



Biomarker Ratios and Stablecarbon Isotopes to Describe Crude Oils Characteristics in the Murzuq Basin (Libya)

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Authors' contributions

This work was carried out in collaboration between all authors. Authors SA and EF suggested and designed the study, performed, wrote the protocol, and wrote the first draft of the manuscript. Authors A. Abdulgader and A. Albaghdady worked Laboratories analysis. Author OH managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

This present paper includes a detailed evaluation of specific biomarkers together with stable carbon isotope ($\delta^{13}\text{C}$) by gas chromatography-mass spectrometry (GC-MS) and Gas Chromatograph-Isotope Ratio Mass Spectrometry (GC-IR-MS). Eight crude oil samples were collected from the A, B, H (east) and H (west) Fields, located in the Murzuq Basin, Libya. Stable Carbon isotope data ($\delta^{13}\text{C}$) together with biomarker ratios data of individual hydrocarbons, n-alkanes, isoprenoids, terpenes, hopanes, steranes and aromatic have been determined in crude oils to delineate their bacterial degradation, source facies, organic matter precursors, depositional conditions and a variation of maturation. Based on source-specific parameters including n-C₁₉ alkane, % C₂₇S, %C₂₈S, %C₂₉S, %C₂₃TT, %C₃₀αβ, %rC₂₈, DBT/P, CPI, Pr/Ph, Ts/Tm, dh 30/h 30, 1 MN, 2 MN, 26-27 DMN, 15 DMN, 236 TMN, 146-135 TMN, 125 TMN, 136 TMN ratios and $\delta^{13}\text{C}_{\text{‰}}$ of saturates and aromatics fractions. Such oils showed non-biodegradation, n-C₁₉ peak proved oils generated from a Lower Palaeozoic source rocks as emphasized n-C₁₉ peak, the dominance of C₂₉steranes

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over C₂₇ and C₂₈ with light Carbon isotope ratio ($\delta^{13}\text{C}\text{‰}$) values. The abundances of isosterane C₂₉, C₂₇, C₂₈-Tricyclohexaprenol and bacteriohopane polyols and aminopolyols, recommended as mixture bioprecursors of tricyclic terpenes and hopanes, furthermore regular sterane ratio gives values characteristic of Lower Palaeozoic marine source rocks and holding green algae and most likely a quantity of contribution from acritarchs. Carbon preference indices (CPIs) > 0.9 pointed to an anoxic deposition, dibenzothiophene to phenanthrene (DBT/Prange 0.49 - 0.58) recommend a siliciclastic source rather than carbonate and/or evaporate saline deposition. The ratios of CPIs, pristane/*n*-C₁₇ and phytane/*n*-C₁₈, *n*-alkanes (C₁₆ to C₂₂) against (C₂₃ to C₃₃), Ts/Tm, C₃₀diahopane/C₃₀hopane, methyl naphthalene, dimethyl naphthalene and trimethyl naphthalene indicated that the oils analysed are mature except the B Field oil being slightly less mature than the A, H (east) and H (west) Fields oils.

Keywords: Murzuq basin; crude oils; Libya; isoprenoids; biomarkers.

1. INTRODUCTION

Despite the geochemical studies around crude oils of Murzuq basin, still, more information can be obtained from biomarkers of saturated and aromatic hydrocarbons in terms of the source facies, depositional environment, Organic Matter Precursors and thermal maturity of organic matter. In a study by Volkman, et al. [1], demethylated hopanes are biological markers for bacterial degradation occurrence. Demethylation of the hopanes is extensively considered to occur as an effect of bacterial degradation, and demethylated hopanes have been widely reported in biodegraded oils, seeps and bitumens [2,3,4,5,6]. In a recent geochemical study of East Sirte Basin to investigate bacterial degradation occurrence, the oils analysed appear to be non-biodegraded on the basis of their high relative abundance of biomarkers [7].

Source facies of oils such as Lower Palaeozoic and older source rocks which earlier than the evolution of the higher plants may contain relatively abundant C₂₉steranes [8]. Variations in sterane carbon number distributions with respect to geological time were well-known for oils derived from marine source rocks [9]. Many published monographs of 3-methylesterases are typically linked to occurrences in oils and source rocks of Palaeozoic facies and older age [10, 11,12,13,14]. The ratio of dibenzothiophene and phenanthrene (DBT/P) recommended as an indicator of the availability of low sulfur for incorporation into organic matter and therefore is a valuable carbonate/shale facies discriminator [15]. Ratios of dibenzothiophene to phenanthrene (DBT/P) and pristane/phytane (Pr/Ph) are indicating oil source rock depositional environment and lithology.

Biomarker of tricyclic terpenes occurrence in geological samples was reported by [16]. The

tricyclohexaprenol have been suggested as organic matter precursors of the C₁₉-C₃₀ tricyclic terpenes series [17]. Tricyclic terpenes series (C₁₉ to C₄₅) from petroleum samples were recognized [18]. In extracts of saline lacustrine rock from Hartford in the USA, a large quantity of tricyclic to pentacyclic terpenes within a range from C₁₉ to C₄₁ was identified [19]. De Grande, et al. [20] reported extended series of tricyclic terpenes from C₁₉ up to C₅₄ in Brazilian source rocks and crude oils by using mass spectrometry (MS-MS) transitions and molecular ions of *m/z* 191. An extended tricyclic terpenes series (C₁₉TT to C₄₅TT), correlated with marine and/or lacustrine shales demonstrated as result of a marine environment for the reduced depositional conditions was recognized in crude oils from the East Sirte Basin, Libya [7,21]. Hopanoids are biological precursor have been identified as crucial compounds of metabolites in cell membranes of bacteria [22]. The significance of a bacterial input to the sedimentary organic matter is reported the occurrence of different hopanoid alkanes and derivative in source rocks and crude oils by [23].

The C₂₇ 18a(H)-22,29,30-trisnorhopane (Ts) is thermally more stable than C₂₇ 17a(H)-trisnorhopane(Tm) and their ratio typically raises from low values at immaturity organic matter and reaches unity within the major oil window. At higher levels of maturity, the value usually rises at an increasing rate and may reach high values (5-10) at late maturity [24]. Aromatic biomarkers such Methylphenanthrenes have been known as maturation parameters, and empirical correlations with vitrinite reflectance [25,26,27,28], while Ethylphenanthrene and dimethylphenanthrene isomers are identified by Radke, et al. [29]. The stable carbon ($\delta^{13}\text{C}$) value depends on the types of organisms preserved in the kerogen and on depositional environmental conditions [30,31] as well as a

useful parameter for establish oil–source rock correlations, in conjunction with other geochemical properties. It can indicate the possible age and depositional environment of source rocks. This paper aims to provide a detailed description of the geochemical characteristics of oils in the Murzuq Basin, utilizing 8 oils from the A, B, H (east) and H (west) Fields (Fig. 1). Molecular indicators *n*-alkanes, isoprenoids, terpenes, steranes and aromatic, together with stable carbon ($\delta^{13}\text{C}$) used to investigate a number of aspects of crude oils such as bacterial degradation occurrence, source facies, organic matter precursors, depositional environment and maturation for these oils.

1.1 Geological Setting

The studied felids are located in the Intracratonic Murzuq Basin (Fig. 1), which is separated by the Atshan Saddle, an anticlinal structure trending approximately east northeast to west south-west which leads into the Northwest end of the Al Qarqaf High. Since basin explored, there have been a number

of publications concerned with the structural/stratigraphic framework of the region, including geochemical studies on the basin sediments such [32]. Across the studied region, the environmental deposition of Quaternary is between 20 and 55 m thick, came with by nonattendance of the Miocene, Eocene and Oligocene clear formations with over unclear Mesozoic sediments, clarified by [33]. The formations of Cretaceous are destroyed and truncated by an escarpment to the southeast of the basin. The formations of Cretaceous are destroyed and truncated by an escarpment to the southeast of the basin with Jurassic Taouratine Formation nearly 200m thickness towards the northwest and is greatest to the south and southeast of the basin. The Triassic Formation is between 250 and 300 m thickness [33], resting on the Upper Carboniferous in the fields sampled. The sedimentary section is the central part of the basin with mainly composed of Palaeozoic and Mesozoic deposits (Fig. 2). The Carboniferous formations in the studied zone are four sediments, the Carboniferous consists of Tiguentourine, Dembaba Assedjefar and Marar Formations.

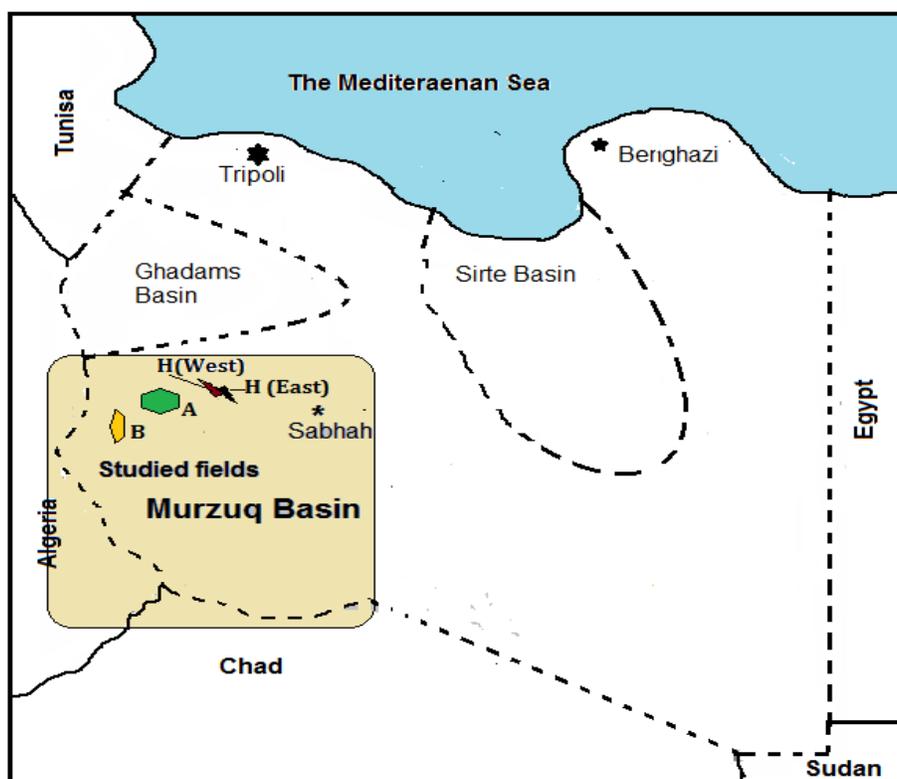


Fig. 1. Map shows the location of the Murzuq basin and studied fields modified from [34] and [32]

A number of variations in the thicknesses among formations across the province, even though the common depth of the Carboniferous preserved is approximately comparable, ranging from 501 m to 548 m, overlies a group of Devonian formations (Fig. 2). Tanezzuft and Akakus Formations of Llandovery age (Silurian) are a preserved thickness among 200 and 250 m. The Tanezzuft Formation contains the Hot Shale Member which is present over approximately half of the search area in thicknesses of up to 30 m and separated from the underlying Ordovician by an unconformity [33]. The Ordovician Mamuniyat Formation is present across the basin with depth up to 240 m, following by MelezShuqran, Hawaz and Ash Shabiyat Formations. The Hasawnah Formation is fluvialite at the base to shallow marine. This formation occurs widely throughout the Murzuq Basin, while Mourizidie Formation is considered to be a lower unit of the Cambrian Formations [34].

2. MATERIALS AND METHODS

2.1 Samples

Eight petroleum samples were selected for geochemical analysis. The samples were obtained from the A, B, H (east) and H(west) Fields in the Murzuq Basin(Fig. 1), to provide a better understanding of a number of geochemical characteristics of crude oil geochemistry.

2.2 Separation of Crude Oils

Crude oils were separated into three fractions using a column chromatographic method [35]. In brief, 10 to 20 mg of crude oil were applied to the top of a small column (5.5 cm x 0.5 cm i.d.) of activated silica gel (120°C, 8 h). The aliphatic hydrocarbon (saturated) fraction was eluted with n-pentane (2 mL); the aromatic hydrocarbon fraction with a mixture of n-pentane and

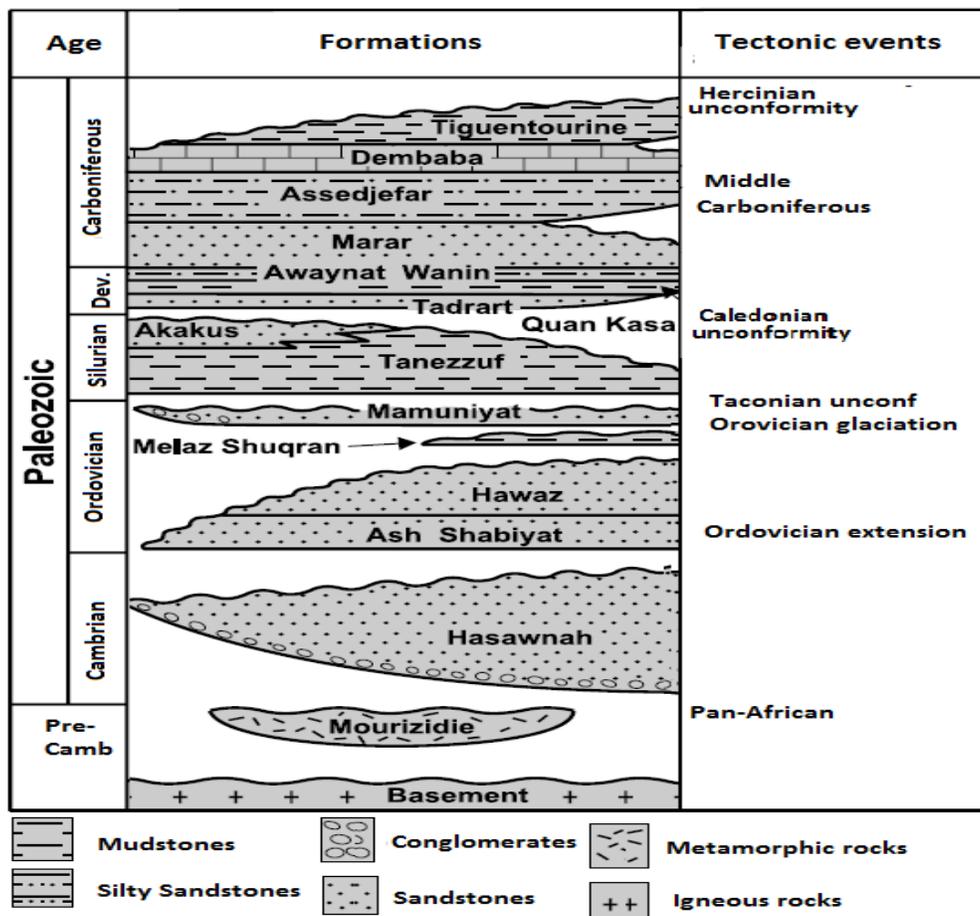


Fig. 2. Stratigraphic column of the Murzuq basin highlighting the lithology of the formations and the reservoir units. Modified from [4]

DCM (2 mL, 7:3 v/v); and the polar (NSO) fraction with a mixture of DCM and MeOH (2 mL, 1:1 v/v).

2.3 Molecular Sieving

Saturated hydrocarbon fractions were subjected to 5 Å molecular sieving as illustrated by [36]. A bit of the aliphatic fraction in cyclohexane was put into a 2 ml vial, filled with an activated sieve (7 g). The vial was sealed and placed into a pre-heated aluminium block (85°C, 8 h). The solution was after that cooled and transferred through a small column of silica plugged with glass wool and pre-rinsed with cyclohexane (2 ml). The sieve was after washed well with cyclohexane and the washings filtered during the same silica column. The combined filtrates afforded the branched/cyclic fraction. The *n*-alkanes were recovered HF digestion of the sieve as described previously [37].

2.4 Gas Chromatography - Mass Spectrometry (GC-MS)

A Hewlett Packard (HP) 5890 mass-selective detector (MSD) interfaced to an AMS 92 gas chromatograph (GC) was used to analyse Aliphatic and aromatic fractions. The gas chromatograph oven was programmed from 30°C to 310°C at 3°C/min, after which it was held isothermal for 30 min. Dissolved Samples by *n*-hexane were introduced via the HP 5890 sampler into a split-splitless injector operated in the pulsed-split less mode. The biomarker data was acquired in a full-scan mode *m/z* 50 to *m/z* 500. The mass spectrometer is linked to a gas chromatograph in order to provide separation of the sample. The technique is widely used in petroleum geochemistry for detailed analyses of oils, oil stains and source rock extracts. Selected ion monitoring mode (SIM GC-MS), the mass spectrometer is tuned to a selected number of

certain *m/e* values, which are diagnostic of the specific biomarker compounds such terpenes, steranes and aromatic compounds.

2.5 Gas Chromatograph –Isotope Ratio Mass Spectrometry (GC-IR-MS)

A Hewlett Packard (HP) 5890 gas chromatograph (GC) with autosampler was used in tandem with a Micromass isotope ratio mass spectrometer (IR-MS) for carbon isotope measurements and the same type of column used in GC-MS analysis was employed for GC-IR-MS. The $\delta^{13}\text{C}$ data were obtained by integrating the ion currents for masses 44, 45 and 46 from the CO_2 produced by oxidation of each chromatographically separated component, after passing through a quartz furnace packed with copper oxide pellets heated at 850°C. The accuracy and precision of $\delta^{13}\text{C}$ measurements were monitored by analysing a mixture of organic reference compounds with known $\delta^{13}\text{C}$ values.

3. RESULTS AND DISCUSSION

3.1 Fractionation Results

To isolate Saturates, Aromatics, Polaris, Resenes, a Column chromatography was used to separate compounds from their mixture. The data of isolation are shown in Table 1.

3.2 Bacterial Degradation

The data of analysed petroleum showed non-biodegradation, on the base of their high relative profusion of *n*-alkanes, isoprenoids, terpenes, steranes and aromatic. Nonappearance an obvious unresolved complex mixture (UCM) in the total alkane chromatograms and absence of 25-norhopanes. The next sections, therefore, focus on the study objective.

Table 1. Result of isolation via column chromatography (% deasphalted oil)

Field	Saturated	Aromatic	Polar	Resenes
A	68.6	20.4	4.7	6.3
	68.3	20.7	4.4	6.6
B	65.3	21.7	6.0	7.0
	65.0	22.0	6.0	7.0
H(W)	57.9	19.2	4.5	18.4
	57.5	19.6	4.2	18.7
H(E)	60.6	18.7	4.6	16.1
	60.3	19.0	4.5	16.2

3.3 Source Facies

A selection of gas chromatograms showing the difference in saturated hydrocarbon distributions found in the crude oils. The quantification of the alkane gas chromatography data shows a pronounced $n\text{-C}_{19}$ peak which is characteristic of oils generated from Lower Silurian Tanezzuft Formation/Hot Shale Member (Lower Palaeozoic source rocks), consistent with the findings of a previous study by Hallett, [34] who confirmed that the Lower Palaeozoic is the main hydrocarbon source. A dominance of C_{29} steranes over C_{27} and C_{28} (Table 2) and the relative abundances of the three isostere groups is roughly 50% C_{29} , 30% C_{27} and 20% C_{28} , typical features for a Lower Palaeozoic sourced oil. Carbon isotope ratio ($\delta^{13}\text{C}\%$) data is presented in Table 2. The oils are isotopically light, characteristic of oils sourced from Lower Palaeozoic rocks and a cross-plot of stable carbon isotope ratios for the alkane fraction vs.data for the aromatic fractions of the oils shows a relatively tight cluster demonstrating the similarity of source material as it is extremely obvious in Fig. 3. Ternary variation diagrams of C_{27} , C_{28} & C_{29} isosterane composition can be used as correlation parameters, where all oils showed a plot in a close cluster potentially indicating a uniform source faces. The relative abundances of the three isostere groups are approximately 50% C_{29} , 31% C_{27} and 19% C_{28} , typical values for a Lower Palaeozoic sourced oil (Fig. 4).

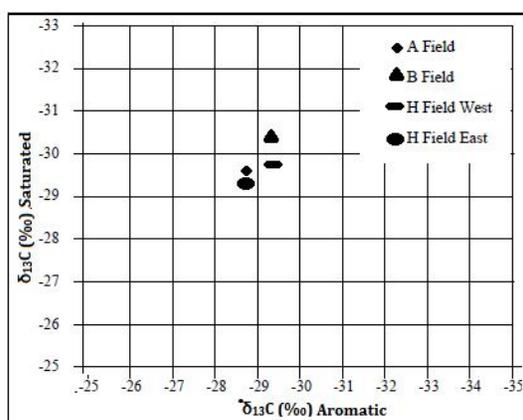


Fig. 3. Cross plot of $\delta^{13}\text{C}$ values of saturated and aromatic hydrocarbon fractions of selected oils

3.4 Organic Matter Precursors

Both tricyclic terpenes and hopanes considered to be the most significant petroleum compounds

that reserved characteristic structure of the original biological components and commonly used to delineate organic matter precursors. The tricyclohexaprenol have been suggested as precursors of the tricyclic terpenes series [17,7]. Hopanoids are biological precursor have been known as crucial compounds of metabolites in prokaryotic cell membranes [22,23]. distributions of tricyclic terpenes and hopanes show the massive similarity between the studied petroleum in terms of organic matter source. High relative abundances of C_{23}TT and C_{30} hopane (Table 2)are typically derived from mixed precursor source within different ratios, more likely tricyclohexaprenol and bacterio hopane polyols and amino polyols, existed as mixture biomarkers of tricyclic terpenes and hopanes. The ratio of C_{28} to C_{29} regular steranes is a function of geological time due to evolutionary changes in photosynthetic organisms, where quantifiable for the oils (Table 2). The $\text{C}_{28}/\text{C}_{29}$ regular sterane ratio gives values characteristic of Lower Palaeozoic marine source rocks and holding green algae and probably a quantity of contribution from acritarchs.

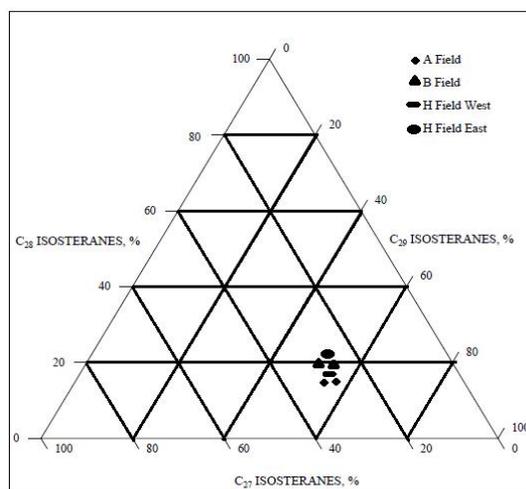


Fig. 4. Ternary variation diagrams of C_{27} , C_{28} and C_{29} isosteranes, showing a uniform source faces

3.5 Depositional Environment

The carbon preference indices (CPIs) measure the ratio of alkanes with an abnormal number of carbon atoms to those with an even number. The CPIs Values <0.9 suggest rapid deposition into an anoxic environment, associated with very salty carbonate and evaporate saline

environments [38,39]. The studied oils have consistent CPIs (Table 2) within Values <0.9, indicating an exception of salty carbonate and evaporate saline deposition. Dibenzothiophene to phenanthrene (DBT/P) ratio is as well related to depositional environment pointer (Table 2). According to [15], the DBT/P and Pr/Ph ratios of crude oils can be used to identify their source lithofacies. The DBT ratios with range (0.49 - 0.58) are approximated indicating a similar source for organ organic matter, suggest a siliciclastic source rather than carbonate and demonstrate to have originated from marine shale deposited under sub-anoxic conditions (Fig. 6). The oils related to depositional organisms were derived from a mix of prokaryotic and eukaryotic. This, where partial mass chromatograms showing convergent distributions of tricyclic and tetracyclic terpenes and hopanes (m/z 191) and steranes (m/z 217) for oils (Fig. 7).

3.6 Biomarkers as an Indication of Organic Matter Maturity

The amount of lower n -alkanes (C_{16} to C_{22}) against the amount of higher carbon number n -alkanes (C_{23} to C_{33}) (Fig. 8). Values of bias increase with maturity and these results indicate the oils analysed are mature. further confirmed via the pristane/ n - C_{17} and phytane/ n - C_{18} ratios, show consistent results of high maturity except the B Field oil being slightly less mature than the other oils. The oils of fields A, H (west) and H(east), show consistent values of bias between 2.20 - 2.61 with a mean of 2.40. The B Field oil

shows the lowest value of bias (1.88), indicating it is the least mature of selected oils. This consistent with a biomarker of C_{27} trisnorhopane ratio (Ts/Tm) $h_{27} s/h_{27} m$ (m/e 191) which typically increases with increasing maturity [24]. The Ts/Tm ratio is considerably lower in the oil from the B Field (1.20) than those from the other fields (Table 2), indicating that the oil from B Field is less mature than the other three oils. The dihopanes are rearranged hopanes, with the C_{30} homologue having the structure 17a(H)-15A-methyl-27-norhopane, thermally more stable than regular hopanes and Ratio of C_{30} diahopane/ C_{30} hopane raises with increasing maturity [40]. In the oils of A, H (east) and H (west) fields, the C_{30} diahopane/ C_{30} hopane ratios show consistent results of high maturity while B Field oil (0.13) shows lower than the other oils (Table 2). Aromatic biomarkers such as naphthalene compounds (methyl naphthalene, dimethyl naphthalenes, trimethyl naphthalene) have been suggested as strong maturation indicators [41,42,29,43,44]. Results of aromatic fraction gas chromatography-mass spectrometry (Fig. 9) are presented in Table 2. The ratios of methyl naphthalene, dimethyl naphthalene and trimethyl naphthalene (236 TMN/146,135 TMN) are certainly increasing through increasing maturity while a second trimethyl naphthalene ratios (125 TMN/136 TMN) reduces with increasing maturity. The results show that the B Field oil is considerably less than the other three oil results, all four trimethyl naphthalene consistently show the B Field oil to be the least mature of the four oils.

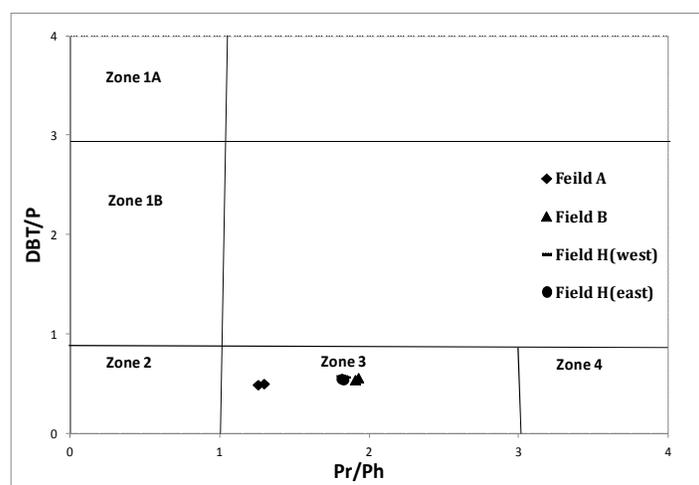


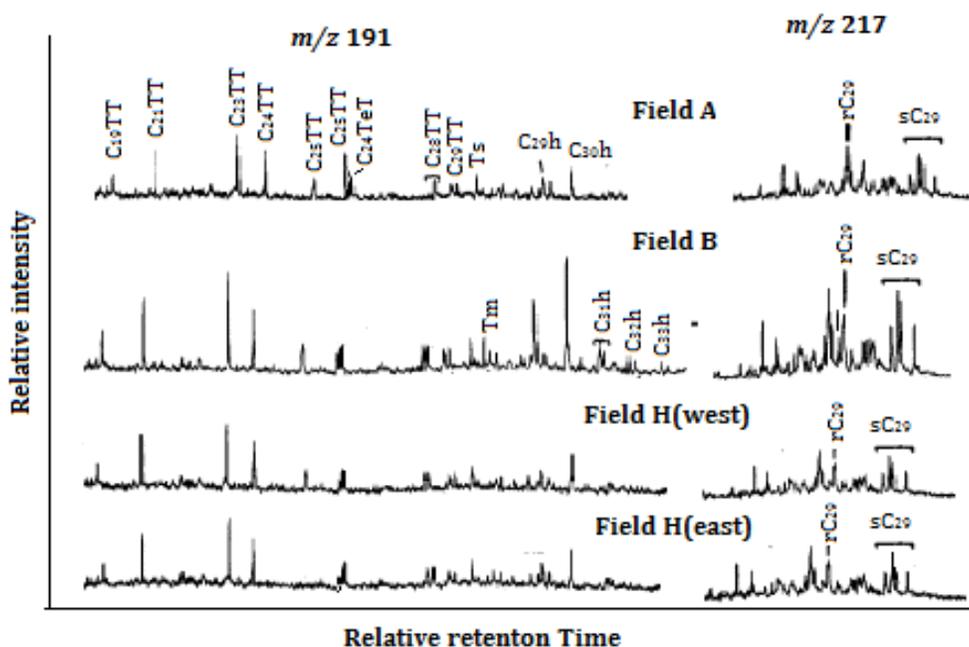
Fig. 6. The cross-plot of DBT/P versus pristane/phytane (Pr/Ph) for crude oils showing the source rock depositional environments and lithologies

Zone 1A = marine carbonate; Zone 1B = marine carbonate and marl; Zone 2 = marine hypersaline; Zone 3 = marine shale and lacustrine; Zone 4 = fluvio-deltaic shale [15]

Table 2. Geochemical data for selected oils from the Basin

component	Field A		Field B		Field H(west)		Field H(east)	
<i>n</i> -C ₁₉ (%)	7.2	7.2	6.7	7.72	6.4	6.4	6.8	6.9
C ₂₇ S (%)	30.1	30.0	31.8	32.8	30.3	n.d.	30.1	n.d.
C ₂₈ S (%)	19.0	19.2	20.1	21.0	19.0	n.d.	19.0	n.d.
C ₂₉ S (%)	50.9	50.8	48.1	46.2	51.7	n.d.	50.9	n.d.
C ₂₃ TT (%)	59.9	n.d.	39.4	n.d.	57.4	n.d.	63.9	n.d.
C ₃₀ αβ (%)	40.1	n.d.	60.7	n.d.	42.6	n.d.	36.1	n.d.
rC28 (%)	n.d.	25.6	n.d.	26.2	n.d.	25.3	n.d.	26.1
δ ¹³ C (‰)	Sat	Aro	Sat	Aro	Sat	Aro	Sat	Aro
	-29.55	-28.71	-30.37	-29.24	-29.51	-28.80	-29.82	-29.11
DBT/P	0.49	0.50	0.56	0.54	0.57	0.58	0.54	0.55
CPI	1.00	1.01	0.99	0.99	1.00	1.00	1.09	1.10
Pr/Ph	1.26	1.30	1.93	1.91	1.84	1.82	1.83	1.82
Ts/Tm	4.72	n.d.	1.20	n.d.	4.60	n.d.	3.25	n.d.
dh30/h30	0.57	n.d.	0.12	n.d.	0.42	n.d.	0.55	n.d.
2MN/1MN	1.58	n.d.	1.56	n.d.	1.66	n.d.	1.76	n.d.
26,27DMN/15DMN	8.65	n.d.	3.53	n.d.	8.11	n.d.	7.80	n.d.
236TMN/146,135TMN	1.30	n.d.	1.02	n.d.	1.09	n.d.	1.20	n.d.
125TMN/136TMN	0.05	n.d.	0.10	n.d.	0.06	n.d.	0.06	n.d.

n-C₁₉ (%) = *n*-C19 alkane, C₂₇S (%) = s27b/(s27b+s28b+s29b), C₂₈S (%) = s28b/(s27b+s28b+s29b), C₂₉S (%) = s29b/(s27b+s28b+s29b), C₂₃TT (%) = C₂₃ tricyclic terpene/C₂₃ tricyclic terpene+C₃₀ 17a hopane, C₃₀αβ (%) = C₃₀ 17a hopane/C₂₃ tricyclic terpene+C₃₀ 17a hopane, rC₂₈ (%) = (r28d,c)/(r27d,c+r28d,c+r29d,c), δ¹³C(‰)PeeDeeBelemnite, DBT/P(dibenzothiophene/phenanthrene), CPI(carbon preference indices), Pr/Ph(Pristane/Phytane), Ts/Tm(C27 18a-22,29,30-trisnorhopane/C27 18a-22,29,30-trisnorhopane), dh30/h30(), 1MN(methylnaphthalene), 2MN (methylnaphthalene), 26-27DMN(2,6-dimethylnaphthalene & 2,7-dimethylnaphthalene), 15DMN (1,5-dimethylnaphthalene), 236TMN(2,3,6-trimethylnaphthalene), 146-135TMN(1,4,6-trimethylnaphthalene&1,3,5 trimethylnaphthalene), 125TMN(1,2,5-trimethylnaphthalene), 136TMN(1,3,6-trimethylnaphthalene)



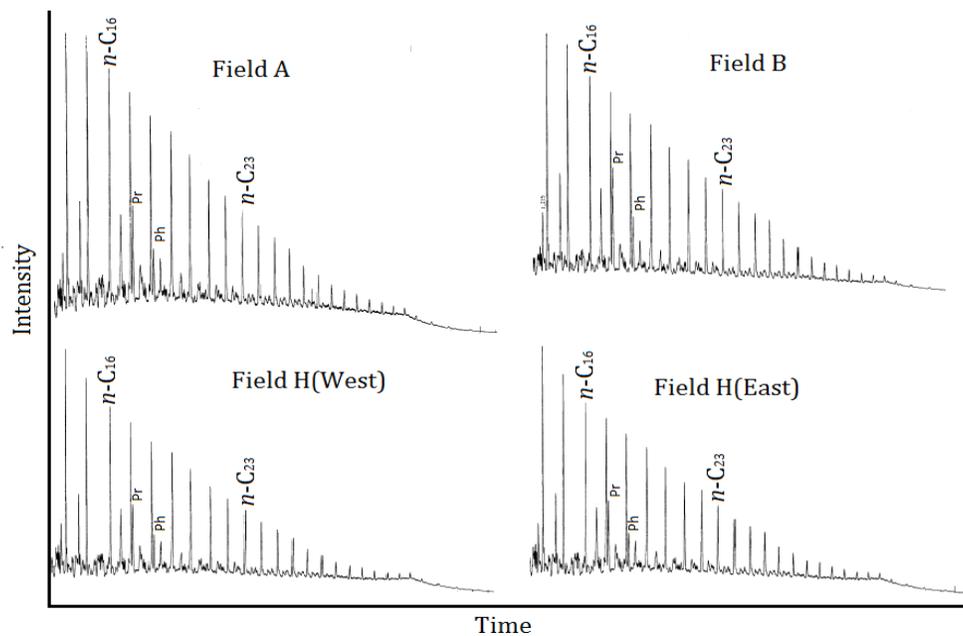


Fig. 8. Partial mass chromatograms showing distributions of Alkane component gas chromatograms

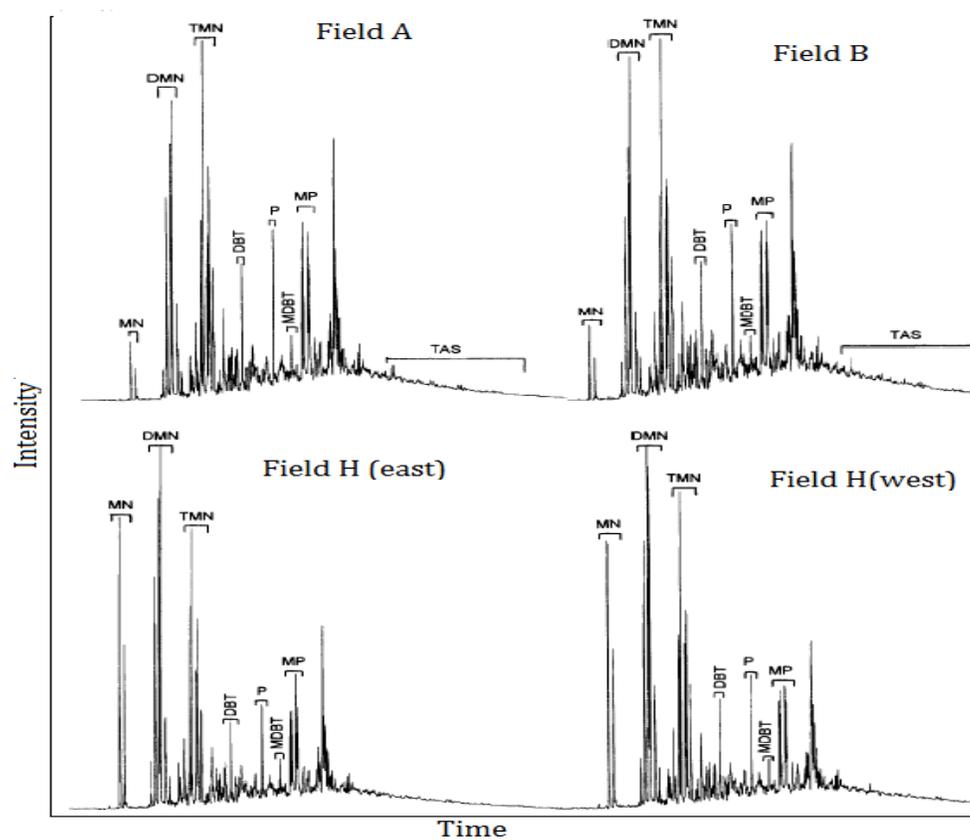


Fig. 9. Aromatic fraction GC-MS reconstructed ion chromatogram

4. CONCLUSION

The main conclusion of this study are:

1. Oils showed non-biodegradation, on the base of their high relative profusion of *n*-alkanes, isoprenoids, terpenes, steranes and aromatic.
2. The alkane *n*-C₁₉ peak, a dominance of C₂₉ over C₂₇ and C₂₈ steranes and light carbon isotope revealed that studied oils are sourced from Lower Palaeozoic facies
3. Tricyclic terpenes and hopanes biomarkers are evidence of tricyclohexaprenol and bacterio hopane polyols and amino polyols precursors.
4. All samples dropped in zone 3 as the siliciclastic environment and revealed marine shale deposited under sub-oxic conditions.
5. On the base of the biomarkers as an indication of organic matter maturity, all oils sourced from a mature source rock with the exception of the B Field oil, showed the lower source maturity.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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