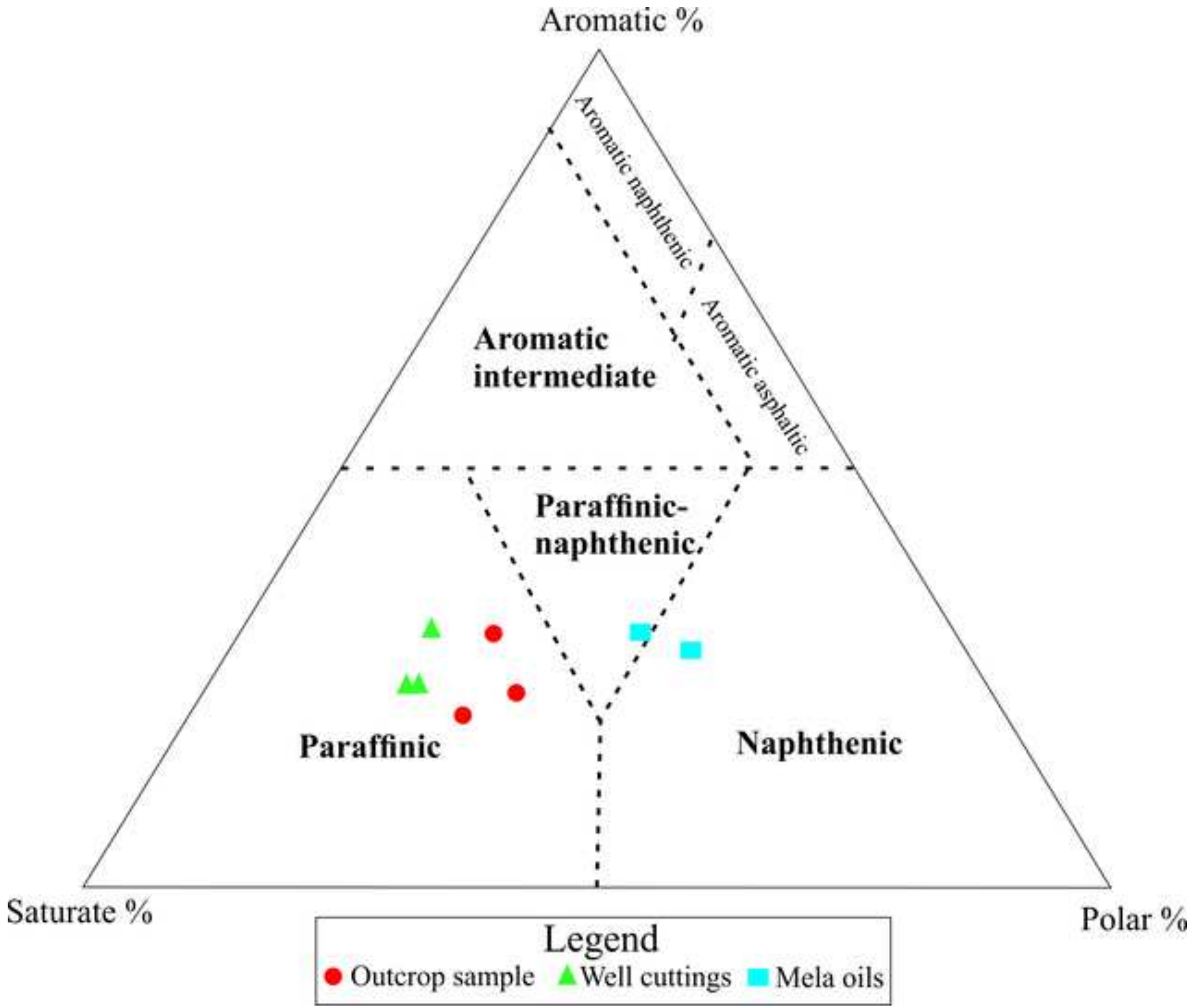
Aromatic %
Aromatic naphthenic
Aromatic asphaltic
Aromatic intermediate
Paraffinic-naphthenic
Paraffinic
Naphthenic
Saturate %
Polar %
Legend
Outcrop sample
Well cuttings
Mela oils

Figure 4 Click here to access/download;Figure;Fig. 4.jpg

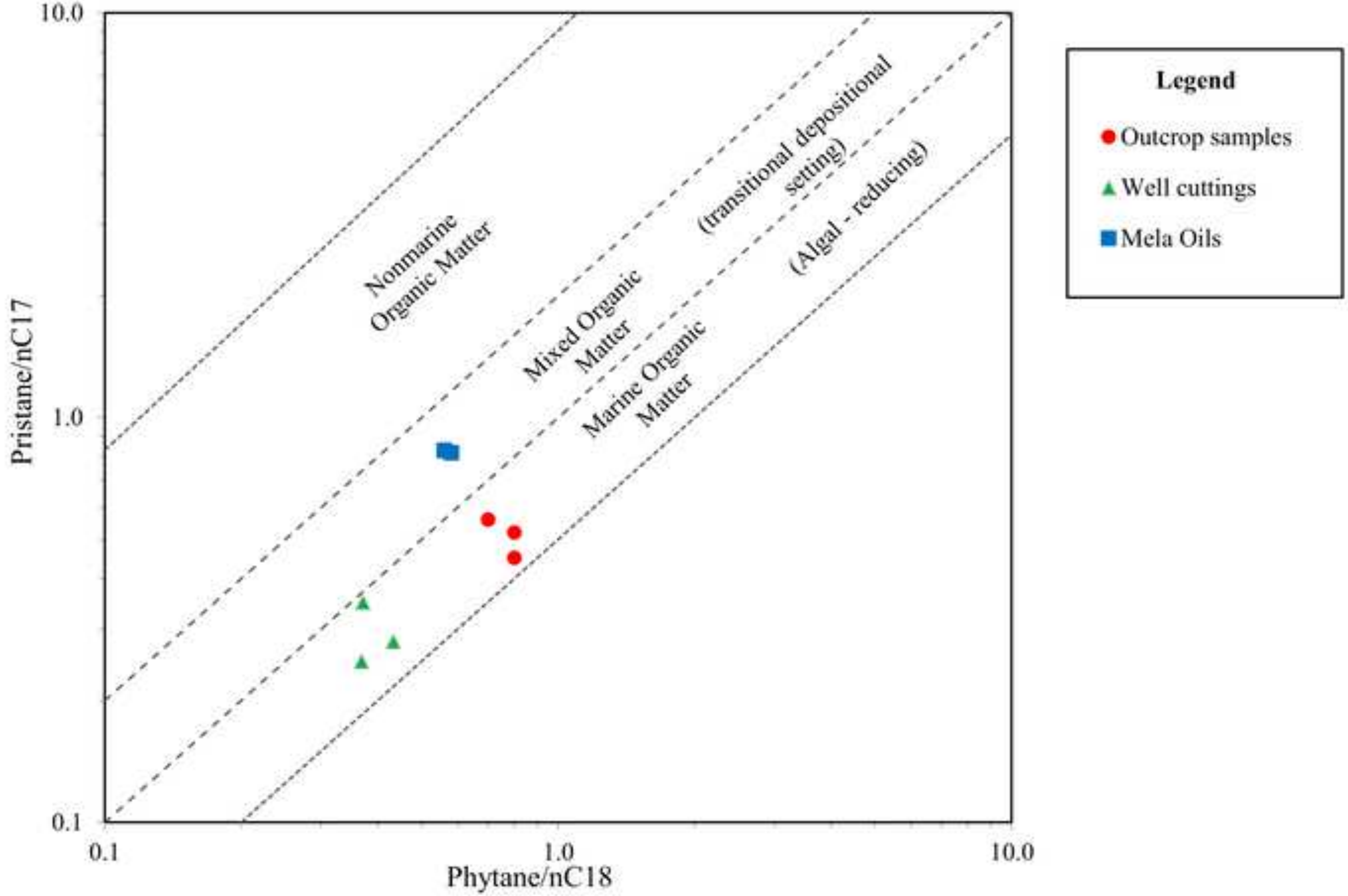

Figure 5

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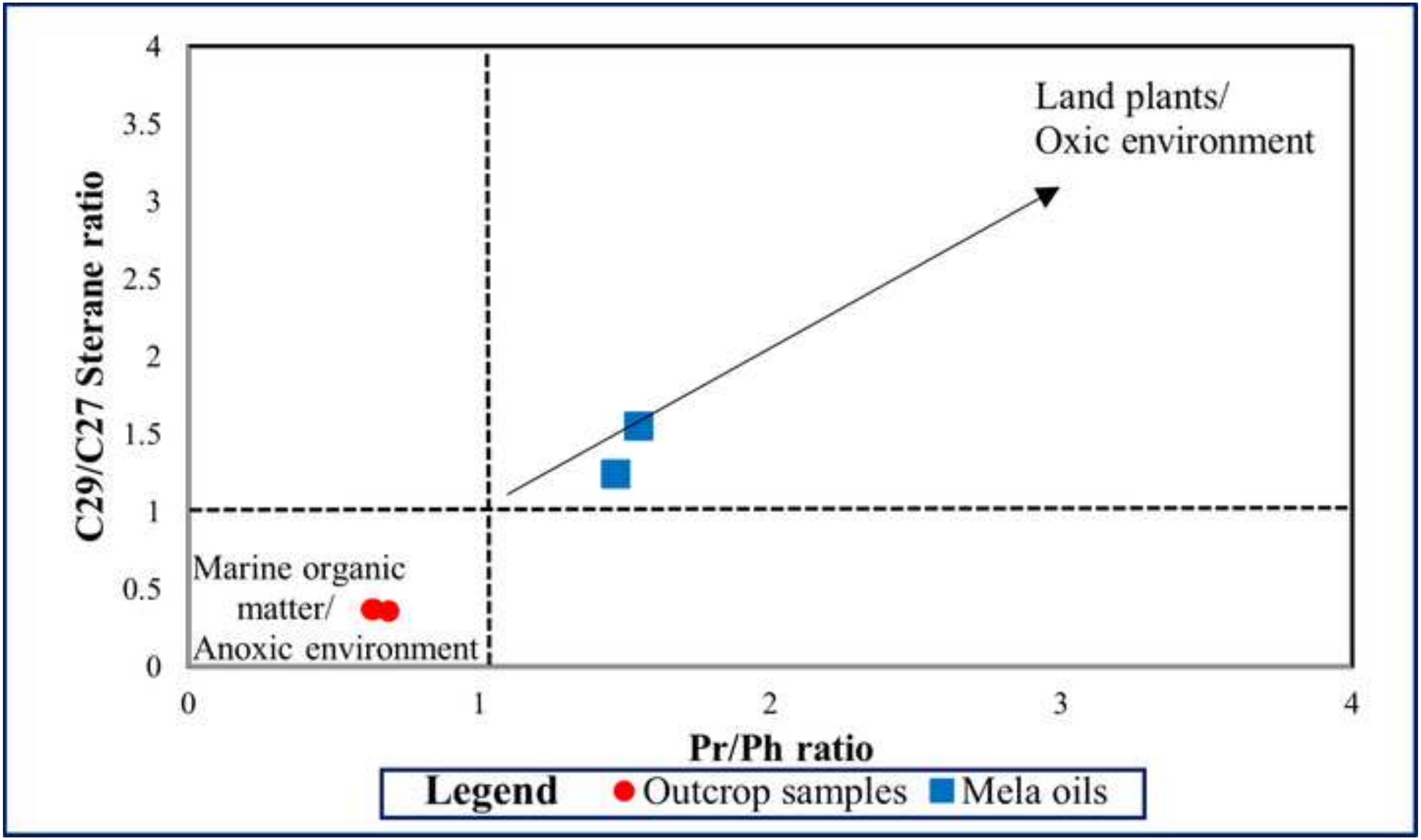

Figure 6

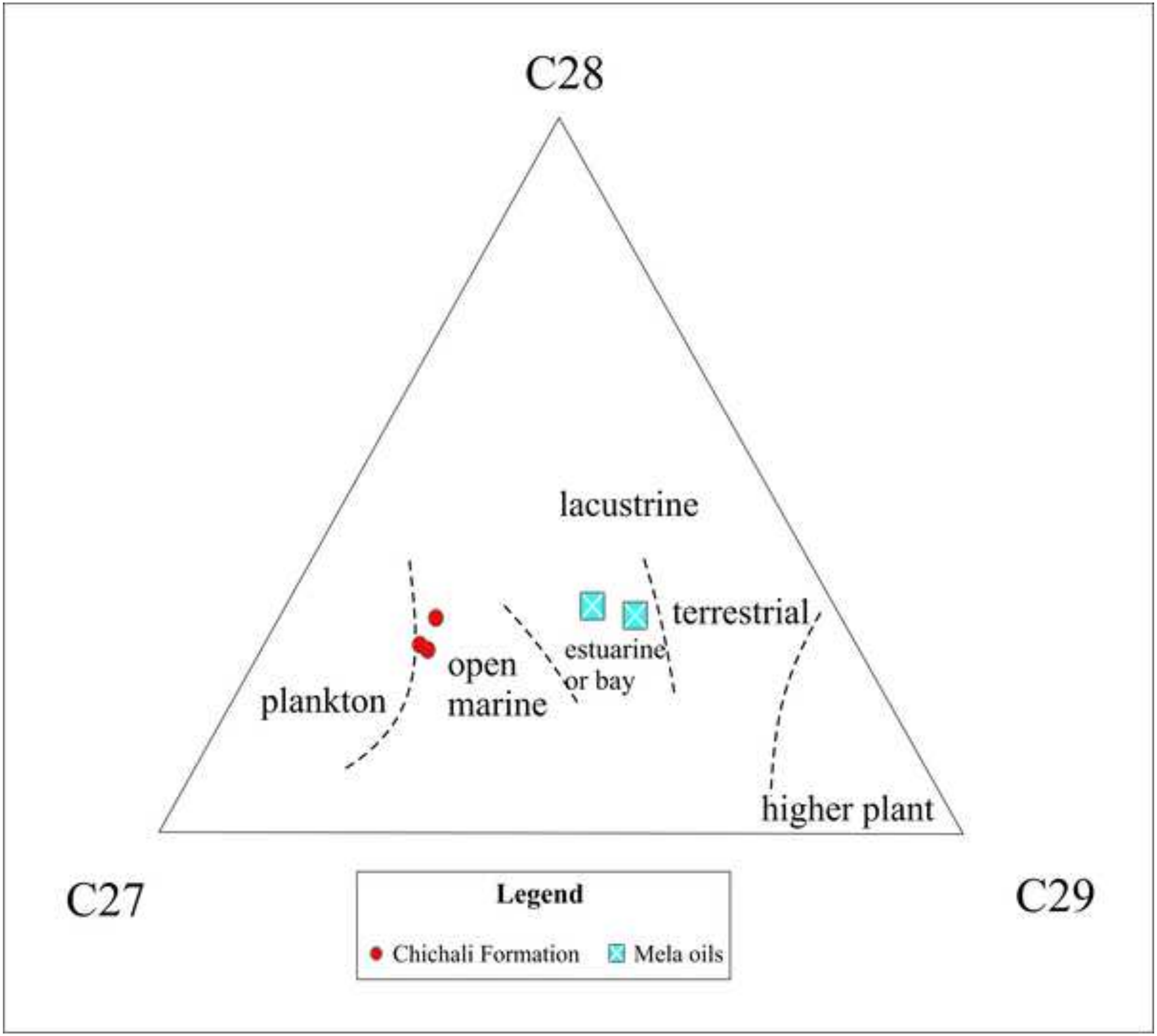
C28
lacustrine
terrestrial
estuarine
or bay
open
marine
plankton
higher plant
C27
C29
Legend
Chichali Formation
Mela oils

Figure 7

Click here to access/download;Figure;Fig. 7.jpg

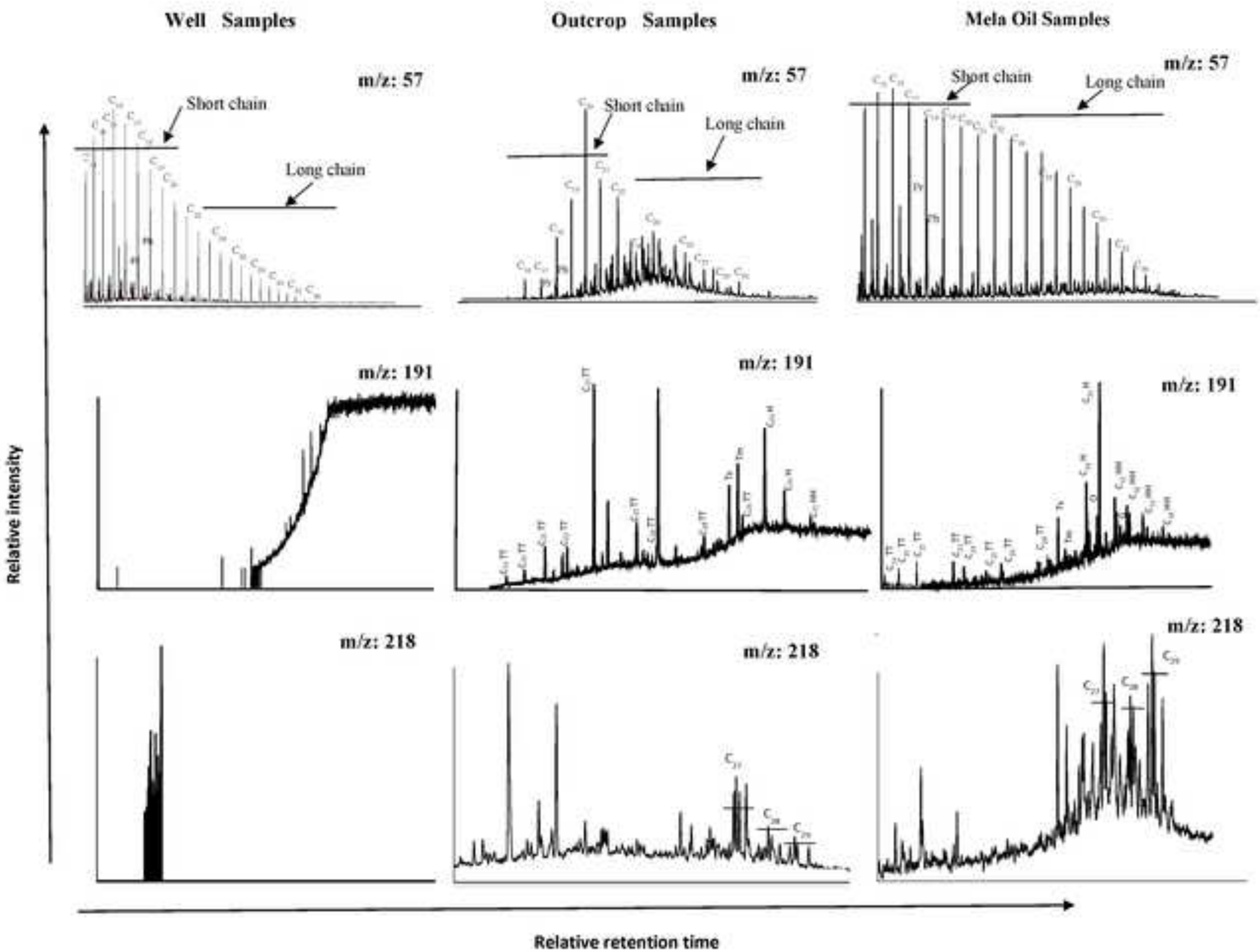

Figure 8

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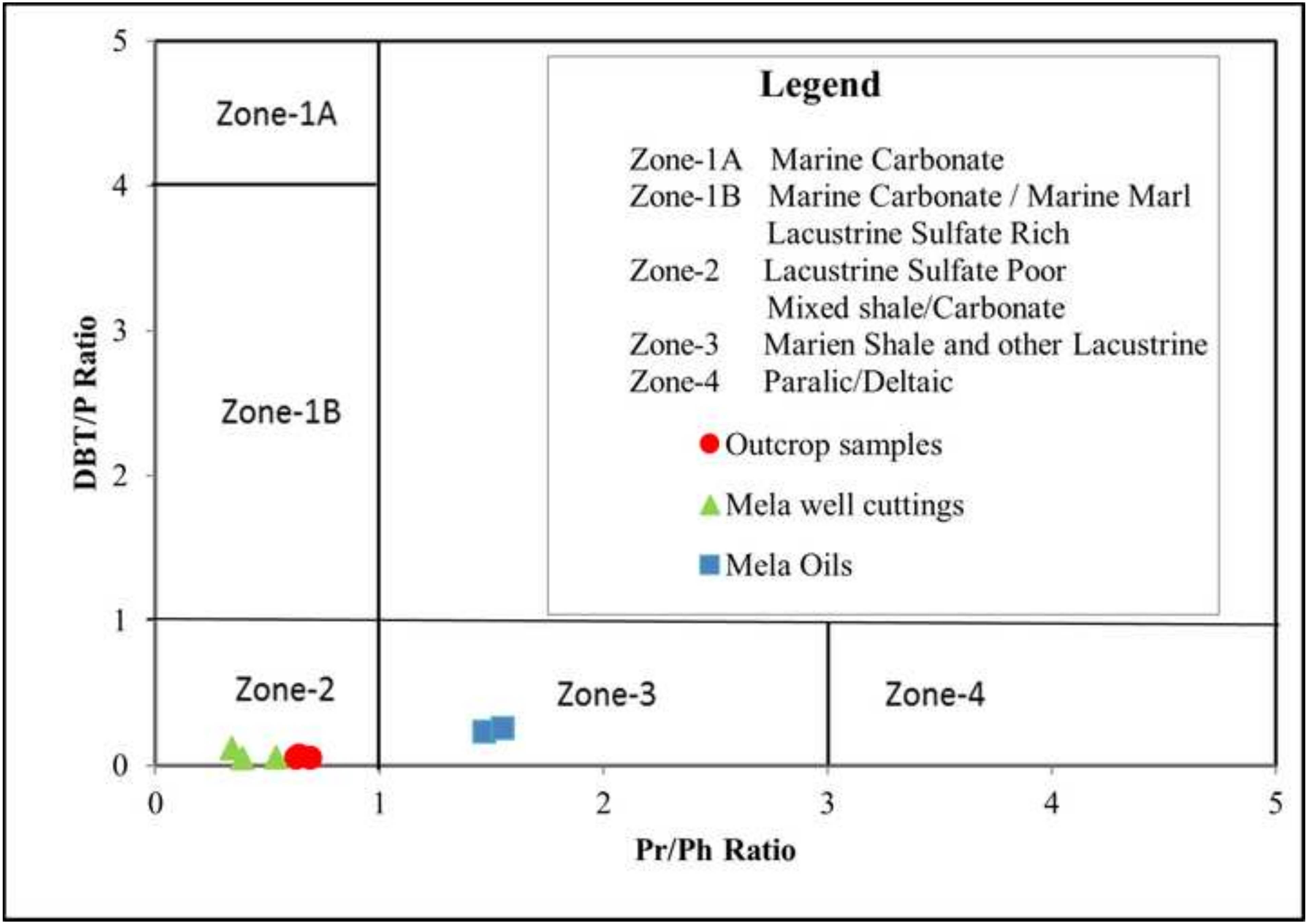


Figure 9

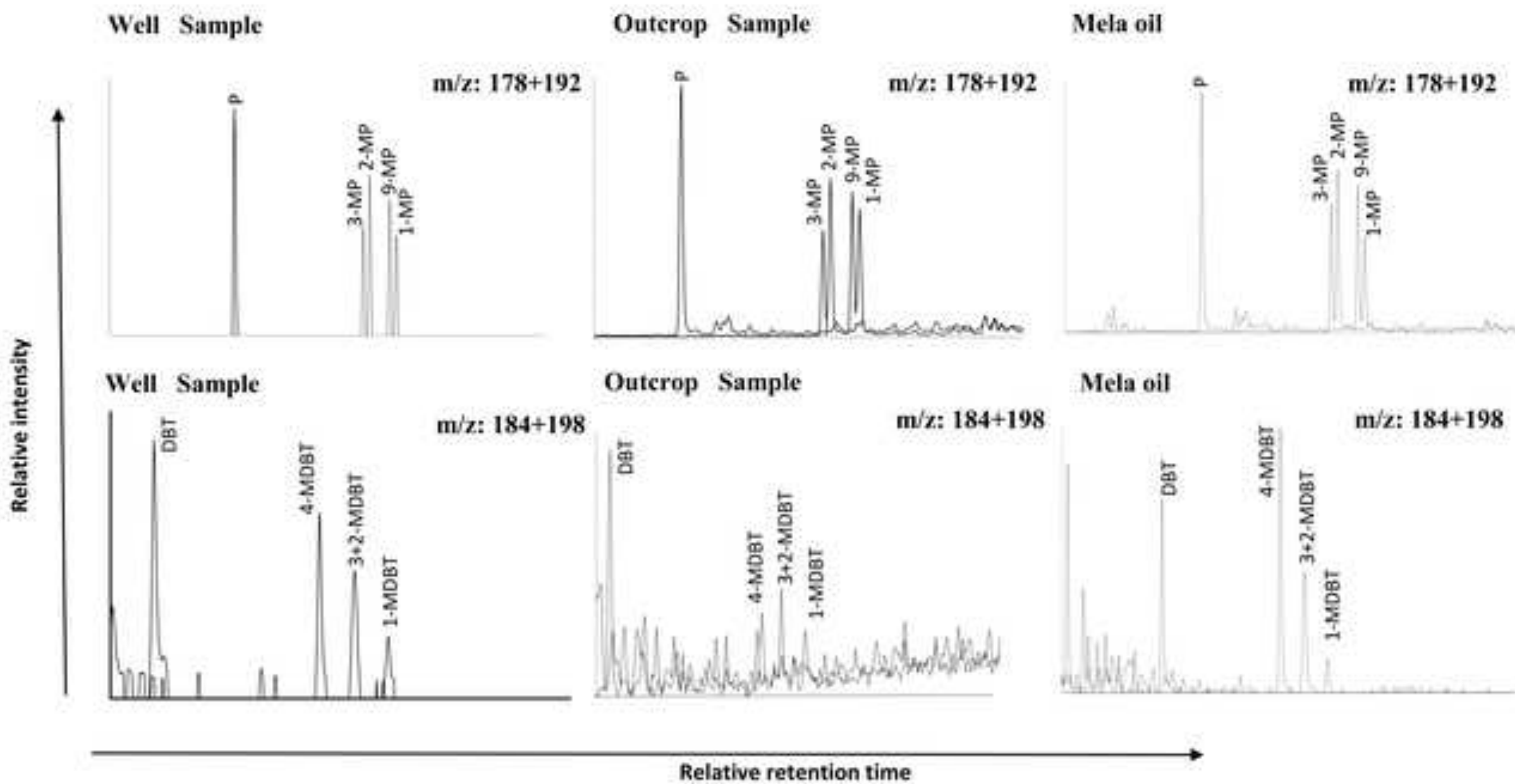
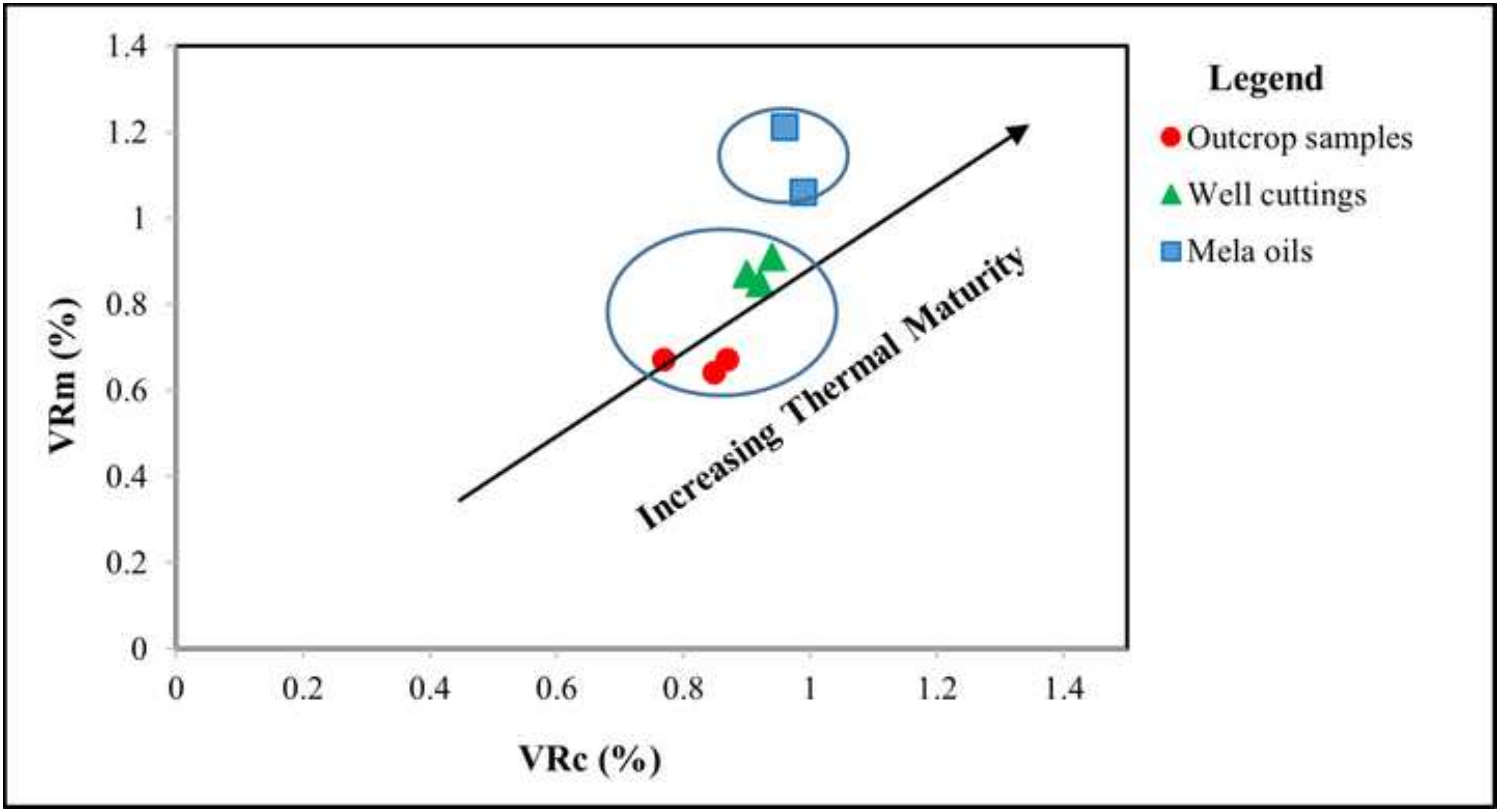

Well Sample
m/z: 178+192
P
3-MP
2-MP
9-MP
1-MP
Outcrop Sample
m/z: 178+192
P
3-MP
2-MP
9-MP
1-MP
Mela oil
m/z: 178+192
P
3-MP
2-MP
9-MP
1-MP
Well Sample
m/z: 184+198
DBT
4-MDBT
3+2-MDBT
1-MDBT
Outcrop Sample
m/z: 184+198
DBT
4-MDBT
3+2-MDBT
1-MDBT
Mela oil
m/z: 184+198
DBT
4-MDBT
3+2-MDBT
1-MDBT
Relative intensity
Relative retention time

Figure 10



Legend
Outcrop samples
Well cuttings
Mela oils
Increasing Thermal Maturity
VRm (%)
VRc (%)
0
0.2
0.4
0.6
0.8
1
1.2
1.4

Table 1

Sample type	Formation	Sample ID	Sample depth (m)	Sample ID	% TOC
Mela-05	Chichali Formation	ChF-01	4760	ChF-01	1.08
		ChF-02	4766	ChF-02	1.2
		ChF-03	4772	ChF-03	1.40
		ChF-04	4776	ChF-04	0.90
		ChF-05	4782	ChF-05	1.04
		ChF-06	4784	ChF-06	1.02
		ChF-07	4786	ChF-07	1.06
		ChF-08	4788	ChF-08	1.04
		ChF-09	4790	ChF-09	1.08
		ChF-10	4802	ChF-10	1.18
Mela-01	Chichali Formation	ChF-11	4688	ChF-11	0.70
		ChF-12	4694	ChF-12	0.66
		ChF-13	4708	ChF-13	0.60
		ChF-14	4718	ChF-14	0.75
		ChF-15	4728	ChF-15	0.61
		ChF-16	4734	ChF-16	0.61
		ChF-17	4740	ChF-17	0.73
Outcrop	Chichali Formation	CF-18	----	CF-18	0.57
		CF-19	----	CF-19	0.43
		CF-20	----	CF-20	0.29
		CF-21	----	CF-21	0.55
		CF-22	----	CF-22	0.45
		CF-23	----	CF-23	0.53
		CF-24	----	CF-24	0.59

Sample No.	Saturate (%)	Aromatic (%)	Polar (%)	TAR	CPI	Pr/Ph	Pr / nC_{17}	Ph/nC_{18}
ChF-03	45.30	30.21	24.49	0.18	1.1	0.54	0.15	0.37
ChF-07	46.73	23.09	30.18	0.10	1.1	0.39	0.10	0.37
ChF-10	53	20.63	26.35	0.08	1.0	0.34	0.10	0.43
CF-18	51.10	30.75	18.15	Np	np	0.69	0.28	0.08
CF-21	55.62	24.07	20.21	Np	np	0.64	0.45	0.05
CF-24	56.79	24	19.20	np	np	0.64	0.07	0.24
Mela-01	27.20	28.10	44.50	0.51	0.99	1.55	0.83	0.56
Mela-05	31.70	31.03	39.25	0.63	1.0	1.47	0.82	0.58

TAR: $(C_{27} + C_{29} + C_{31})/ (C_{15} + C_{17} + C_{19})$; CPI: $(2[C_{23}+C_{25}+C_{27}+C_{29}]/[C_{22}+2\{C_{24}+C_{26}+C_{28}\} +C_{30}])$; np: not present

Table 3 Click here to access/download;Table (Editable version);Table 3.docx

Sample ID	Terpanes								Steranes			
									Steranes (%)			C_{29}/C_{27}
	C_{19}/C_{23} TT	C_{20}/C_{23}TT	C_{26}/C_{25} TT	TT/H	C_{23}TT/H	C_{29}/C_{30}H	GI	OI	C_{27}	C_{28}	C_{29}	Sterane
CF-18	0.02	0.07	0.62	10.51	4.63	2.89	Np	np	55	25	20	0.36
CF-21	0.03	0.09	0.29	6.99	2.51	2.47	Np	np	54	25	20	0.37
CF-24	0.03	0.08	0.16	6.40	2.66	2.29	Np	np	51	30	19	0.37
Mela-01	0.40	0.60	1.03	0.50	0.11	0.45	0.10	21.45	28	28	44	1.55
Mela-05	0.39	0.62	1.35	0.57	0.11	0.52	0.15	20.63	31	31	38	1.24

Table 4

Sample ID	CPI	S/(S + R) C_{31}HH	Ts/(Ts + Tm)	C_{29} S/S+ R	MPI-1	Rc(%)	DBT/P	MDR	Rcs(%)
CF-18	1.1	0.47	0.46	0.46	0.62	0.77	0.05	2.23	0.67
CF-21	1.1	0.52	0.37	0.51	0.79	0.87	0.05	2.15	0.67
CF-24	1.0	0.58	0.38	0.47	0.74	0.85	0.07	1.73	0.64
ChF-03	np	Np	np	np	0.83	0.90	0.06	4.97	0.87
ChF-07	np	Np	np	np	0.86	0.92	0.05	4.59	0.85
ChF-10	np	Np	np	np	0.90	0.94	0.12	5.52	0.91
Mela-01	0.99	0.62	0.77	0.60	0.99	0.99	0.33	7.55	1.06
Mela-05	1.0	0.63	0.72	0.58	0.93	0.96	0.26	9.55	1.21

Declaration of interests

☒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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: