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Biomarker Characterization of Crude Oils from Basement Reservoirs, East of Bombay High, Western Offshore - India.

Abstract

A suite of 6 crude oil samples of basement reservoirs from different wells, east of Bombay High - Mumbai Offshore Basin were analysed using gas chromatography-mass spectrometry. Biomarker compositions and parameters were used to understand their origin, depositional environment, maturity and to correlate oils with each other. All the studied oil samples show unimodal n-alkanes distribution and are characterized by carbon number ranging from n-C₁₁ to n-C₃₆ with a maximum abundance between n-C₂₀ and n-C₂₈. The investigated oils have carbon preference index (CPI) and odd-to-even predominance (OEP) values of ~1. The analysed oil samples have pristane/phytane (Pr/Ph) ratio of 1.60 to 3.40 suggesting high thermal maturity and suboxic conditions during deposition of source sediments. The cross plot of Pr/n-C₁₇ versus Ph/n-C₁₈ indicate Type II/III kerogen. Tricyclic terpanes are present in low abundance suggesting lesser input by algae and/or bacteria. A dominance of C₂₉ steranes suggests a strong terrestrial contribution to the organic matter. The C₂₉ steranes 20S/(20S+20R) and 66/(66+αα) ratios ranges from 0.54 to 0.65 and 0.54 to 0.70, respectively, suggesting thermal equilibrium and the main phase of oil generation has reached or surpassed. The oleanane index (OI/C₃₀-hopane) ranges from 0.35 to 0.53 indicating a significant input of angiosperm material. The bicadinanes/(bicadinanes+C₃₀-hopane) and BMI ranges from 0.32 to 0.73 and 2.41 to 4.85, respectively. The oils have moretane/hopane ratio of 0.15 to 0.31, Ts/Tm ratio in the range 0.37 to 1.05, C₃₀-diahopane/C₂₉Ts ratio of 0.76 to 1.32, C₃₀-diahopane/(diahopane+normoretene) ratio of 0.37 to 0.56, and C₃₂ 22S/(22S+22R) ratio of 0.47 to 0.58.

The biomarker data indicates that the oils have originated from a mature Tertiary source rock with a predominantly terrestrial origin for the precursor organic matter and subsidiary algal/bacterial input, deposited under suboxic conditions.

Introduction

The Mumbai offshore basin is a Tertiary pericratonic rift basin (Biswas & Singh, 1988) located off the west coast of India. It is bounded in the east by the coastline of India, in the north by the Saurashtra arch, in the south by the Vengurla arch, and in the west by the west margin basement arch. The basin covers an area of about 116,000 km² from coast to 200 m isobaths and has a sedimentary fill of about 1100-5000 m ranging from Paleocene to Holocene epoch.

The Mumbai offshore basin has been a prolific hydrocarbon producer for more than 40 years and accounts for nearly 44% of the annual petroleum production of India (Wood Mackenzie, 2017). The first oil in this basin was discovered in 1974 which led to the discovery of giant "Bombay High" field. Since then intense hunt for hydrocarbon in this basin has led to the discovery of several significant oil and gas fields, namely the Bassein, Heera, Mukta, Neelam, Panna, Ratnagiri and recently the D1 and Tapti fields.

The basin has evolved as a result of rifting and separation of Seychelles from Indian plate in late Cretaceous (Norton and Sclater, 1979). Several previous workers (Rao, 1984; Bhattacharya and Subrahmanyam, 1986; Biswas and Singh, 1988; Kolla and Coumes, 1990; Singh and Lal, 1993; Subrahmanyam et al., 1993) have studied the tectonic framework of the basin and have presented geophysical evidence on the extension of structural trends from the Indian subcontinent into the shelf areas. Accordingly, three prominent Precambrian structural trends are observed in the basin, the NW-SE to NNW-SSE Dharwar trend; NE-SW Aravalli trend; and ENE-WSW to E-W Satpura trend. On the basis of its configuration, the basin can be subdivided into six tectonic blocks: Tapti-Daman, Diu, Heera-Panna-Bassein, Bombay High-Deep Continental Shelf (DCS), Ratnagiri, and Shelf Margin blocks.

The floor of the basin is occupied by Deccan Trap (late Cretaceous) and by granite-granite gneiss (Precambrian). The presence of Mesozoic sediments in this basin has not been established as of date. Mature source rocks occur in three kitchen areas: Surat depression in the north and its southward extension to Ratnagiri, Saurashtra low in the northwest, and Murud and Rajpur lows in the southwest. Good source rocks are present in Panna Formation (Paleocene-early Eocene) and Belapur Formation (middle Eocene). In the Tapti-Daman area, less mature source rocks exist in the Oligocene Formation. In DCS and deeper part of the basin, marginally mature source rocks are found within Neogene Formation. Hydrocarbon reserves have been established in almost all the stratigraphic units of the basin viz. basement (Precambrian, late Cretaceous), Panna (Paleocene to early Eocene), Bassein (middle Eocene), Mukta (early Oligocene), Heera (early Oligocene), Panvel (late Oligocene), Bombay (early Miocene), Ratnagiri (early to middle Miocene), Bandra (middle Miocene) and Chinchini (middle Miocene to Holocene) formations. The generalized stratigraphy of the basin is given in Fig. 2.

In recent years, exploration of unconventional hydrocarbon reservoirs such as fractured basement have gained significant attention. In this paper, six oil samples from basement reservoirs in different wells, east of Bombay High field have been studied using GC-MS, for the analysis of biomarkers to understand their origin, environment of deposition, maturation and to correlate oils with each other.

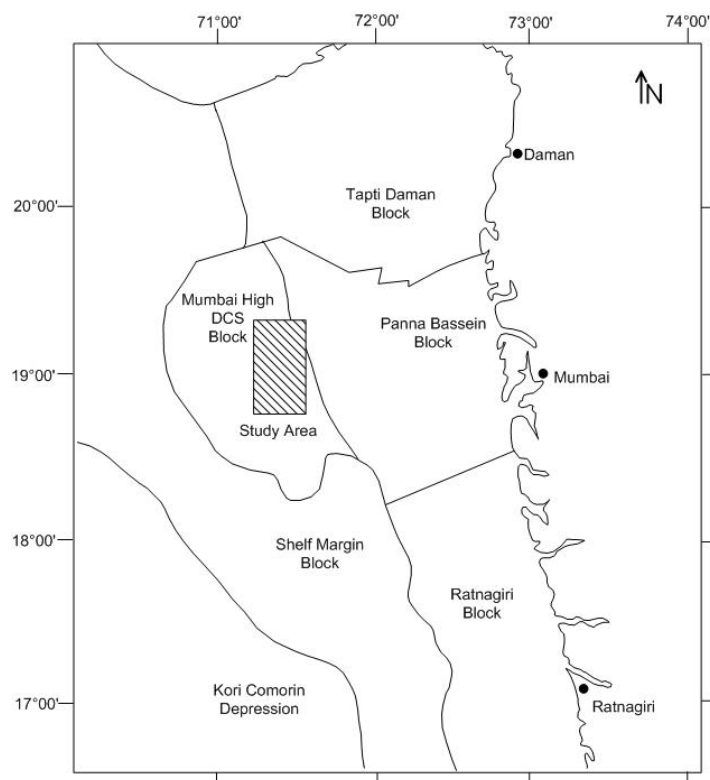


Fig.1. Outline map of Mumbai Offshore Basin. The shaded portion represents the area from which oil samples have been taken for this study.

Samples and Methods

Excess n-hexane was added to ~0.2 ml of oil sample taken in a beaker and left in refrigerator overnight. The asphaltenes precipitated as a dark brown solid. The maltenes obtained above were separated into aliphatic and aromatic fractions by column liquid chromatography using activated silica gel (100-200 mesh). The aliphatic fraction was then separated using n-hexane, and the aromatic fraction was separated using a mixture of n-hexane and dichloromethane in the ratio 4:1. The saturate fractions were then analysed using an Agilent 5975 mass spectrometer attached to a 7890 gas chromatograph with an HP-5 MS fused capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness). Helium was used as a carrier gas with a flow rate of 1 ml/min. The GC temperature was initially held at 40 °C for 5 min and subsequently raised at a rate of 4 °C/min to 310 °C and held for 5.5 min. The mass spectrometer

detector was operated in EI mode with 70 eV ionization energy and the samples were analysed in a full scan mode across a mass range of 50-600 dalton. The data acquisition and processing was done using Chemstation software and the compounds were identified on the basis of their retention time, elution pattern and comparison of the mass spectra with published data.

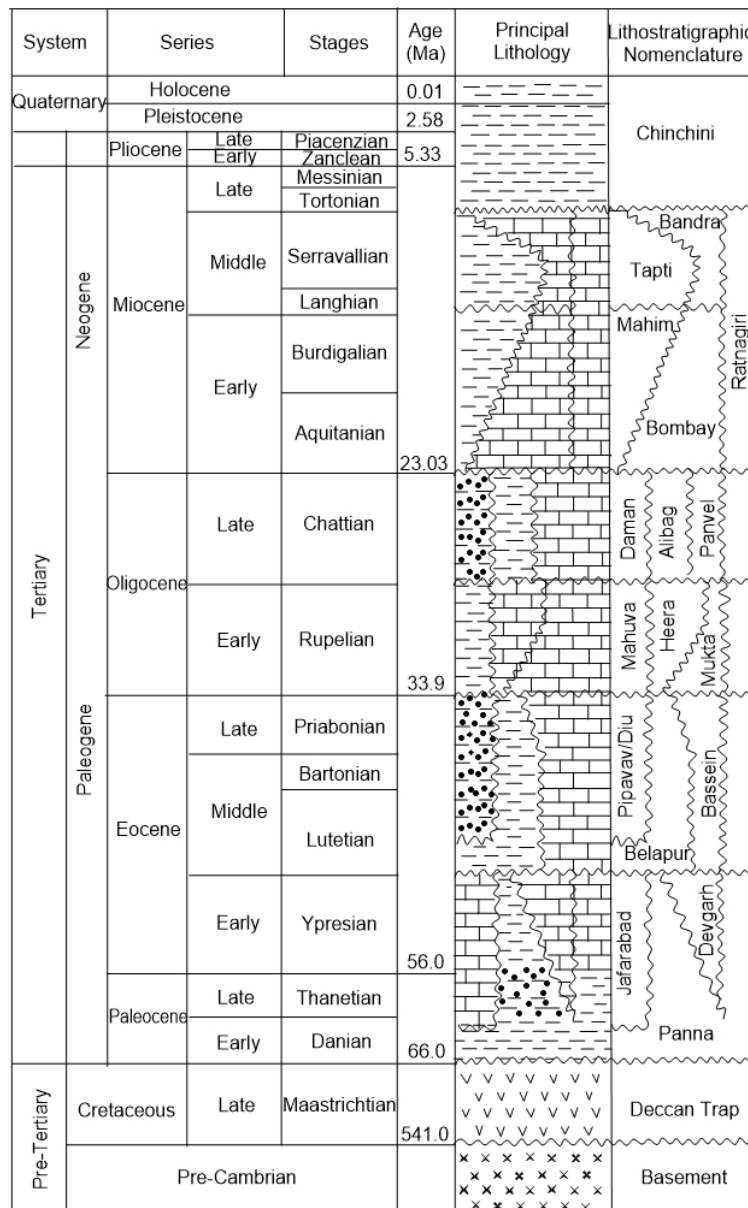


Fig. 2. Generalized stratigraphy of Mumbai Offshore Basin.

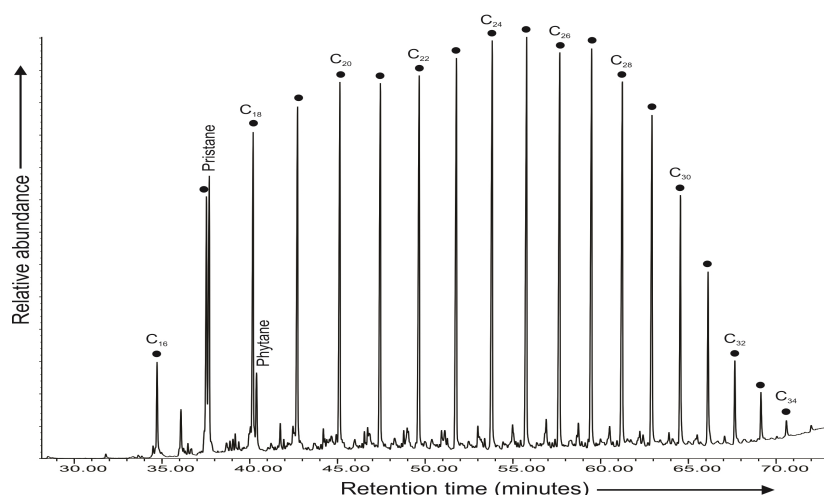


Fig. 3. Gas chromatography trace of a representative oil sample (MO-5). Numbers along the top indicate the number of carbon atoms in the n-alkanes.

Table 1. Gas chromatogram data of n-alkanes and acyclic isoprenoids of the oil samples.

SI No	Sample No	Pr/Ph	Pr/n-C ₁₇	Ph/n-C ₁₈	CPI	OEP	Waxiness
1	MO - 1	1.61	0.36	0.26	1.05	1.01	1.51
2	MO - 2	2.40	0.55	0.26	1.06	1.01	1.54
3	MO - 3	2.11	3.21	1.76	1.06	1.01	1.41
4	MO - 4	2.20	0.45	0.26	1.06	1.01	1.36
5	MO - 5	3.40	4.88	1.28	1.07	1.00	2.65
6	MO - 6	1.60	0.39	0.33	1.05	1.00	0.62

$$\text{CPI} = \frac{1}{2} \left[\frac{(C_{25} + C_{27} + C_{29} + C_{31} + C_{33})}{(C_{24} + C_{26} + C_{28} + C_{30} + C_{32})} + \frac{(C_{25} + C_{27} + C_{29} + C_{31} + C_{33})}{(C_{26} + C_{28} + C_{30} + C_{32} + C_{34})} \right] \text{ (Bray \& Evans)}$$

$$\text{OEP} = \frac{(C_{23} + 6 \cdot C_{25} + C_{27})}{(4 \cdot C_{24} + 4 \cdot C_{26})}$$

The n-alkanes and acyclic isoprenoids are the most abundant components in the aliphatic fraction of the crude oils and are characterized by carbon number ranging from n-C₁₁ to n-C₃₆. All the studied samples shows unimodal n-alkane distribution with a maximum abundance between n-C₂₀ and n-C₂₈ (Fig. 3), indicating high waxiness which is confirmed by $\Sigma(C_{21} - C_{31})/\Sigma(C_{15} - C_{20})$. All the samples have carbon preference index (CPI) and odd-to-even predominance (OEP) values of ~1, suggesting high thermal maturity and contribution from both terrigenous and marine organic matter into source rock. The acyclic isoprenoid ratio Pr/Ph of the studied samples are moderate to high (1.60 to 3.40) indicating suboxic condition during deposition of source sediments (Didyk *et al.*, 1978; Powell, 1988; Lijmbach, 1975; Didyk *et al.*, 1978; Peters and Moldowan, 1991; Hughes *et al.*, 1995). The samples MO-1 and MO-6 have moderate Pr/Ph ratio of 1.60. This suggests a predominantly terrestrial source with relatively higher input of algal matter as compared to other samples. MO-3, MO-4 and MO-2 have relatively high Pr/Ph ratio 2.11 to 2.40. The sample MO-5 has the highest Pr/Ph ratio of 3.40 indicating high terrigenous input into source matter. The cross plot of Pr/n-C₁₇ versus Ph/n-C₁₈ (Fig. 4) indicates that the oils have originated from a mixture of Type II/III kerogen (Shanmugam, 1985). The cross-plot shows that the oil samples MO-1, MO-2, MO-4 and MO-6 have generated from a mixed Type-II and Type-III kerogens and the oils MO-3 and MO-5 have originated from Type-III organic matter.

Among sesquiterpenoids (*m/z* 123), 8β(H)-drimane and 8β(H)-homodrimane are present in considerable amount in all the samples. 4β(H)-eudesmane is relatively less abundant. Apart from these, the samples also exhibit C₁₄-nordrimanes and C₁₅-rearranged drimanes. Diterpenoids are present in very low abundance or are present below the detection limit of the instrument. C₁₉-C₂₁ tricyclic terpanes (*m/z* 123,191), with most abundant being C₁₉ are present in all the studied samples. C₂₃ tricyclic have been detected in samples MO-1, MO-3, MO-4 and MO-6. Among tetracyclic terpenoids (*m/z* 191), C₂₄-des-A-oleanane and C₂₄-secohopane are present in all the analysed samples.

The sterane distribution (m/z 217) of the studied samples shows higher concentrations of C_{29} regular steranes over C_{27} and C_{28} steranes (Fig. 5.) suggesting a strong terrestrial contribution to the organic matter, whereas abundance of C_{27} and C_{28} steranes indicate marine and lacustrine algae inputs, respectively (Huang and Meinshein, 1979; Czochanska et al., 1988; Waples and Machihara, 1991; Schoell et al., 1992; Peters and Moldowan, 1993; Köster et al., 1998; Schouten et al., 2001; Inaba and Suzuki, 2003). The C_{29} steranes $20S/(20S+20R)$ and $\beta\beta/(\beta\beta+\alpha\alpha)$ ratios ranges from 0.54 to 0.65 and 0.54 to 0.70 respectively, suggesting thermal equilibrium and main phase of oil generation has reached.

Oleananes (m/z 191) and bicadinanes (m/z 369) have been detected in all the samples, confirming their terrigenous origin (Ekweozor and Udo, 1988; Alam and Pearson, 1990; Ekweozor and Telnaes, 1990; van Aarssen et al., 1992; Curiale et al., 1994; Murray et al., 1994; Nytoft et al., 2010). Oleananes are formed by the diagenetic and catagenetic alteration of various 3β -functionalised angiosperm triterpenoids (Rullkotter et al., 1994). The oleanane index (Ol/C_{30} -hopane) ranges from 0.35 to 0.53. Bicadinanes are pentacyclic non-hopanoid triterpenoid with six-membered E-ring structure produced from dammar resin, which are produced by Dipterocarpaceae, an angiosperm species found in oil and sediments of SE Asia (Grantham et al., 1983; Alam and Pearson, 1990; van Aarssen et al., 1990, 1992; Curiale et al., 1994; Pearson and Alam, 1993; Murray et al., 1994). Bicadinanes (V, W, T, T1 and R configurations) were identified in all the samples analysed. The bicadinanes/(bicadinanes+ C_{30} -hopane) ratio ranges from 0.27 to 0.81. The bicadinane maturity index ($BMI-I = T/(T+R)$) ranges from 2.41 to 4.85.

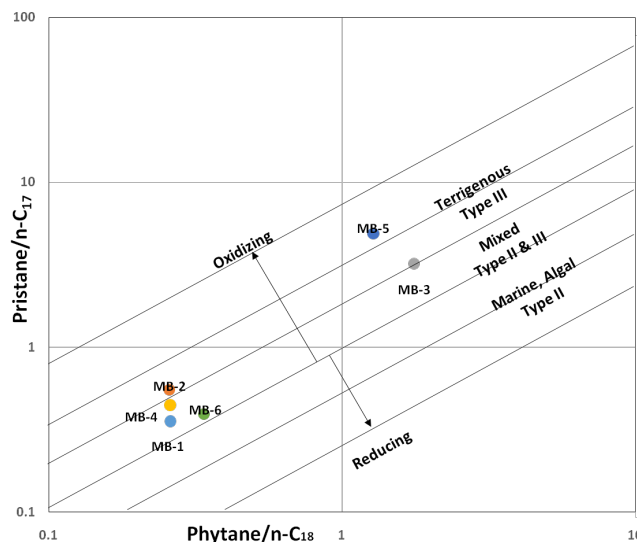


Fig. 4. Cross plot of $Pr/n-C_{17}$ ratio versus $Ph/n-C_{18}$ ratios showing depositional environment conditions and type of organic matter.

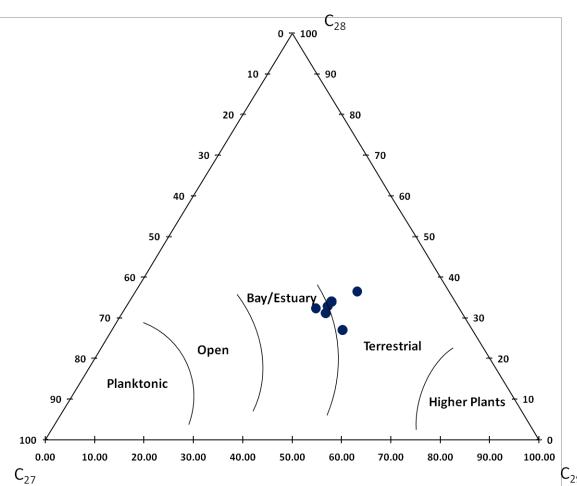


Fig. 5. Ternary diagram of regular steranes (C_{27} - C_{29}) indicating the relationship between sterane compositions in relation to organic matter input and depositional environments.

Table 2. Hopane indices (m/z 191 chromatogram) of crude oil samples.

Sl No	Sample No	T_s/T_m	Mo/Ho	$Ol/Ol+Ho$	$Bc/BC+Ho$	BMI-1	C_{30} -diahopane/ diahopane+normoratane	C_{30} -diahopane/ C_{29} - T_s	C_{29} 20S/ (20S+20R)	C_{29} $\beta\beta$ / ($\beta\beta+\alpha\alpha$)	C_{32} 22S/ (22S +R)
1	MO-1	0.81	0.24	0.35	0.73	4.85	0.56	1.19	0.54	0.63	0.56
2	MO-2	1.05	0.31	0.35	0.45	4.06	0.54	1.32	0.57	0.64	0.54
3	MO-3	0.46	0.27	0.26	0.38	3.61	0.52	0.96	0.55	0.70	0.47
4	MO-4	0.37	0.15	0.26	0.38	2.55	0.44	0.76	0.65	0.54	0.57
5	MO-5	0.76	0.25	0.34	0.34	2.41	0.37	1.07	0.56	0.60	0.48
6	MO-6	0.86	0.26	0.26	0.32	2.92	0.44	0.83	0.54	0.62	0.58

Pentacyclitriterpanes dominated by the C₃₀-hopanes are present in all the samples. C₃₀-Moretane is present in lower concentration in all the studied samples. The ratio of C₃₀-moretane to the corresponding C₃₀-hopane decreases with increasing thermal maturity from 0.80 in immature bitumens to less than 0.15 in mature source rocks and in oils to a minimum of 0.05 (Seifert and Moldowan, 1980) because moretane is thermodynamically less stable than hopane. The moretane/hopane ratio for the oils examined varies between 0.15 and 0.31.

Oils originating from sediments with high clastic contents deposited under mild anoxic conditions are characterised by high C₃₀-diahopane/C₂₉Ts ratios (Peters et al., 2005). Lower values may indicate more reducing depositional conditions. However, the higher values of this ratio could also result from increasing maturity (Peters and Moldowan, 1993). The C₃₀-diahopane/C₂₉Ts ratio of the samples varies from 0.76 to 1.32. The samples MO-1, MO-2 and MO-5 have high C₃₀-diahopane/C₂₉Ts ratios (1.07-1.32) as compared to MO-4 and MO-3 and MO-6 (0.76-0.96). The C₂₉-norhopane/C₃₀-hopane ratio ranges between 0.62-0.70. The low value of C₂₉/C₃₀ 17 α -hopane ratio suggests that these oils have been sourced from marine clay-rich source rocks (Connanet *al.*, 1986). The analysed samples have Ts/Tm ratio 0.37-1.05 and C₃₀-moretane/C₃₀-hopane ratio 0.15-0.31. Homohopanes are present in lower concentration and are dominated by C₃₁-homohopane. C₃₁-C₃₂ homohopanes 22S/(22S+22R) isomerization ratios can be used to assess the thermal maturity, which commonly ranges from 0.57 to 0.62 during thermal maturation (Seifert and Moldowan, 1986). The C₃₂-homohopane ratio in the samples analysed are in the range of 0.47 to 0.58, indicating main phase of oil generation.

The oils have tricyclitertanes/hopane ratio of 0.54 to 3.87. The samples MO-1 and MO-6 have high tricyclitertanes/hopane ratio (1.04 and 0.59 respectively) suggesting relatively greater contribution from marine algal matter to source as compared to other samples. This is in agreement with low Pr/Ph ratio of MO-1 and MO-6. The sample MO-1 has high tetracyclic terpanes/hopane ratio of 2.10 whereas all other samples have tetracyclic terpanes/hopane ratio from 0.47 to 0.61 thereby, suggesting high relative maturity of MO-1.

The cross plot of BMI-I versus diahopane/(diahopane+normoretane) (Fig. 6), shows the oils samples MO-1 and MO-2 have relatively high maturity and MO-5 has the lowest maturity. The plot of Pr/Ph versus C₃₀-diahopane/C₂₉-Ts (Fig. 7) of the studied oils, indicate suboxic depositional environment. The oils MO-1 and MO-2 are relatively more mature and are characterised by high diahopane/(diahopane+normoretane) ratio (Fig. 7).

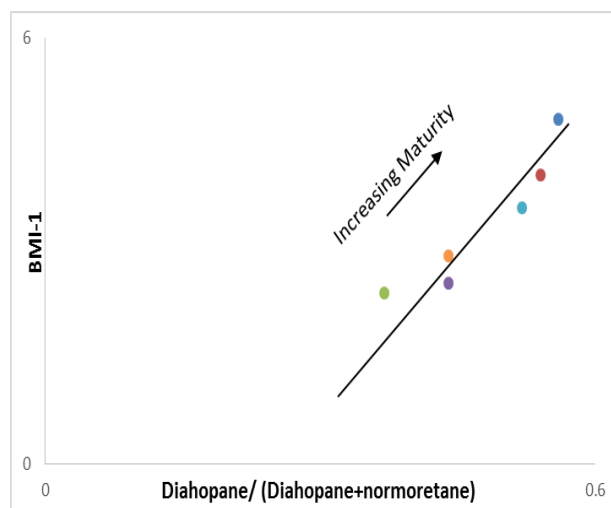


Fig. 6. Cross plot of bicadinane maturity index (BMI-1) vs C₃₀-diahopane/(C₃₀-diahopane+C₂₉-moretane).

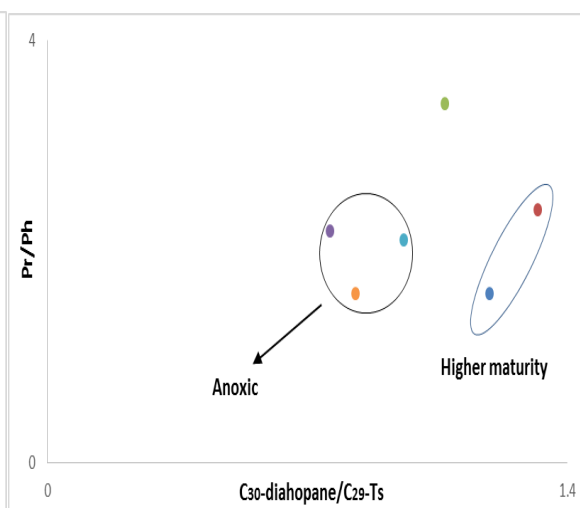


Fig. 7. Cross plot of pristane/phytane (Pr/Ph) vs C₃₀-diahopane/C₂₉-Ts.

Conclusions

The following conclusions can be drawn from the biomarker studies of oil samples from basement reservoirs east of Bombay High field, Mumbai Offshore Basin:

1. The analysed oils have originated from a mixture of type II-III and type III kerogens. The oil samples MO-3 and MO-5 have a predominance of terrigenous sediments derived from type-III organic matter. The samples MO-1, MO-2, MO-4 and MO-6 contain terrestrial organic matter with a substantial algal/bacterial input derived from type II-III kerogen.
2. The source sediments were deposited in a suboxic environment.
3. The oils were generated from a mature source that have entered the main oil window.
4. The oils were generated from a Tertiary source characterised by significant input of angiosperms.
5. The oil samples MO-1 and MO-2 are relatively more mature as compared to other samples.
6. The oil samples MO-1, MO-2, MO-4 and MO-6 are genetically co-relatable and have generated from the same source rock. The samples MO-3 and MO-5 are supposed to have generated from a different source or there could be charging from another source.