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Occurrence of rare biomarker in crude oil from fractured basement reservoir of Mumbai Offshore Basin, west coast India

Swaraj Kumar Jena[1], Suryendu Dutta
[1]Email: jena_swaraj@ongc.co.in, Oil and Natural Gas Corporation Limited

Abstract

Chemotaxonomic applications of flora based on extractible biomarkers can be used to understand more precisely the provenance of organofacies. In this paper a detailed biomarker study of an oil sample from Basement reservoir of Mumbai Offshore Basin have been made. The crude oil sample is characterized by high abundance of angiosperm biomarkers such as oleananes and bicadinanes. Steranes are present in low concentrations dominated by C_{29} constituent. Diterpenoids are represented by 8β(H)-labdane, 4β(H)-19-norisopimarane, rimuane, *ent*-beyerane, rosane, iso-pimarane, 16β(H)-phyllocladane, *ent*-16β(H)-kaurane, 16α(H)-phyllocladane and *ent*-16α(H)-kaurane. A conifer origin possibly is suggested for the diterpenoids. Onocerane was reported for the first time in crude oils from SE Asia. Occurrence of onocerane isomers I and II in oil sample from Mumbai Offshore suggest an input from angiosperm precursor, and/or humid tropical fern-related plants deposition in a restricted/lacustrine environment. High OI along with abundance aryl isoprenoids in oil sample indicate marine condition and photic zone anoxia coeval with the deposition of rich source rocks in the source pods.

1. Introduction

Biomarkers not only preserve the carbon skeleton of the precursor fossil life from which they were derived but also provide valuable information about the ancient ecosystem and thermal maturity of the source rocks by means of their chemical composition. The Indian subcontinent was positioned just over the equator during Late Palaeocene–Early Eocene period (Scotese and Golanka, 1992; Sluijs et al., 2007). The prevailing warm humid equatorial conditions with exceptionally high mean annual precipitation (MAP) (Prasad et al., 2009; Dutta et al., 2009, 2011; Paul et al., 2015) gave rise to luxuriant growth of flora and fauna along the western continental margin of the Indian plate. In this paper a crude oil sample from Basement reservoir from north of Bombay High field have been studied in detail to understand more precisely the provenance of paleogene organofacies in Mumbai Offshore Basin using biomarkers.

2. Regional geology and stratigraphy

The depositional history and tectonic framework of Mumbai Offshore Basin have been extensively studied by various authors (Rao and Talukdar, 1980; Basu et al., 1982; Roychoudhury and Deshpande, 1982; Biswas and Deshpande 1983; Biswas and Singh, 1988; Biswas, 1989). The basin is located on the Western Continental Margin of India between the Deccan Trap in the east, Kori-Comorin ridge in the west, Saurashtra arch in the north and Vengurla arch in the south (Bhattacharya and Chaubey, 2001). The basin covers an area of about 1,16,000 km² in shallow water of Arabian sea between 0–

200m isobaths. Granite-granite gneiss, syenite and granodiorite of Precambrian age and/or Deccan Trap of Late Cretaceous age forms the technical basement of the basin. The entire sedimentary fill in the basin has been divided into two 1st order sequence, the rift sequence of Paleocene age and the Passive margin sequence of Eocene to Recent age. The generalized stratigraphy of Mumbai Offshore Basin is shown in Fig. 1 (Zutshi et al., 1993). The structural element of the basin has been affected by three prominent Precambrian structural trends, viz. the NW-SE to NNW-SSE Dharwar trend; NE-SW Aravalli trend and ENW-WSW to E-W Satpurs trend (Biswas, 1987; Rao, 1984; Bhattacharya and Subrahmanyam, 1986; Biswas and Singh, 1988; Kolla and Coumes, 1990; Singh and Lal, 1993; Subrahmanyam et al., 1993). Furthermore the basin has sub-divided into six tectonic blocks based on its structural configuration, namely Tapti-Daman block, Diu block, Heera-Panna-Bassein block, Bombay High-Deep Continental Shelf (DCS) block, Shelf Margin block and Ratnagiri block.

Fig. 1. Generalized stratigraphy of Mumbai Offshore Basin (Modified after Zutshi et al., 1993).

3. Samples and Methods

Asphaltenes were precipitated from oil sample by adding excess *n*-hexane. The deasphalted maltenes were separated into aliphatic and aromatic fractions by column liquid chromatography technique using activated silica (100–200 mesh). The saturate and aromatic fractions were separated using *n*-hexane and a mixture of *n*-hexane and dichloromethane (DCM) in the ratio 4:1, respectively. The resultant fraction was subjected to GC-MS analysis.

Hydrocarbon extracts were analysed using Agilent 5975 mass spectrometer attached to a 7890 gas chromatograph with an HP– 5MS 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 programmed at 40 °C for 5 min and was then raised to 310 °C at a rate of 4 °C/min and was held for 5.5 min at final temperature. The mass spectrometer detector was operated in EI mode with 70 eV ionization energy and the samples were analysed in full scan mode across a mass range of 50–600 dalton. The data acquisition and processing were done using Chemstation software. Individual compounds were identified on the basis of their retention time in the total ion chromatogram (TIC) and comparison of their mass spectra with available literature. Relative percentages of different compounds and compound groups in the saturated and aromatic fractions were calculated using peak areas from the gas chromatograms in relation to those of internal standards.

4. Results and Discussion

Aliphatic fraction

n-Alkanes and isoprenoids. The TIC of the oil sample from Basement reservoir display unimodal pattern with carbon number distribution between C_{14}–C_{35} and maxima in the range *n*-C_{21}–*n*-C_{26}, together with well-preserved acyclic isoprenoids; pristane and phytane. The *n*-alkane distribution pattern suggests that no biodegradation has occurred. The oil sample have Pr/Ph ratio of 1.33, Pr/*n*-C_{17} and Ph/*n*-C_{18} ratios of 2.28 and 1.09, respectively. The crude oil sample have CPI and OEP values of 1.04 and 1.01, respectively.

Sesquiterpenoids. C_{14} to C_{17} bicyclic sesquiterpanes denoted by 4β(H)-eudesmane, 8β(H)-drimane and 8β(H)-homodrimane along with its isomers are present in the oil sample. Eudesmane is present in relatively less abundance than drimane.

Bi-, tri- and tetracyclic diterpanes. The diterpenoids (Fig. 2) are represented by 8β(H)-labdane, 4β(H)-19-norisopimarane, rimuane, *ent*-beyerane, rosane, iso-pimarane, 16β(H)-phyllocladane, *ent*-16β(H)-kaurane, 16α(H)-phyllocladane and *ent*-16α(H)-kaurane. Diterpenoids are the diagnostic biomarkers of conifers and their resins (Otto and Wilde, 2001) and are eventually detected in oils and coals from regions which were heavily forested in the past (Shanmugam, 1985). They are especially derived from conifer families Cupressaceae, Pinaceae and Podocarpaceae.
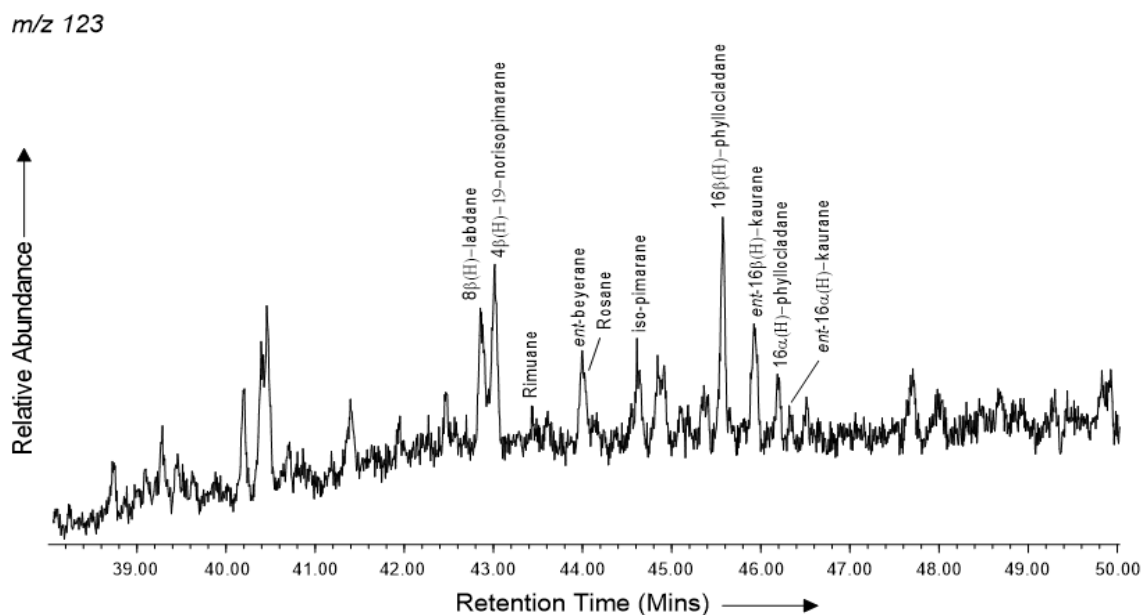
Fig. 2. Partial mass chromatogram at *m/z* 123 of the aliphatic fractions showing distribution of diterpenoids in crude oil sample from Basement reservoir, Mumbai Offshore Basin, India.

Tricyclic terpanes. The tricyclic terpanes are represented by a homologue series of C_{19} to C_{25} except the members C_{22} and C_{24}, amongst which the C_{19} and C_{20} members predominate. The C_{19}–C_{20} tricyclic terpanes are commonly found in oils originated from terrestrial organic matter and are believed to have originated mainly from diterpenoids produced by vascular plants (Peters et al., 2005), whereas the C_{23} tricyclic terpane is the dominant homologue present in crude oils generated from marine source rock (Aquino Neto et al., 1983; Peters and Moldowan, 1993; Peters et al., 2005). The $C_{19}/(C_{19}+C_{23})$ tricyclic ratio of the oil sample is 0.62.

Tetracyclic terpanes. The tetracyclic terpanes are represented by C_{24} and C_{26} members. Ring-A degraded tetracyclic terpanes; $10\beta(H)$des-A-oleanane, $10\beta(H)$des-A-lupane and ring-E degraded 17,21-secohopane are the C_{24} tertracyclic terpanes identified in the oil samples, amongst which $10\beta(H)$des-A-oleanane and 17,21-secohopane have relative higher abundance whereas, $10\beta(H)$Des-A-lupane occurs as a minor peak next to $10\beta(H)$des-A-oleanane. The oil sample have C_{24} TeT/(C_{24} TeT + C_{23} TT) ratio of 0.86.

Steranes and diasterane. Diasteranes are more abundant than steranes and the ratio of disterane/(diasterane + regular sterane) of the oil sample is 1.46. The occurrence of diasternanes in crude oils and source rocks has been attributed to clay catalysed rearrangement of sterenes to diasteranes during diagenesis (Rubinstein et al., 1975; Sieskind et al., 1979; Grantham and Wakefield, 1988; Peters and Moldowan, 1993). The steranes are dominated by the C_{29} regular steranes which can be taken as an unequivocal evidence for terrestrial organic matter input. The $C_{27}/(C_{27} + C_{29})$ sterane ratio of the oil is have value 0.30.

Hopanes. Series of $\alpha\beta$-hopanes have been detected in all the oil samples using the fragment at *m/z* 191. The hopanes are derived from bacteriohopanepolyols found in specific bacteria, such as bacteriohopanetetrol (Peters and Moldowan, 1991). Hopanes are present in relative higher

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concentration as compared to tricyclic and tetracyclic terpanes. The bisnorhopane/hopane ratio of the oil sample equals 1.06. The *m/z* 191 mass chromatogram shows exponential decrease in peak heights of homohopanes with increasing molecular weight.
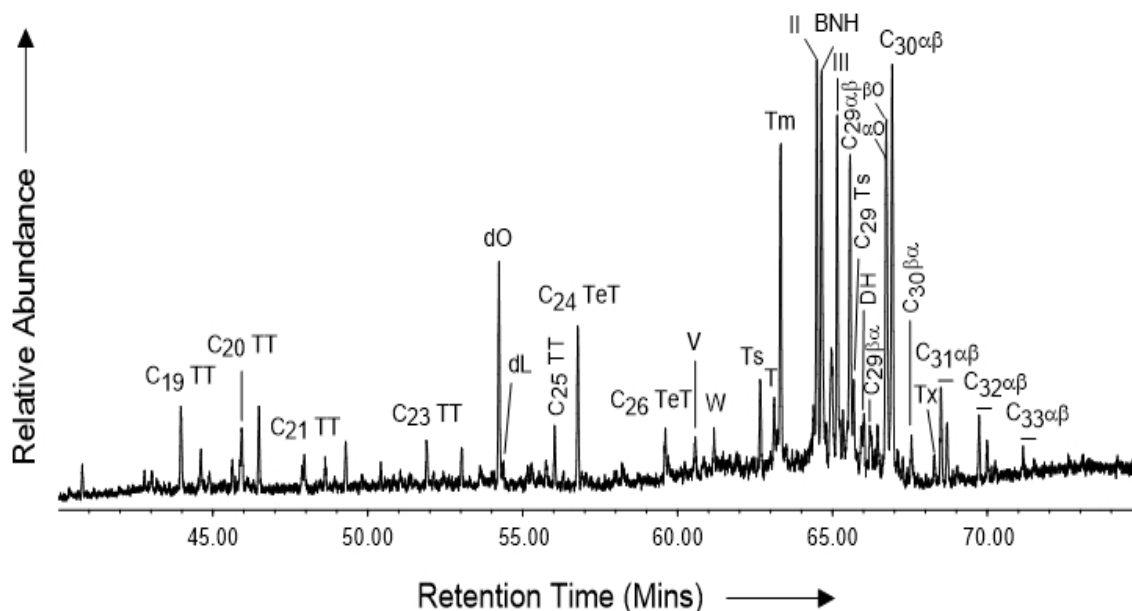

Fig. 3. Partial mass chromatogram at *m/z* 191 of the aliphatic fractions showing distribution of terpanes in crude oil sample from Basement reservoirs, Mumbai Offshore Basin, India.

Oleananes. Oleananes are the product of diagenetic and catagenetic alteration of various 3P-functionalised angiosperm triterpenoids (Rullkotter et al., 1994). Oleananes are source and age specific diagnostic biomarkers as they are sourced from land plants predominantly angiosperms (Philp and Gilbert, 1986; Peters and Moldowan, 1993; Moldowan et al., 1994). They are abundant in oils and sediments of Late Cretaceous and Tertiary age owing to the fact that angiosperm diversification occurred during Late Cretaceous (Ekweozor and Udo, 1988; Moldowan et al., 1994; Murray et al., 1994; Peters et al., 2005). The oil sample have exceptionally high OI of 0.88.

Bicadinanes. Bicadinanes are the catagenetic product of dammar resin of the angiosperm family Dipterocarpaceae which are ubiquitously present in tropical rain forests of SE Asia, India and Sri Lanka (van Aarssen et al., 1992). Bicadinanes with cis-cis-trans (V, W, W1 and W2) configuration and trans-trans-trans (T, T1 and R) configuration have been identified in the mass spectra *m/z* 369. In addition to this different isomers of homobicadinanes (MeW, MeT and MeT1) (Murray et al., 1994) and secobicadinanes were noted in abundance in the oils at *m/z* 383 and 151.

Onoceranes. One significant observation made in the oil from north of Bombay High field was the detection of onoceranes (8,14-seco-gammaceranes). Onocerane and onocerane related compounds are rare in geological record and to the best of our knowledge, onocerane was not reported earlier in crude oils or sediments from SE Asia. Ring C-opened pentacyclic triterpane- 8α(H), 14β(H)-onocerane I and 8α(H), 14α(H)-onocerane II were identified in the characteristic ion fragmentogram (Fig. 4) with a base peak at *m/z* 123, M+. 414 and another intense fragment at *m/z* 191 that exceeds *m/z* 193.
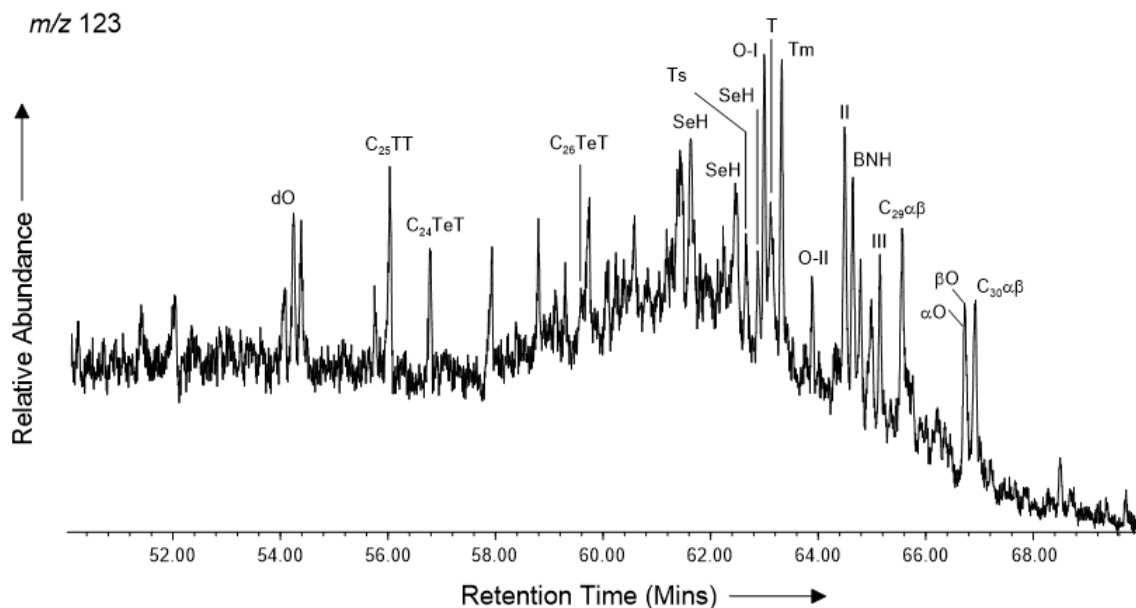
Fig. 4. Partial mass chromatogram at *m/z* 123 of the aliphatic fractions showing distribution of onocerane isomers in crude oil sample from Basement reservoir, Mumbai Offshore Basin, India.

The occurrence of onocerane isomers in oil from north of Bombay High suggest that these compounds would have generated from angiosperm precursor, possibly from family Fagaceae, and/or humid tropical fern-related plants deposited in a restricted/lacustrine environment.

Aryl isoprenoids. The presence of aryl isoprenoids are biomarker evidence for phototrophic green/brown sulfur bacteria thriving on sulfide penetrating the shallow, anoxic photic zone. The oil sample have high abundance of aryl isoprenoids. Apart from this, the oil sample also contain one novel bicyclic monoaromatic aryl isoprenoids C_{18} with base peak at *m/z* 173. In addition to this, 2,3,6/ 2,3,4-trimethyl substituted C_{32} triaryl isoprenoid was also identified in the oil sample.
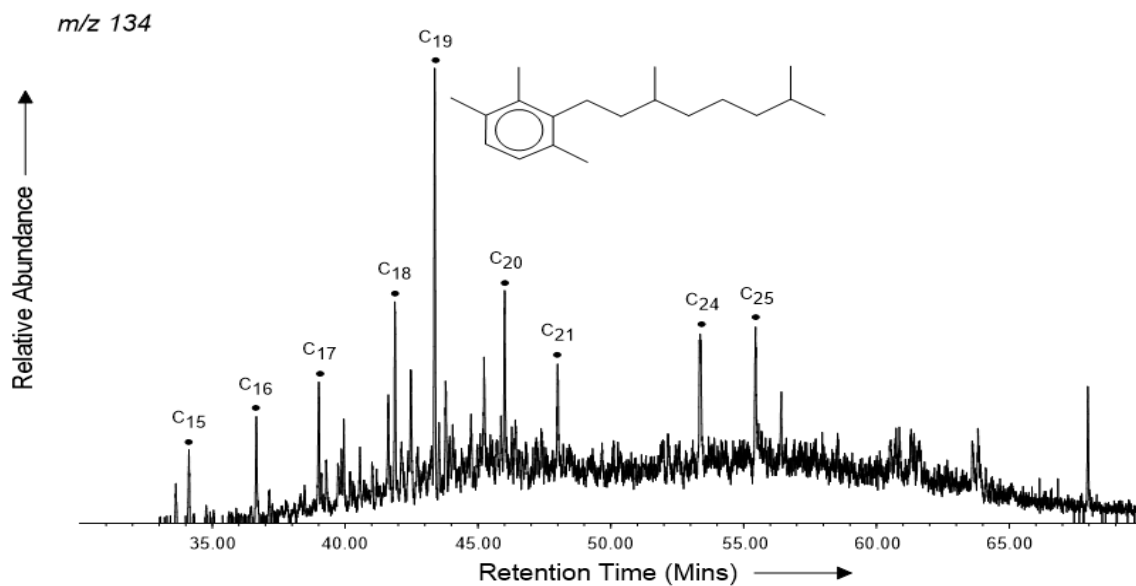

Fig. 5. Partial mass chromatogram at *m/z* 134 of the aromatic fractions showing distribution of aryl isoprenoids in crude oil sample from Basement reservoir, Mumbai Offshore Basin, India.

5. Conclusions

The following principal conclusions are made:

1. Pr/Ph, Pr/n-C_{17} and Ph/n-C_{18} ratios indicate type-II kerogen deposited under oxic-suboxic conditions.

2. The C_{19}/(C_{19}+C_{23}) tricyclic ratio and C_{27}/C_{29} sterane ratio specify mixed organic facies with significant contribution of terrigenous organic matter to the source pods.

3. Presence of oleanane and bicadinanes suggest a strong angiosperm input to the source sequence.

4. Oleanane index (> 0.2) assigns a Tertiary age to the source rock.

5. The presence of diterpenoids indicates a conifer origin possibly from Araucariaceae and Podocarpaceae family.

6. The omnipresence of onocerane isomers in good amounts in oil sample suggests an input from angiosperm precursor, and/or humid tropical fern-related plants deposition in a restricted brackish/lacustrine environment.

6. High OI (0.88), low Pr/Ph (1.33) along with abundance aryl isoprenoids in oil sample indicate marine condition and photic zone anoxia coeval with the deposition of rich source rocks in the source pods.

7. High OI and occurrence of onocerane isomers (I and II) in oil from north of Bombay High and its absence in oils from east-southeast-south of Bombay High-DCS block and Panna-Bassein block (not included in the present study) revealed difference in source pods. Accordingly, the oil from Basement reservoir north of Bombay High field have generated from a lacustrine source rock with high angiosperm input deposited under specific conditions.

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