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ORIGINAL PAPER--EXPLORATION GEOLOGY

Integrated geochemical study of Chichali Formation from Kohat sub-basin, Khyber Pakhtunkhwa, Pakistan

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Abstract

An integrated geochemical study was performed for the assessment of the hydrocarbon potential, environment of deposition, thermal maturity and the organic matter's source of the Chichali Formation in the Kohat sub-basin of Pakistan. The analytical techniques used included the total organic carbon (TOC), Rock–Eval (RE), organic petrography, column chromatography (CC) and gas chromatography mass spectrometry (GC–MS). The quantity of the organic matter (i.e., TOC), Rock–Eval parameters (such as the original hydrogen index, oxygen index and T_{max}) and maceral analyses revealed that the shales of the Chichali Formation have poor to good petroleum source potential with Kerogen type II presently shown as type III (hydrogen index, oxygen index and T_{max}) due to thermal maturation and with higher marine organic matter. The extracts of the rock samples have high amount of short-chain n-alkanes with high ratios of tricyclic terpanes to hopanes (TCT/H), C_{27} to C_{29} stranes and low ratios of pristane to phytane (Pr/Ph), C_{19}/C_{23} TCT and C_{20}/C_{23} TCT. These ratios and lack of terrestrial biomarker (oleanane) are pointing toward algal/marine organic source deposited under anoxic environment. The dibenzothiophene-to-phenanthrene ratios (DBT/P) versus Pr/Ph cross-plot also confirms the anoxic environment with sulfate poor mixed shale/carbonate lithology. The drill cuttings show relatively high maturity compared to outcrop samples indicated by n-alkanes ratios, isoprenoids vs n-alkanes cross-plot, methyl-phenanthrene index (MPI-1), methyl-dibenzothiophene ratios and absence of saturate biomarkers. All the above findings reveal that the Chichali Formation had mature algal source with anoxic environment of deposition and may prove to be a poor to good hydrocarbon source rock.

Keywords Chichali Formation · Geochemical study · Kohat sub-basin · Pakistan

Introduction

The EW-trending Kohat sub-basin is one of the major hydrocarbon-producing areas in northern Pakistan having various proven and potential plays. The sedimentary succession of the Kohat sub-basin was deposited on the northwestern margin of the Indian plate, ranging in age from Jurassic to Quaternary (Wandrey et al. 2004). According to Meissner et al (1974), the total stratigraphic thickness of this basin is greater than 7700 m. The major hydrocarbon discoveries

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in the basin include Chanda, Nashpa, Mela, Makori and Manzalai oil–gas–condensate fields. The Samana Suk and Datta formations of Jurassic, Lumshiwal and Kawagarh formations of Cretaceous, and Lockhart and Patala formations of Paleocene age are the main reservoirs in the study area. The limestone of Lockhart Formation and shales of Datta, Chichali, Hangu and Patala formations appear to be the source rocks for hydrocarbons (Table 1).

The organic matter's characterization in the sedimentary rocks is one of the important criteria for the determination of a petroleum prospect in a basin. TOC is a valuable parameter for the evaluation of petroleum source rocks. Rocks with TOC less than 0.5 wt% have poor, with TOC 0.5 to 1 wt% have fair, with TOC 1–2 wt% have good, with TOC 2–4 wt% have very good and with TOC greater than 4 wt% are considered to have excellent potential for hydrocarbons (Peters and Cassa 1994). The Rock–Eval pyrolysis data have been extensively used to evaluate the organic matter type, maturity and its potential for hydrocarbons in different basins (Espitalié et al. 1985; Peters 1986; Peters and Cassa 1994; Langford and Blanc-Valleron 1990). The thermal maturity level is a function of vitrinite reflectance, T_{max} (pyrolysis temperature representing maximum yield of hydrocarbons) and production index (PI), depending upon the nature of the organic matter (Bacon et al. 2000; Peters and Cassa 1994). The specific complex compounds present in the source rocks' extracts derived from the living organisms are called biomarkers which are the survivors of the processes of diagenesis and catagenesis (Peters et al. 2005). Biomarkers can be used for the assessment of depositional environment, maturity, kerogen type and the source of organic matter in sediments (Peters et al. 1993). The commonly applied biomarkers are the n-alkanes, acyclic isoprenoids, terpanes, steranes, dibenzothiophene and phenantrene. The organic compounds produced from the marine algae and photosynthetic bacteria have comparatively more concentration of short-chain n-alkanes (i.e., nC_{15}, nC_{17} and nC_{19}), whereas the organic matter related to vascular plants is dominated by long-chain n-alkanes (nC_{27}, nC_{29} and nC_{31}) (Tenzer et al. 1999; Cranwell et al. 1987). The acyclic isoprenoid compounds such as pristane (Pr) and phytane (Ph) have been applied to know about the environment of deposition of the petroleum's source rocks (Didyk et al. 1978; Powell and McKirdy 1973). The source rock extracts or crude oils derived from marine and saline lacustrine source have abundant C_{23} tricyclic terpanes (C_{23}TCT), whereas the terrestrial oils or source rock extracts are dominated by C_{19} tricyclic terpanes (C_{19} TCT) and C_{20} tricyclic terpanes (C_{20} TCT) (Peters et al. 1993). The saturate biomarker ratio such as C_{31} 22S/(22S + 22R) homohopane ratio attains equilibrium in range of 0.57 to 0.62 and indicates early oil generation phase (Seifert and Moldowan 1980). Similarly, with an increase in thermal maturity, the C_{29} sterane isomerization ratio, i.e., C_{29} 20S/(20S + 20R), rises from 0 to ~0.5, attains equilibrium in the range of 0.52–0.55 and indicates oil generation (Seifert and Moldowan 1986). The C_{29} $\beta\beta/\alpha\alpha + \beta\beta$ sterane ratio rises from 0 to ~0.7 as thermal maturity increases and attains equilibrium in the range of 0.67–0.71 (Peters et al. 2005). Similarly, the most commonly applied aromatic maturity parameters are based on molecular ratios of substituted naphthalenes (N), phenanthrenes (P) and dibenzothiophenes (DBT). The methyl-phenanthrene (MP) isomers abundance changes with variation in source thermal maturity and has therefore been correlated with vitrinite reflectance (R_o) (Radke et al. 1982). A similar trend has been observed by others (Radke 1988; Chakhmakhchev and Suzuki 1995) for methyl-dibenzothiophene (MDBT) with increasing maturity.

The studies related to stratigraphy, sedimentology and structural architecture of the sedimentary succession have been reported with little source rocks' interpretation (based only on the source rock screening analysis such as TOC measurements, Rock–Eval pyrolysis and organic petrography) of hydrocarbons within the Kohat sub-basin (Meissner et al. 1974; Wandrey et al. 2004; Shah 2009; Rehman et al. 2009; Gardezi et al. 2017). The current research work is mainly focused on the source rock's screening as well as biomarkers analysis to provide information about the quality and type of organic matter and its thermal maturity as well as environment of deposition of the Early Cretaceous Chichali Formation within the Kohat sub-basin.

Tectonic and geology of the area

The collision of Indian and Eurasian plates during Cretaceous time has produced compressive tectonic structures on the north and northwest portion of the Indian tectonic plate (Abbasi and McElroy 1991). Since the Cretaceous time, the continuous pushing of the Indian plate created Himalayan orogenic belt with related chain of foreland basins (Wandrey et al. 2004). The Kohat sub-basin is an intricate compressional basin of Himalayan Foreland Belt (Fig. 1). The Main Boundary Thrust (MBT) and Surghar Range Thrust mark the northern and southern boundaries of this basin, respectively. The eastern and western boundaries of this basin are marked by Indus river and Kurram Fault, respectively. The Mesozoic sediments are thrust over Eocene–Miocene along MBT (Yeats and Hussain 1987). Along the Surghar Range Thrust, the Mesozoic sediments are thrust southward over the alluvium of the Punjab Foreland. The Mesozoic sediments are juxtaposing with Eocene–Miocene sediments along Kurram Fault (Ahmad 2003). Surghar Range which represents the leading deformational front of the Kohat sub-basin is separated from the Salt Range Thrust (SRT) by Kalabagh Strike-Slip Fault. The exposed sedimentary rocks (shales,

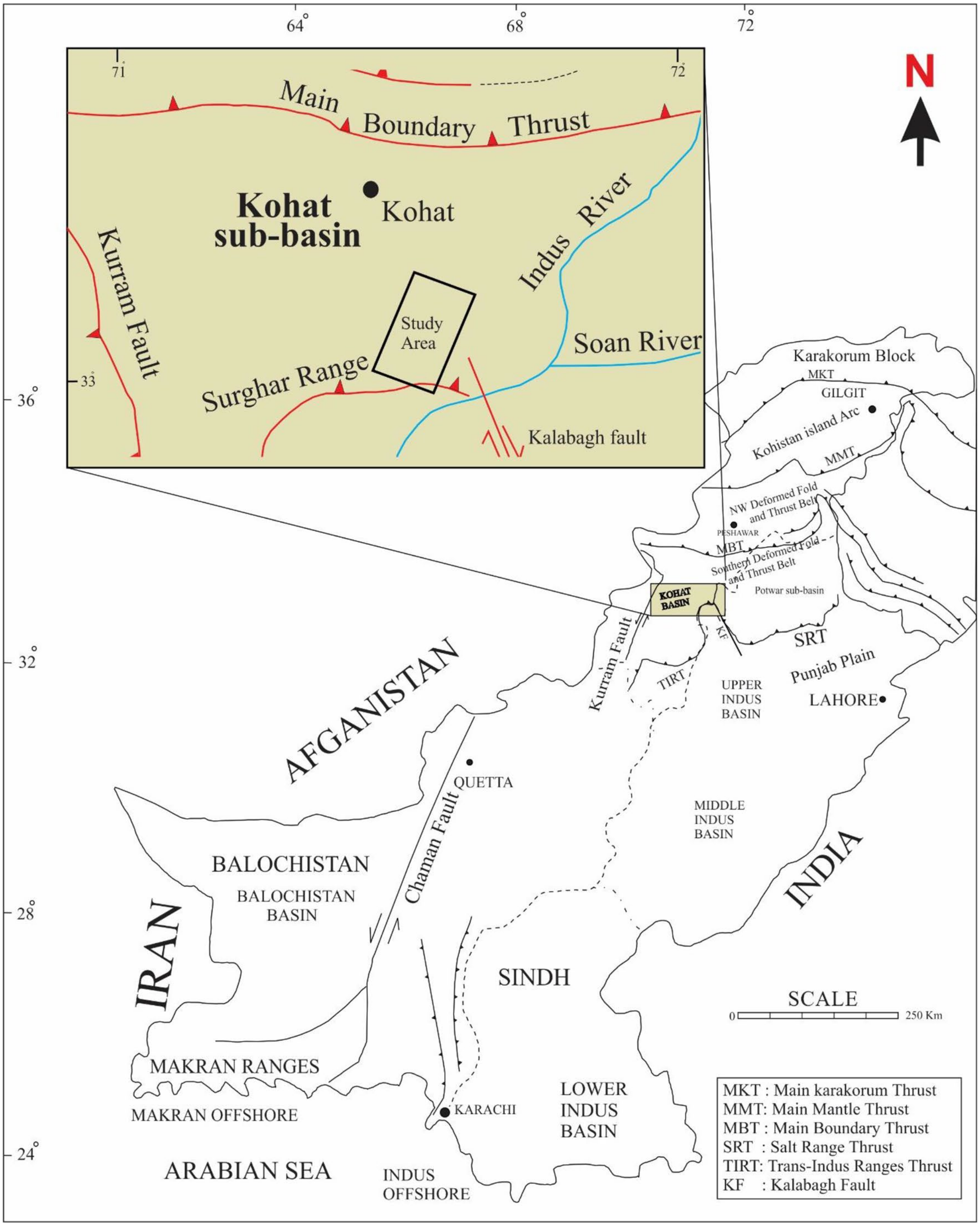


Fig. 1 Tectonic map of Pakistan showing the major tectonic features and the location of the study area (after Ahsan and Chaudhry 2008)

Table 1 The generalized exposed stratigraphy of the Kohat sub-basin (after Kadri 1995)

Era	Period	Epoch	Group	Formation	Lithology
Cenozoic	Quarternary	Pleistocene		Soan Fm	
Cenozoic	Tertiary	Pliocene	Siwalik Group	Dhok Pathan Fm	
Cenozoic	Tertiary	Miocene	Siwalik Group	Nagri Fm	
Cenozoic	Tertiary	Miocene	Siwalik Group	Chinji Fm	
Cenozoic	Tertiary	Miocene	Rawalpindi Group	Kamlial Fm	
Cenozoic	Tertiary	Miocene	Rawalpindi Group	Murree Fm	
Cenozoic	Tertiary	Eocene	Cherat Group	Kohat Fm	
Cenozoic	Tertiary	Eocene	Cherat Group	Mami Khel Clay	
Cenozoic	Tertiary	Eocene	Cherat Group	Jatta Gypsum	
Cenozoic	Tertiary	Eocene		Shekhan Fm	
Cenozoic	Tertiary	Eocene		Bahadur Khel Salt	
Cenozoic	Tertiary	Eocene		Panoba Shale	
Cenozoic	Tertiary	Paleocene	Makarwal Group	Patala Fm	
Cenozoic	Tertiary	Paleocene	Makarwal Group	Lockhart Limestone	
Cenozoic	Tertiary	Paleocene	Makarwal Group	Hangu Fm	
Mesozoic	Cretaceous			Kawagarh Fm	
Mesozoic	Cretaceous			Lumshiwal Fm	
Mesozoic	Cretaceous			Chichali Fm	
Mesozoic	Jurassic			Samana suk Fm	
Mesozoic	Jurassic			Datta Fm	

INDEX

- Sandstone
- Shale
- Salt
- Clay
- Gypsum
- Limestone
- Conglomerate
- Unconformity

sandstones, limestones, gypsum, evaporates) of the Kohat sub-basin are ranging in age from Jurassic to Quaternary (Table 1).

Methods and materials

A total of 17 samples, seven from Chichali Nala section (Surghar Range) and 10 drill cuttings (from Mela-05 well of Mela oil field) of the Chichali Formation, were collected. The techniques performed included TOC, RE, organic petrography, column chromatography and GC–MS. The TOC was carried out for all the samples, and RE was performed for the drill cuttings. The biomarker analysis was applied on six samples, three outcrop samples from the Chichali Nala section and three drill cuttings from Mela-05 well. Four outcrop samples were also studied for macerals by the microscope.

The organic richness was measured by Carbon–Sulfur analyzer CS-580A (Helios). The Rock–Eval analysis was performed on Rock–Eval 6 instrument. Different Rock–Eval parameters and ratios such as S_1(free hydrocarbon at 300 °C), S_2 (hydrocarbons produced due to pyrolysis of kerogen), S_3 (CO, CO_2 produced by the pyrolysis of the samples), oxygen index (OI: S_3/TOC × 100), hydrogen index (HI: S_2/TOC × 100), production index (PI: $S_1/S_1 + S_2$) and the T_{max} were used to determine the source rock potential of the Chichali Formation. The vitrinite reflectance measurement and macerals assessment was performed by Carl Zeiss Axio microscope. The Soxhlet apparatus was used to extract the bitumen through dichloromethane and methanol. The two components of bitumen, i.e., maltenes and asphaltenes, were separated from using n-pentane. Column chromatographic technique was used for the separation of saturates, aromatics and polar (resin) compounds present in maltene. The gas chromatograph mass spectrometer (GC–MS) was used for the biomarkers study in saturate and aromatic fractions.

Table 2 The TOC results of Mela-05 drill cuttings of the Chichali Formation

S. no.	Sample ID	Depth (m)	Sample type	TOC (wt%)
1	CF-1A	4760	Shale	1.08
2	CF-2A	4766	Shale	1.2
3	CF-3A	4772	Shale	1.40
4	CF-4A	4776	Shale	0.90
5	CF-5A	4782	Shale	1.04
6	CF-6A	4784	Shale	1.02
7	CF-7A	4786	Shale	1.06
8	CF-8A	4788	Shale	1.04
9	CF-9A	4790	Shale	1.08
10	CF-10A	4802	Shale	1.18

Table 3 The TOC results of outcrop samples of the Chichali Formation

S. no.	Sample ID	Sample type	TOC (wt%)
1	CF-1B	Shale	0.57
2	CF-2B	Shale	0.43
3	CF-3B	Shale	0.29
4	CF-4B	Shale	0.55
5	CF-5B	Shale	0.45
6	CF-6B	Shale	0.53
7	CF-7B	Shale	0.59

Results and discussion

Source rock screening analysis

Total organic carbon (TOC)

The TOC results of the drill cuttings and outcrop samples of Chichali Formation are presented in Table 2 and 3, respectively. The TOC in drill cuttings from the Mela-05 well ranges from 0.9 to 1.40 wt% (Fig. 2) representing fair to good hydrocarbon potential (Peters and Cassa 1994). The outcrop samples of the Chichali Formation show poor to fair potential of petroleum as the values of TOC are in the range of 0.29–0.59 wt % (Table 3). The low values of TOC in the outcrop samples are probably due to the effect of weathering of the organic constituents.

Hydrocarbon potential and organic matter type

The organic matter type in the source rock determines the types of hydrocarbon products in that source rock (Tissot and Welte 1984; Hunt 1979). The cross-plots of HI versus OI (Espitalié et al. 1977), HI versus T_{max} (Espitalié et al. 1986), TOC versus S_2 (Langford and Blanc-Valleron 1990) and the organic petrographic analysis were used for the assessment of the organic matter's type within the Chichali Formation.

The results acquired from the Rock–Eval of the Chichali Formation's drill cuttings are listed in Table 4. According to Van Krevelen (1984), the Chichali Formation has mainly type III kerogen at present time (Fig. 3a). The T_{max} versus hydrogen index cross-plot designates that all of the samples are present at the boundary of the oil–gas-prone zone and display type III kerogen at current time (Fig. 4a). The TOC versus S_2 cross-plot shows that almost all the samples of the Chichali Formation fall in gas-prone zone with type III kerogen at present time (Fig. 5).

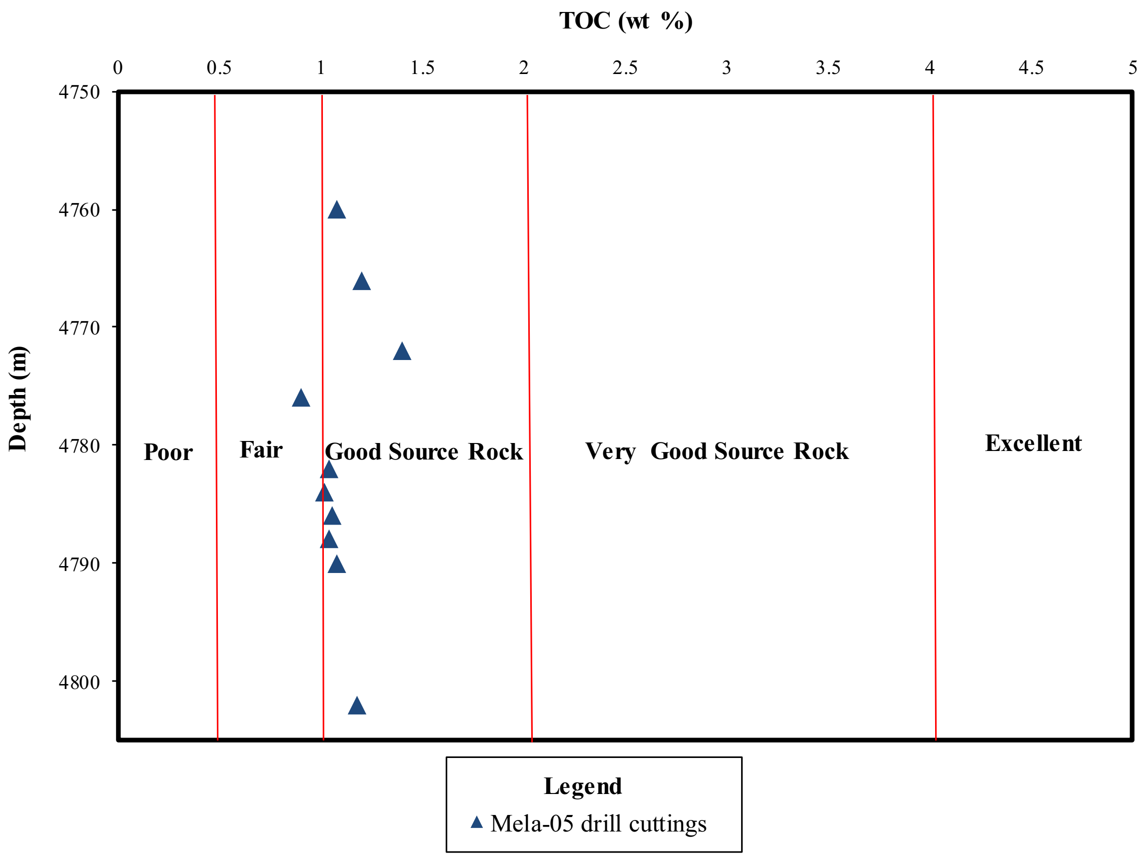


Fig. 2 The cross-plot of depth vs TOC, showing the distribution of TOC (wt%) in the Mela-05 drill cuttings of the Chichali Formation

Table 4 Rock–Eval pyrolysis results of the Chichali Formation from Mela-05

S. no.	Sample ID	Sample depth	S_1	S_2	S_3	OI	HI	HI_o	T_{max}	PI
1	CF-1A	4760	0.35	0.81	0.50	46	75	300	451	0.30
2	CF-2A	4766	0.76	1.48	0.87	73	123	436	438	0.34
3	CF-3A	4772	0.8	1.28	0.81	58	91	349	449	0.39
4	CF-4A	4776	0.55	0.86	0.54	60	96	364	452	0.39
5	CF-5A	4782	1.11	0.95	0.65	63	91	349	451	0.54
6	CF-6A	4784	0.99	0.98	0.78	77	96	364	448	0.50
7	CF-7A	4786	0.92	1	0.65	61	94	358	451	0.48
8	CF-8A	4788	0.84	0.95	0.62	60	91	349	452	0.46
9	CF-9A	4790	0.82	0.99	0.68	63	92	352	453	0.45
10	CF-10A	4802	1.16	1.18	0.81	69	100	375	447	0.51

However, the cross-plots of original hydrogen index (HI_o) (calculated, using ZetaWare software; https://www.zetaware.com/utilities/srp/index.html) against OI (Fig. 3b) and T_{max} (Fig. 4b) indicate type II kerogen formation during the deposition of Chichali Formation. It is also evident from compositional analysis of macerals where major macerals are liptinite derived from marine organic source (Table 5).

Thermal maturity of the organic matter

The organic matter thermal maturation level was assessed through T_{max}, PI and vitrinite reflectance. All the drill cuttings from the Mela-05 well show peak to late thermal maturity stage based on the T_{max} and production index values (Fig. 6, Table 4).

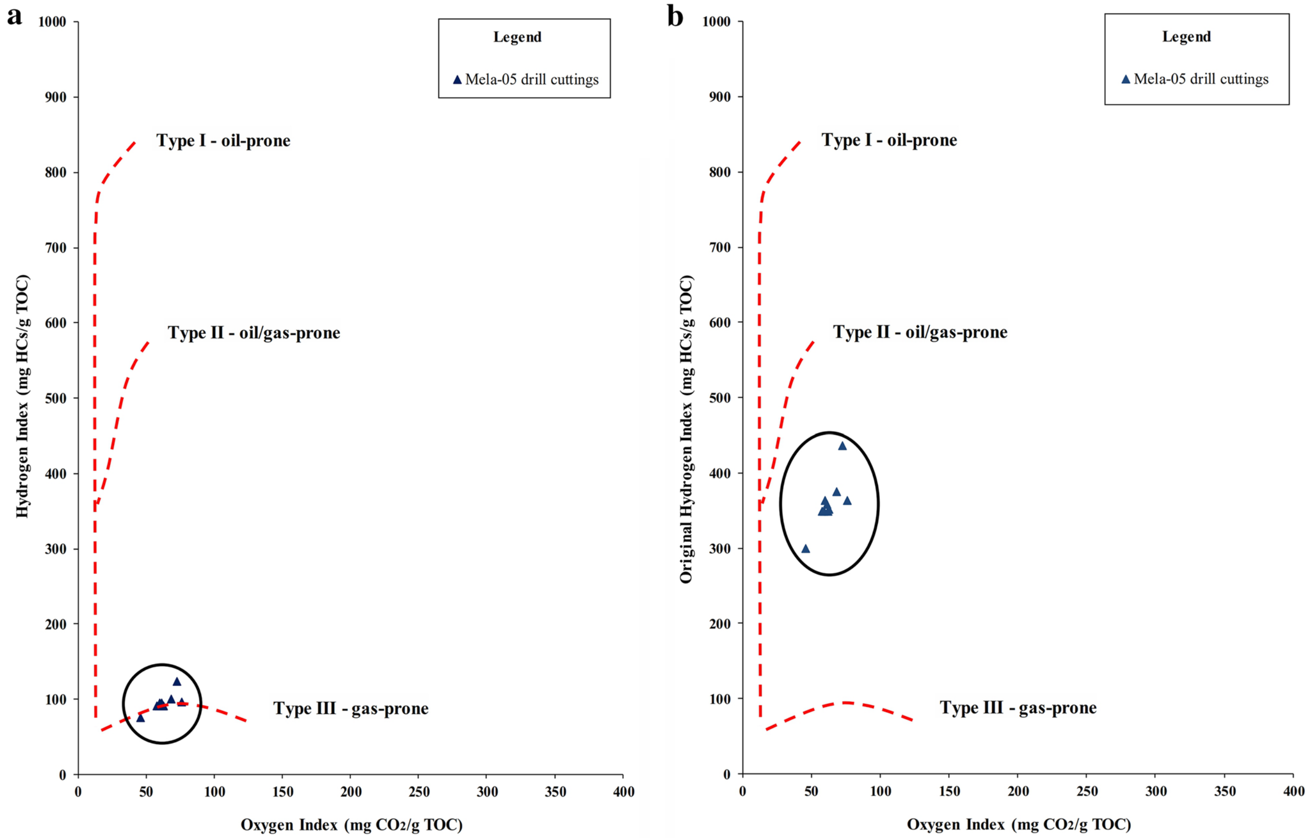


Fig. 3 **a** The HI versus OI cross-plot (modified after Van Krevelen Diagram), showing the present kerogen type in the Mela-05 drill cuttings of the Chichali Formation (after Espitalié et al. 1977). **b** The HI_o versus OI cross-plot (modified after Van Krevelen Diagram), showing the original kerogen type in the Mela-05 drill cuttings of the Chichali Formation (after Espitalié et al. 1977)

The Chichali Formation's outcrop samples have vitrinite reflectance (Ro) values in the range of 0.76–0.84 (Table 5), show thermal maturity in the oil window phase and have not reached peak oil production phase (> 0.9% Ro).

Biomarkers: Environmental conditions and organic matter input

n-alkanes and isoprenoids distribution

The terrigenous-to-aquatic ratio (TAR) determines the relative amount of the terrestrial versus marine organic matter (Bourbonniere and Meyers 1996). The Chichali Formation's drill cuttings obtained from Mela-05 well have TAR values in the range of 0.08—0.18 signifying more algal organic matter input as compared to vascular plants (Fig. 7, Table 6). The same comparable tendency is shown by the n-alkanes chromatograms of the Chichali Formation's outcrop samples where short-chain n-alkanes have more concentration compared to long-chain n-alkanes (Fig. 7).

Pristane and phytane are the acyclic isoprenoid compounds present in the source rock extracts and crude oils. The most abundant source of pristane and phytane is the phototrophic organisms and purple sulfur bacteria (Brooks et al. 1969; Powell and McKirdy 1973). In oxic environment, the decarboxylation within the side chain of phytyl yields pristane (Pr), while in the anoxic environment dehydration and reduction within the phytyl side chain yield phytane (Ph) (Didyk et al. 1978; Powell and McKirdy 1973). The Chichali Formation's samples (drill cutting as well as the outcrop samples) have Pr/Ph ratios less than 1 (Pr/Ph < 1) and indicate anoxic environment of deposition (Table 6).

A cross-plot of phytane/nC_{18} versus pristane/nC_{17} shows that Chichali Formation samples (outcrop samples and drill cuttings) have more marine organic input (Fig. 8).

Terpanes and steranes distribution

The low ratios of the C_{19}/C_{23} TCT and C_{20}/C_{23} TCT in the studied Chichali Formation's samples indicate marine

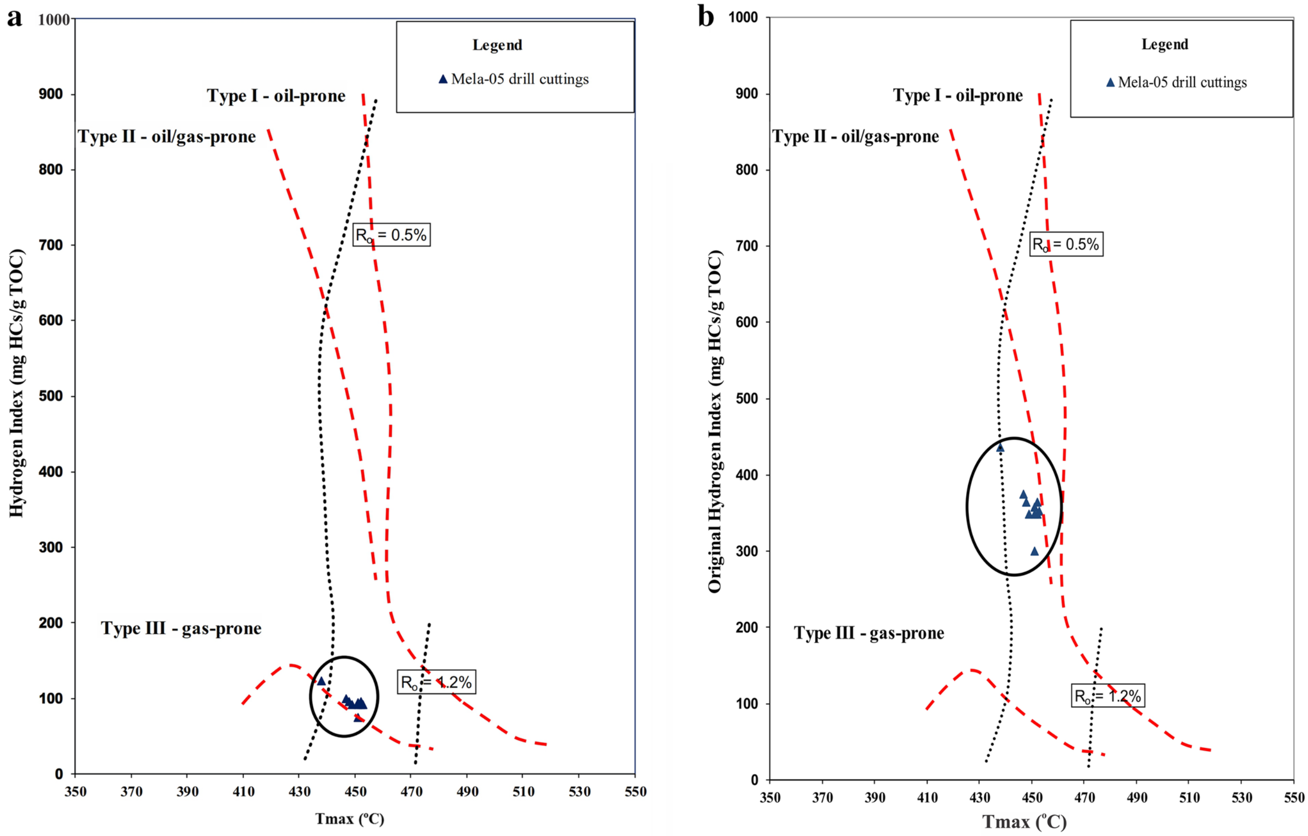


Fig. 4 **a** The HI versus T_{max} cross-plot, showing present kerogen type in Mel-05 drill cuttings of the Chichali Formation (after Espitalié et al. 1986). **b** The HI_o versus T_{max} cross-plot, showing original kerogen type in Mel-05 drill cuttings of the Chichali Formation (after Espitalié et al., 1986)

organic source (Fig. 9, Table 7) (Hao et al. 2010). Similarly, the low values of C_{26}/C_{25} TCT ratios in the Chichali Formation's outcrop samples indicate marine depositional environment (Fig. 9, Table 7). The lack of gammacerane in the Chichali Formation's outcrop samples depicts non-hypersaline environment at the time of organic matter deposition and is supported with low C_{26}/C_{25} ratios. The Chichali Formation's outcrop samples have high tricyclic terpanes-to-hopanes (TCT/H) ratios, indicating higher algal input (Table 7, Fig. 9). Similar trend is shown by the ratios of C_{23} tricyclic terpane to hopane (C_{23}TCT/H; Table 7). The absence of terrestrial biomarker (oleanane) also justifies marine environment of deposition for Chichali Formation. However, no terpanes were identified in drill cuttings from Chichali Formation of Mela-05 well (Fig. 9). The lack of terpanes and low concentration of long-chain n-alkanes suggest high thermal maturity of the drill cuttings which is in conjunction with thermal maturity determined by the T_{max} and production index values (Fig. 6).

The abundance of different steranes can also point toward marine or terrestrial nature of the organic matter (Peters et al. 2005). The higher values of C_{27} steranes compared to C_{29} steranes in the Chichali Formation's outcrop samples indicate marine algal origin for the organic matter (Figs. 10, 11, Table 7). The steranes were not identified in the extracts of Mela-05 drill cuttings of the Chichali Formation, probably due to higher thermal cracking of the organic matter (Fig. 10).

Aromatic compounds distribution

The source rock paleo-environment and lithology can be determined through the cross-plot of dibenzothiophene-to-phenantrene versus Pr-to-Ph ratios (Hughes et al. 1995).

The Chichali Formation's samples (outcrop samples and drill cuttings) fall in Zone 2, depicting anoxic sulfate poor depositional environment with mixed shale and carbonate lithology (Fig. 12).

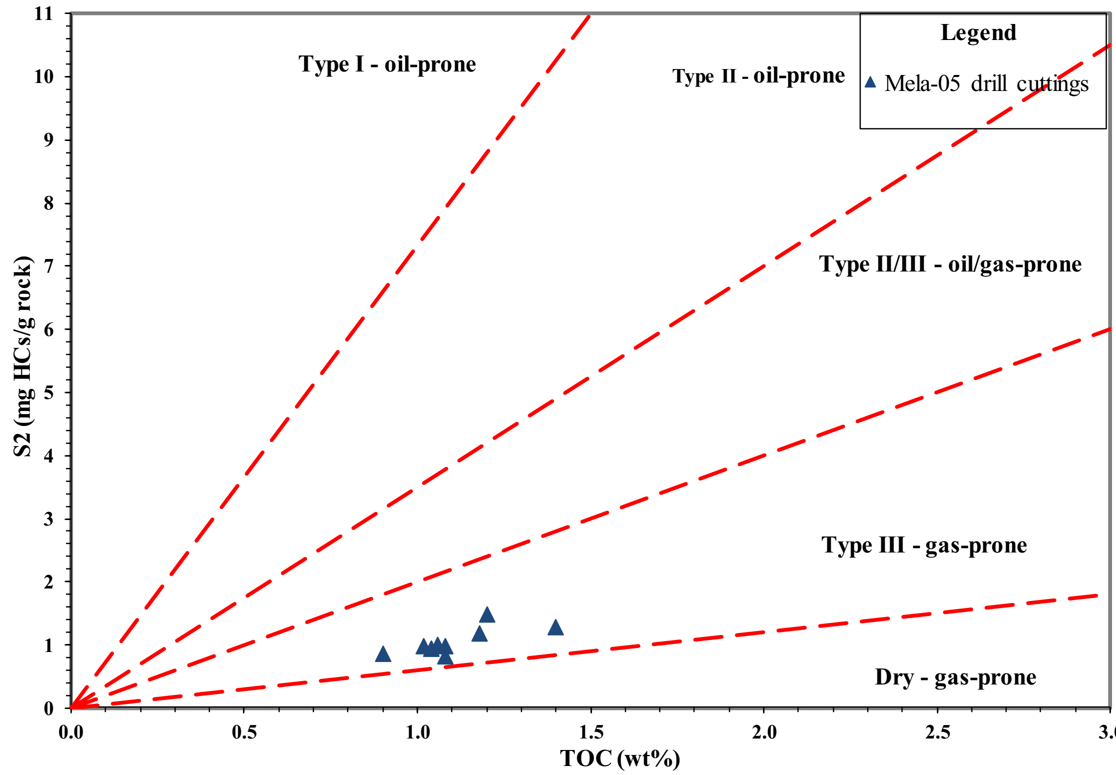


Fig. 5 The S_2 versus TOC cross-plot, showing the current kerogen type in the Mela-05 drill cuttings of the Chichali Formation (after Langford and Blanc-Valleron 1990)

Biomarkers: thermal maturity

To evaluate the organic matter thermal maturity level, different saturate and aromatic compound's ratios of Chichali Formation's extracts were used in this research work. The results of column chromatography reveal that saturates (SAT)-to-aromatics (ARO) ratios are higher (> 1.49) for the Chichali Formation, indicating mature organic matter (Table 6) (Tissot and Welte 1984). Similarly, the carbon preference index (CPI) values or odd-to-even predominance (OEP) values are nearly equal to 1; homohopane ratios [C_{31} 22S/(22S + 22R)] ranging from 0.47 to 0.58 and C_{29} ββ/αα + ββ sterane isomer ratios ranging from 0.56 to 0.65 for the Chichali Formation confirm thermally mature nature of the organic matter (Tables 6, 8).

The isomerization ratio of C_{29} steranes [C_{29} 20S/(20S + 20R)] in the Chichali Formation's outcrop samples is in the range of 0.46 to 0.51, indicating thermally mature organic matter and thus pointing to the oil generation phase (Table 8).

The calculated vitrinite reflectance (VR_c) derived from methyl-phenanthrene index (MPI-1) has values in the range of 0.77–0.85 for outcrop samples and 0.90–0.94 for Mela-05 drill cuttings. The Chichali Formation's outcrop samples indicate comparatively low thermal maturity, based on VR_c, whereas the Chichali Formation's drilled cuttings have VR_c values greater than 0.9 and show postmature stage for the generation of hydrocarbons (Figs. 13, 14, Table 8).

Similarly, the calculated vitrinite reflectance (VR_m) values based on methyl-dibenzothiophene ratio (MDR) also indicate low thermal maturity of the outcrop samples compared to drill cuttings (Figs. 13, 14, Table 8).

Table 5 Organic petrographic results of samples from Chichali Formation

Sample ID	Observations	Vitrinite	Liptinite	Quantities of Liptinite	% Ro
CF-1B	10	O	X	4	0.76
CF-4B	9	O	X	4	0.78
CF-6B	24	O	X	4	0.84
CF-7B	13	O	X	3	0.80

The relative abundance is described by (O = 5- < 20%, X = > 50%), organic matter; 3 = common, 4 = abundant

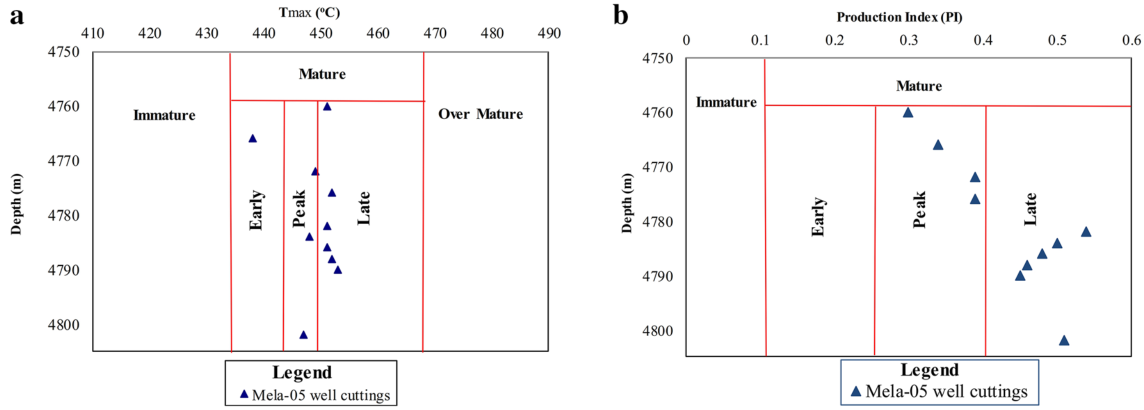


Fig. 6 The organic matter's thermal maturity within drill cuttings of Chichali Formation using **a** depth versus T_{max} and **b** depth versus PI cross-plots (after Peters and Cassa 1994)

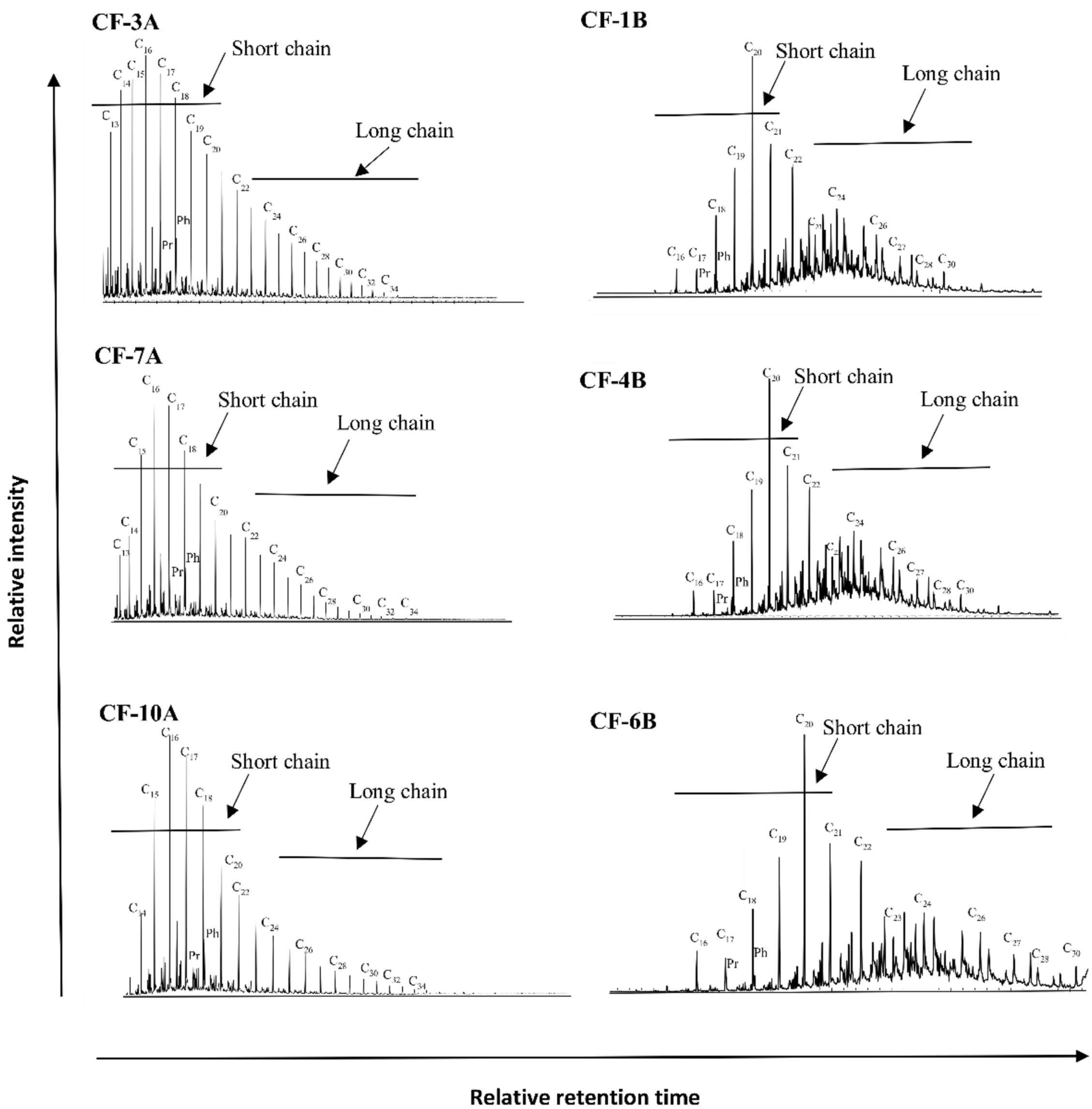


Fig. 7 m/z 57 chromatograms of Mela-05 drill cuttings (left) and outcrop samples (right) showing distribution of n-alkanes and isoprenoids

Table 6 The molecular composition as well as geochemical parameters based on n-alkanes and isoprenoid of the Chichali Formation

Sample ID	Type	Saturate (%)	Aromatic (%)	Resin (%)	SAT/ARO	TAR	CPI	OEP-1	Pr/Ph	Pr/nC17	Ph/nC18
CF-3A	Cuttings	45.30	30.21	24.49	1.49	0.18	1.1	0.98	0.54	0.25	0.37
CF-7A	Cuttings	46.73	23.09	30.18	2.02	0.10	1.1	1.1	0.39	0.35	0.37
CF-10A	Cuttings	53	20.63	26.35	2.57	0.08	1.0	1	0.34	0.28	0.43
CF-1B	Outcrop	51.10	30.75	18.15	1.66	nd	nd	0.98	0.69	0.52	0.76
CF-4B	Outcrop	55.62	24.07	20.21	2.31	nd	nd	0.96	0.64	0.45	0.78
CF-6B	Outcrop	56.79	24	19.20	2.36	nd	nd	0.99	0.63	0.56	0.70

TAR = $(nC_{27}+nC_{29}+nC_{31})/(nC_{15}+nC_{17}+nC_{19})$, *CPI* = ½ $[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33}/C_{24}+C_{26}+C_{28}+C_{30}+C_{32})+(C_{25}+C_{27}+C_{29}+C_{31}+C_{33}/C_{26}+C_{28}+C_{30}+C_{32}+C_{34})]$, *OEP-1* = $(C_{21}+6C_{23}+C_{25})/(4C_{22}+4C_{24})$, nd = not determined

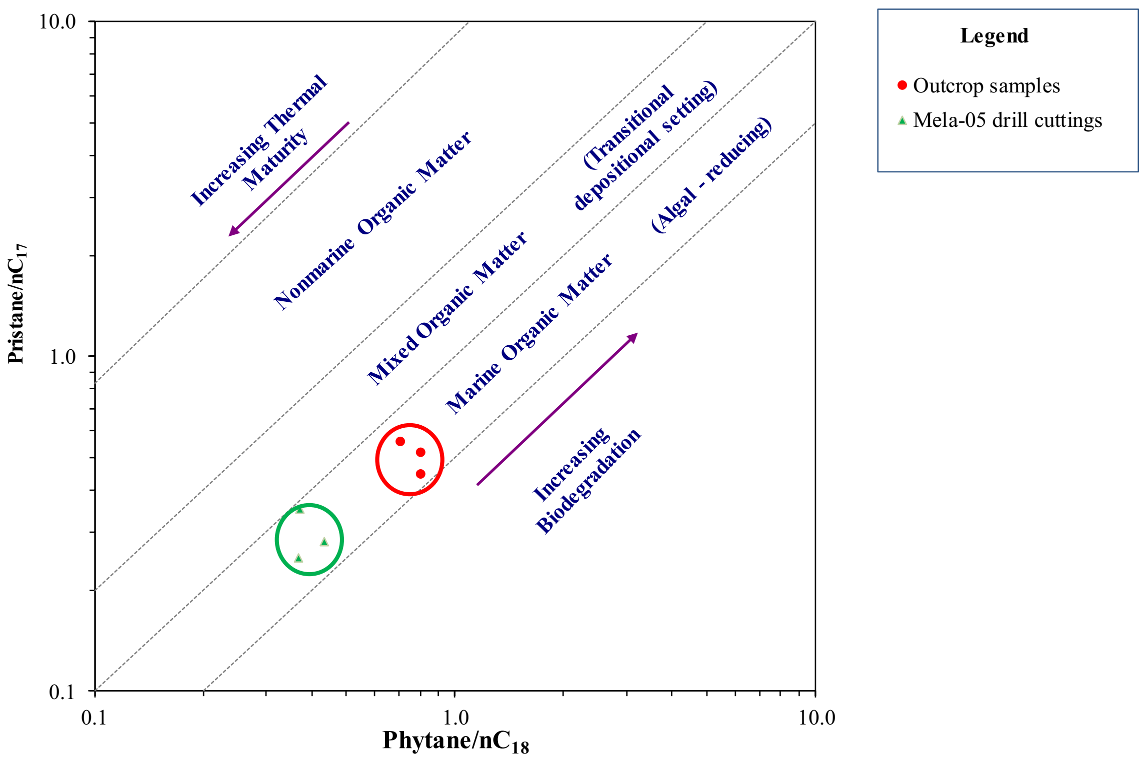


Fig. 8 The cross-plot of Ph/nC_{18} versus Pr/nC_{17} indicates the environment of deposition, source input and thermal maturation level of the samples (after Shanmugam 1985)

Conclusions

The Rock–Eval data indicate the type III kerogen at present time and has the potential to generate gas. The vitrinite reflectance values, C_{31} 22S/(22S + 22R) homohopane ratios, C_{29} sterane isomerization ratios, MPI-based calculated vitrinite reflectance values (VR_c) and DMR-based calculated vitrinite reflectance values (VR_m) indicate oil window phase of the outcrop samples of the Chichali Formation. The production index values, T_{max} values, MPI-based calculated vitrinite reflectance values (VR_c) and DMR-based calculated vitrinite reflectance values (VR_m) indicate gas window phase of the drill cuttings of Chichali Formation. The high thermal maturity of the drill cuttings compared to outcrop samples is also evident from the cross-plot of isoprenoids vs n-alkanes and absence of saturate biomarkers (terpanes, steranes) in the drill cuttings. All these geochemical parameters of thermal maturity for outcrop samples indicate that the Chichali Formation was already in oil window phase during the uplift of the Surghar Range, while the Chichali Formation (drill cuttings) in Kohat sub-basin had been overburdened later on and, therefore, entered into post-oil window phase and cracking of hydrocarbons that probably leads to condensate and gas formation in the Kohat sub-basin. The cross-plots of

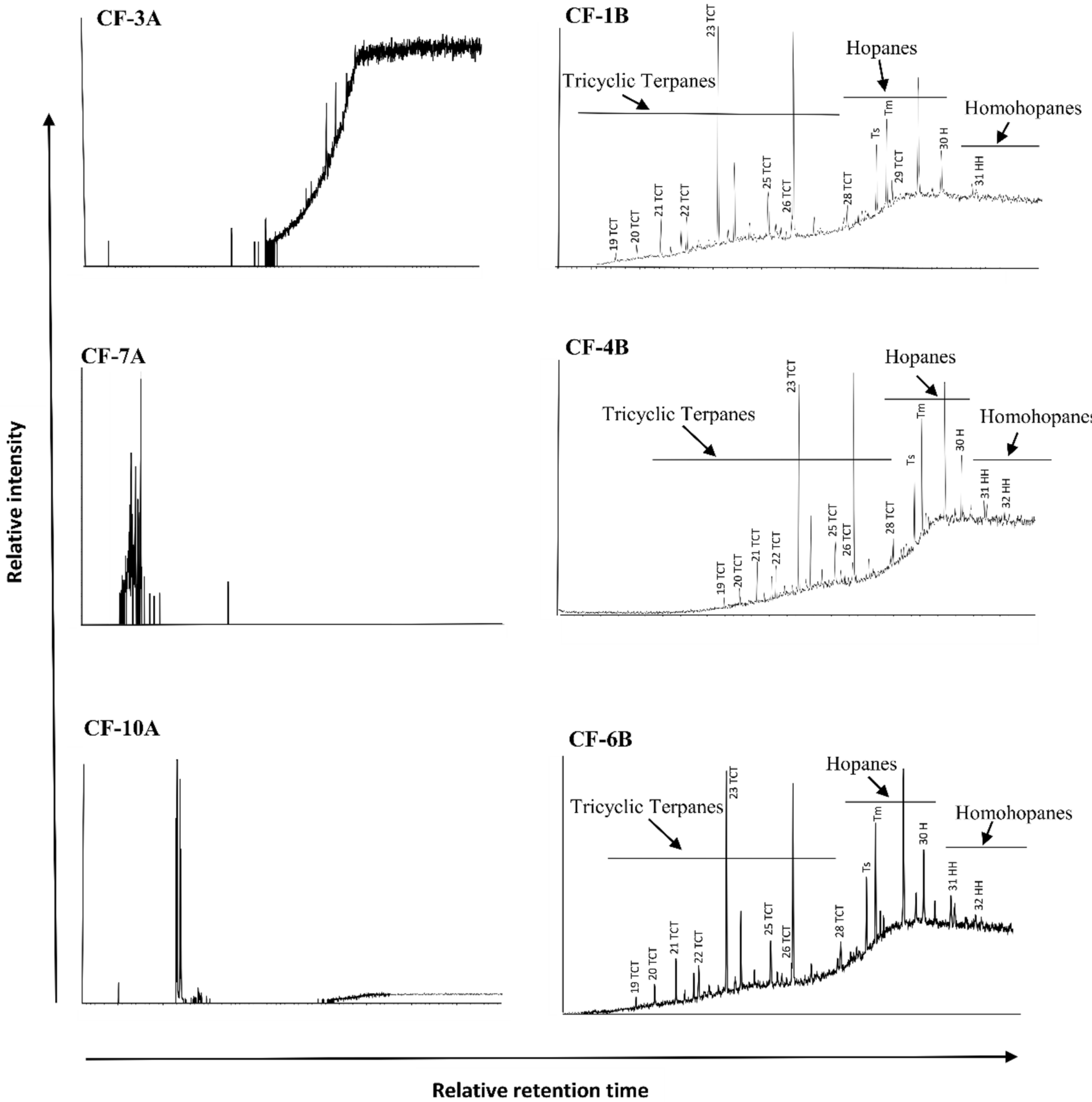


Fig. 9 m/z 191 chromatograms of Mela-05 drill cuttings (left) and outcrop samples (right) showing distribution of TCT and hopanes

Table 7 Terpane and sterane biomarker parameters used in this study

Sample ID	Terpanes					Steranes (%)			C_{29}/C_{27} Sterane
	C_{19}/C_{23} TCT	C_{20}/C_{23} CT	C_{26}/C_{25} TCT	TCT/H	C_{23}TCT/H	C_{27}	C_{28}	C_{29}	
CF-1B	0.02	0.07	0.62	10.51	4.63	55	25	20	0.36
CF-4B	0.03	0.09	0.29	6.99	2.51	54	25	20	0.37
CF-6B	0.03	0.08	0.16	6.40	2.66	51	30	19	0.37

OI versus HI_o and HI_o versus T_{max} indicate that the original kerogen was type II. The low percentage of vitrinite macerals (< 20%) and high quantity of liptinite macerals indicate a marine organic input for the Chichali Formation. The extracts of Chichali Formation have algal/marine organic matter (type II kerogen) that was deposited in anoxic environment. Marine input as well as anoxic environment is also evident from the presence of high abundance of short-chain

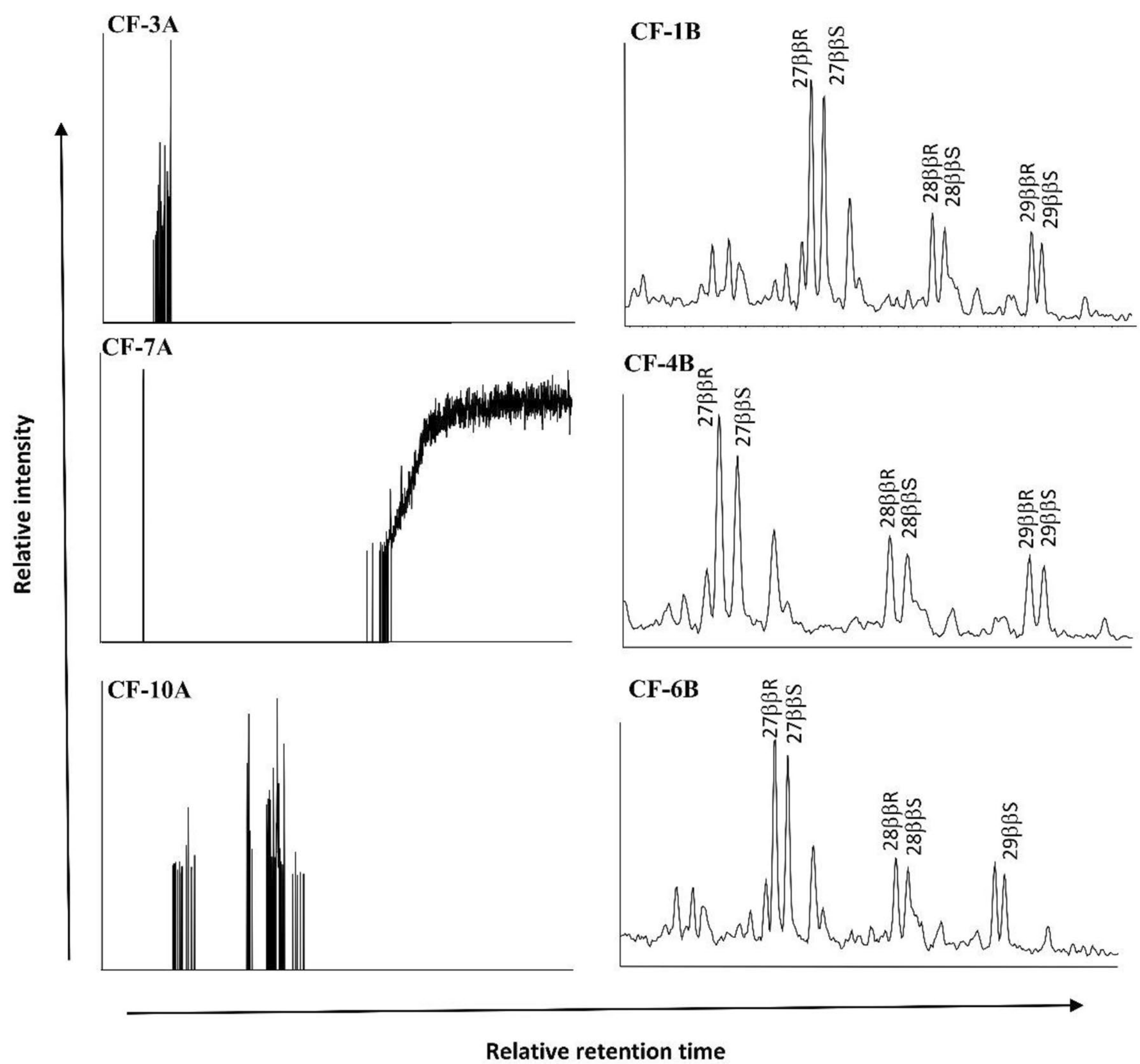
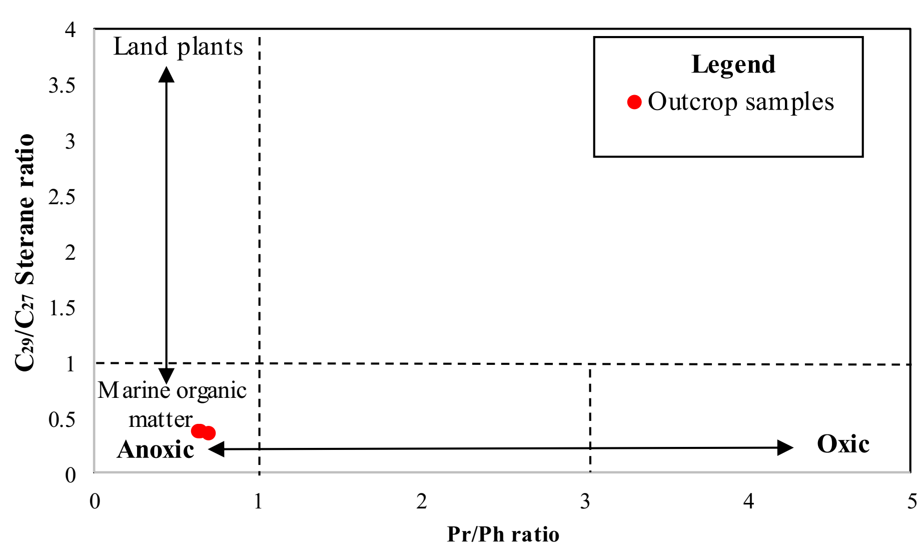


Fig. 10 m/z 218 chromatograms of Mela-05 drill cuttings (left) and outcrop samples (right) showing distribution of steranes

Fig. 11 The Pr/Ph ratio versus C_{29}/C_{27} steranes ratio cross-plot provides information about the environment of deposition and type of organic input (after Peters et al. 2005)



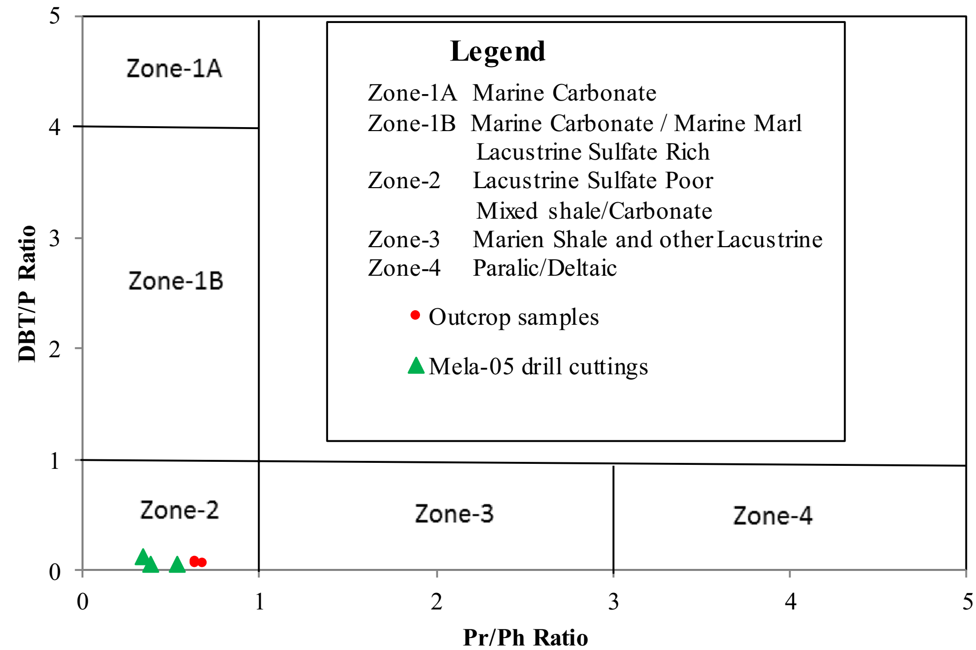


Fig. 12 The Pr/Ph versus DBT/P cross-plot of the drill cuttings and outcrop samples of the Chichali Formation (after Hughes et al. 1995)

Table 8 Thermal maturity and environment of deposition parameters based on saturate and aromatic hydrocarbons in the Chichali Formation

Sample ID	S/(S+R) C_{31}Homohopane	C_{29} S/(S+R) sterane	C_{29} ββ/αα+ββ sterane	MPI-1	VRc(%)	MDR	VRm(%)	DBT/P
CF-1B	0.47	0.46	0.56	0.62	0.77	2.23	0.67	0.05
CF-4B	0.52	0.51	0.65	0.79	0.87	2.15	0.67	0.05
CF-6B	0.58	0.47	0.65	0.74	0.85	1.73	0.64	0.07
CF-3A	Absent	Absent	Absent	0.83	0.90	4.97	0.87	0.06
CF-7A	Absent	Absent	Absent	0.86	0.92	4.59	0.85	0.05
CF-10A	Absent	Absent	Absent	0.90	0.94	5.52	0.91	0.12

MPI-1 = {1.5 × [3-MP + 2-MP]/[P + 1-MP + 9-MP]}, *VRc* = (0.6 × MPI-1 + 0.4), MDR = 4-MDBT/1-MDBT, *VRm* = 0.073 × MDR + 0.51

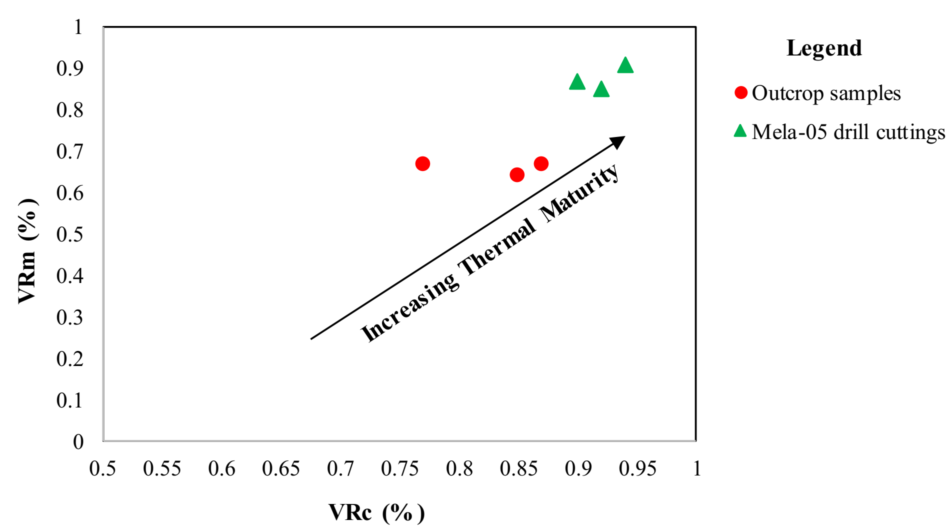


Fig. 13 The VRc% versus VRm% cross-plot, showing the maturity difference in the drill cuttings and outcrop samples of the Chichali Formation

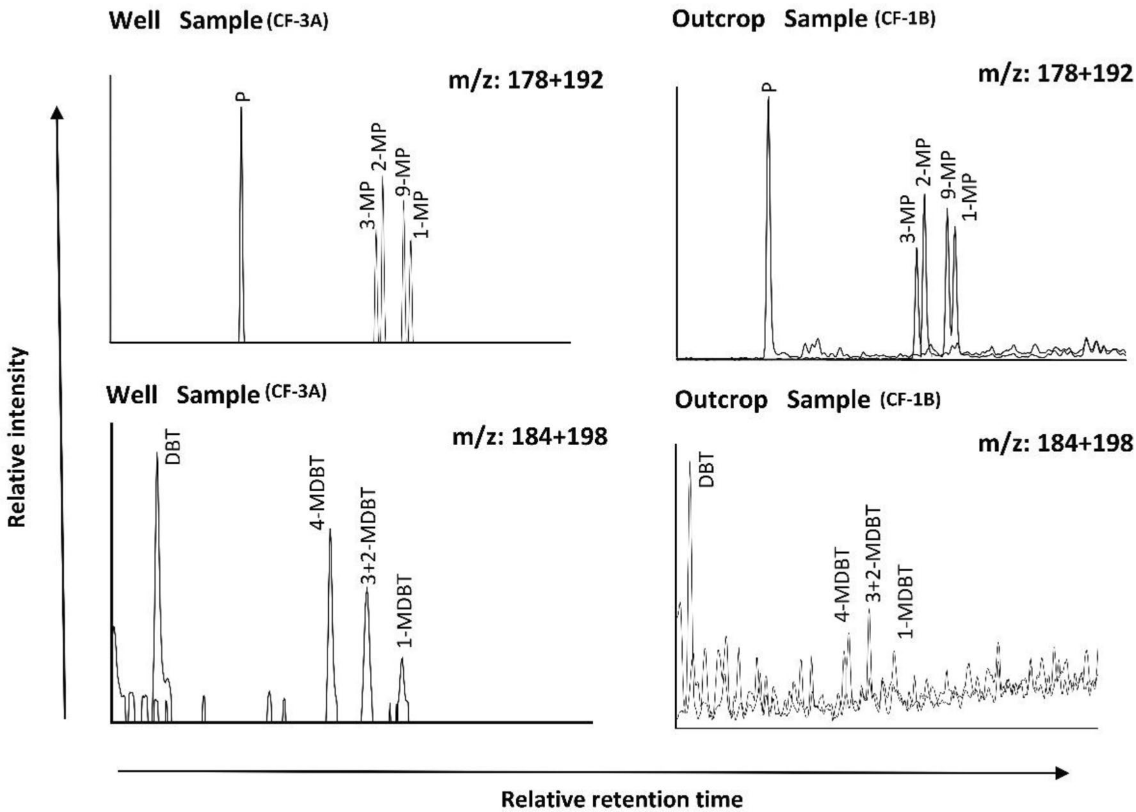


Fig. 14 Aromatic hydrocarbon composition; top 2 are the representative chromatograms that show distribution of P and MP, and bottom 2 are the representative chromatograms that show relative abundance of DBT and MDBT

n-alkanes, low values of Pr/Ph (< 1), low values of different tricyclic terpanes (i.e., C_{19}/C_{23}, C_{20}/C_{23}, C_{26}/C_{25}), high TCT/H ratios, high C_{27} steranes as compared to C_{29} steranes and absence of terrestrial biomarker (oleanane). The integrated geochemical and petrographical studies reveal that the shales of the Chichali Formation were deposited in anoxic environment with type II kerogen having poor to good hydrocarbon potential.

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