Biogeochemical Analyses of Four Crude Oil Samples to Confirm the Presence of Terrestrial-organic Matter, Collected from the Murzuq Basin- Libya

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Authors' contributions

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

Article Information

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ABSTRACT

The Murzuq Basin, in Southwestern Libya, is one of Libyan's most productive petroleum basins, with reserves estimated at 23 billion barrels recoverable of hydrocarbon equivalent within giant oil fields. Four crude oil samples collected from A1-NC186, E1-NC101, E2-NC101, H10-NC115 wells from Murzuq Basin, Libya, were suggested for bulk analysis and physical proprieties, alkane distribution and isoprenoids and the hopane, tricyclic terpane and sterane distributions of the oils, to confirm the presence of non-marine organic matter sources and/or any evidence of its existence. The oils show no significant variation in the ratios of the carbon, hydrogen, nitrogen and sulfur content (CHNS) composition. All samples recorded high to very high API° gravity, ranges 33.8 to 40.3; the sulfur values ranged from 0.31 to 0.45%, the wax ratio in crude oils is showing a great variety, E1-NC101and E2-NC101 oils show higher wax content, ranging from 6.1 to 6.7%. Pristine

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to Phytane ratios (Pr/Ph) range from 1.61 to 2.22 and the Pr/n-C17, Ph/n-C18, n-C17/n-C27 and CPI values determined as indicators of the depositional environment of the crude oils. The data of search confirmed that the crude oils were derived from marine, mixed and terrestrial sediments.

1. INTRODUCTION

The Murzuq Basin, in southwestern Libya, is one of the Libyan most productive petroleum basins and the Africans largest petroleum province, with reserves estimated at 23 billion barrels recoverable of hydrocarbon equivalent within giant oil fields and 23relatively large oil fields [1]; Fig. 1. A series of published research was carried out over the past few years based on the use of modern geochemical technic. The manuscripts revealed many characteristics regarding ancient environments and the prevailing ecosystem by analyzing rocks and crude oil. Geochemical characteristics of six rock formations were studied based on organic geochemical parameters from the Murzuq Basin [2]. The study detected that the most rock kerogen is type II with a slight of Kerogen Type III in the mature situation, generating and expel liquid of hydrocarbons. Aromatic hydrocarbon ratios also revealed different levels of thermal maturity between studied formations, where hot shale (Lower Silurian) showed high aromatic content, pointed to a high level of thermal maturity whereas the rest formations showed low aromatic hydrocarbon, reflected their marginal thermal maturity. Further information 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 [3]. In this study, the samples were collected from the A, B, H (east) and H(west) Fields, NC-115. The main conclusion of the oil investigations was unremarkable biodegradation, a relative profusion of *n*-alkanes, isoprenoids, terpanes, steranes and aromatic, a dominance of C_{29} over C_{27} and C_{28} steranes and light carbon isotope. The results have suggested that the marine shale source rocks of Lower Palaeozoic facies deposited under sub-oxic conditions and all oils were sourced from a mature source rock with the exception of the B Field oil that showed the lower source maturity. An another search achieved by [4], based on geochemical parameters of TOC, RockEval analysis, detailed-various biomarkers and stable carbon isotope of source rock and crude oils assembled from a number of basin concessions. This study was to confirm if their further hydrocarbon accumulations from extra sources. The results confirmed that the hot shale facies at the base of the Silurian Tanezzuft Formation as the principal source rock in addition to contribution of the Paleozoic Devonian, Carboniferous strata and possible Ordovician facies was predictable. Slight amount of phytoclasts and palynomorphs was distinguished, pointed to deposition of non-marine sources. Trailed by study was to evaluate organic matter type, and thermal maturity based on geochemical parameters of Silurian Tanezzuft and Devonian Awaynat Wanin Formations from northern edge of the Basin [5]. The results of this paper were consistent with the above studies in terms of organic matter characteristics and it proposed mainly marine kerogen type II as the source of organic matter, even though kerogen II/III organic matter was notable. The series of research published over the last few years (cited above), encouraged our team to confirm the presence of non-marine organic matter sources and/or any evidence of its existence.

1.1 Regional Tectonic Setting

The Murzuq Basin is one of several intracratonic basins of North Africa, covers an area of over 350000 km2, and it is sedimentary fill reaches a maximum thickness in the basin center of about 4000 m, including a predominantly marine Palaeozoic sector covered by a continental Mesozoic section [6]. The present borders of the Murzuq basin have been delimited by tectonic uplifts and the actual structural framework is a consequence of the cumulative tectonic movements ranging from Palaeozoic through to Tertiary times. The basic tectonic events are related to the Caledonian (late Silurian-early Devonian), Hercynian (end Carboniferous-Permian) and Alpine (early Tertiary) orogenies. Though the contemporary arranging is related mostly to Hercynian compressional movements and the later tectonic activity, the regional lineaments (NW-SE) are probably related to late Precambrian Pan-African fault systems, which largely controlled the early Palaeozoic structural and deposition evolution of this basin [7].

1.2 Stratigraphy

The stratigraphic column in the Murzuq Basin comprises deposits that range from the Precambrian to the Quaternary and a acoustic basement comprises Precambrian meta sediments. It is covered by Cambrian fluvial and braid plain quartzite of the Hasawnah Formation and covering Lower Ordovician Ash Shabiyat Formation that represented by similar facies while the conformable Middle Ordovician, Hawaz Formation. The Upper Ordovician Shuqran and Mamuniyat Formations felt the incised valleys and rest uncomfortably on the Hawaz Fm. The Shuqran Formation.the Lower Silurian

Tanezzuft Formation (shales) deposited in restricted to open marine conditions present organic-rich shale levels at the base termed "hot shales" that constitute the main source rock for the area (REF). The Tanezzuft Formation grades up into the overlying Acacus Formation that is generally absent in the sub-surface due to truncation. Overhead, the Devonian Tahara Formation is represented by sequences of shales, sandstones and minor carbonates. Lower Carboniferous Marar Fm., comprising deltaic and shallow marine shales with inter-bedded sandstones. It is overlain by lagoonal mudstones and algal limestones of the Colonia Beds and
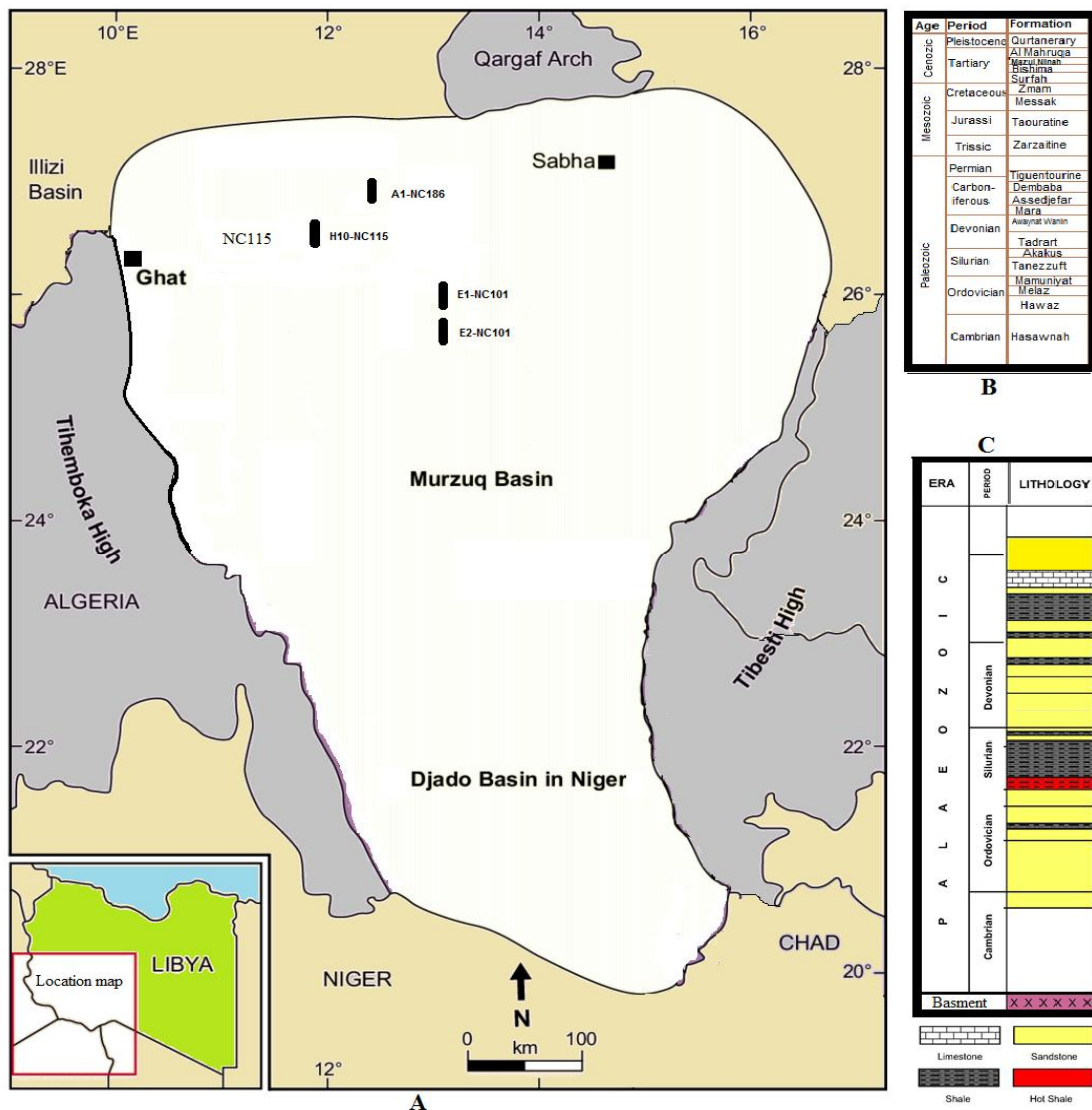

Fig. 1. (A) The location map of the studied wells, (B) The stratigraphic column and (C) The lithologies of the formations in the murzuq basin. modified from [2,3,4,5]

these represented by the Assedjefar Formation, which covering by a final widespread marine transgression (Dembaba Formation). The superimposing continental red-bed structure, include Upper Carboniferous (Stephanian) at the base but comprises mainly Triassic, Jurassic, and Cretaceous sediments. The finally fills are Quaternary, that recent aeolian dune sands and alluvium cover large parts of the basin [6,7,8,9,10].

2. MATERIALS AND METHODS

2.1 Samples

Four Crude Oil Samples Collected from A1-NC186, E1-NC101, E2-NC101, H10 NC115 to search for the presence of non-marine organic matter, Murzuq Basin, Libya.

2.2 Crude Oil Fractionation

The detailed materials and analysis methods were introduced in the series of published articles [2,3,4,5]. Briefly, the oil samples were separated into saturated, aromatic and polar fractions and analyzed by gas chromatography-mass spectrometry (GC-MS). 10 to 20 mg of crude oil was applied to the top of a small column (5.5 cm x 0.5 cm i.d.) of activated silica gel (120ºC, 8 h). The aliphatic hydrocarbon (saturated) fraction was eluted with n-pentane (2 mL); the aromatic hydrocarbon fraction with a

Fig. 2. Photos of the testing laboratory and crude oil samples were taken from the national oil corporation (NOC)

mixture of n-pentane and 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 Gas Chromatography-mass Spectrometry (GC-MS)

A Hewlett Packard (HP) 5890 mass-selective detector (MSD) interfaced with an AMS 92 gas chromatograph (GC) was used to analyses Aliphatic 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. Selected ion monitoring mode (SIM GC-MS), the mass the spectrometer is tuned to a selected number of certain m/e values, which are diagnostic of the specific biomarker compounds such terpanes, steranes, and aromatic compounds.

2.4 Physical Properties

The elemental (CHNS) composition, wax content, API gravity, and kinematic viscosities at 25ºC, 40ºC, and 60ºC of the oil samples, were determined by the staff of the National Oil Corporation (NOC).

3. RESULTS AND DISCUSSION

3.1 Bulk Analysis and Physical Properties of Crude Oils

The composition of oil contents is used to define the physical and chemical properties of oil such as oil density, oil viscosity, water-solubility, evaporation average, and emulsion-forming potential among others. The quantitative definition of bulk composition for crude oil is the first-geochemical step in the study, taking up for the crude petroleum description. In the studied crude oils, the carbon, hydrogen, nitrogen and sulfur content (CHNS) composition, wax content, API gravity, kinematic viscosities at 25ºC, 40ºC, and 60ºC, were analyzed (Table 1). The oils show no significant variation in the ratios of CHNS, while the API° gravity as the reverse of exact gravity and a label of oil proprieties such as light oil, medium, heavy and/or extra heavy oil. This indication has been used to determine the

commercial importance and the market value of crude oils. All samples have high to very high API° gravity, ranges 33.8 to 40.3 point to light oil and high-quality. The sulfur content of the studied crude oil samples is approximately identical. The values ranged from 0.31 to 0.45%, reflecting the low percentage of sulfur compounds in sweet crude oils, as containing less than 0.5% sulfur. The wax ratio in crude oils is showing a great deal of variety. The two oil samples from E1-NC101and E2-NC101 show higher wax content, ranging from 6.1 to 6.7%, indicating their increased waxiness compared with the other oils and may suggesting deposition in a restricted distal marine environment removed from active sources of terrestrial organic matter. Crude oil's viscosity can vary from a low-viscosity liquid to up to tar-like, closely solid procedure, rendering to the API degree (Table 1). This is supported by [4], who indicated Type II oil-prone kerogen of Tanezzuft Formation (Hot shale member), contains 80% amorphous organic matter and minor quantities of phytoclasts and palynomorphs.

3.2 Alkane and Isoprenoid Distribution

The *n*-alkane and isoprenoid are the main components in the saturated hydrocarbon portion. The *n*-alkanes hold abundant information about organic matter characteristics of oil such as oil thermal maturity, biodegradation, source rock organic-matter type and depositional conditions [11,12]. The Gas chromatogram of saturated of a representative crude oil sample is presented in Fig. 2. The *n*-alkanes extended to *n*-C_{33}or more are notable in the chromatograms with low molecular weight *n*-alkanes (<*n*-C12) were detected for all samples, as indication of evaporative defeat during oil sample processing.

A number of ratios of *n*-alkanes and isoprenoids to n-alkanes were calculated for instance the Pr/Ph, Pr/*n*-C_{17}, Ph/*n*-C_{18}, n-C_{17}/n-C_{27} and CPI (Table 2). Pr/Ph ratios have been used as indicator of the depositional environment of the crude oils [11,12]. In representative crude oil samples, a high Pr/Ph values which ranges from 1.61 to 2.22, suggest these oils are derived from marine source rock with a significant contribution of terrigenous source affinity, deposited in anoxic Pale-ecosystem. Data of Table 2 and a plot of Pr/*n*-C_{17} against Ph/*n*-C_{18} are responsible parameters of source, maturation, migration and biodegradation, categorized oil samples in different distribution Fig. 3. The values of Pr/*n*-C_{17} and Ph/$_n$-C_{18} are less <1, which revealing of

non-biodegraded oils, indistinguishable with Aboglila et al. 2019. The Pr/n-C$_{17}$, Ph/n-C$_{18}$ and n-C17/n-C27ratios as well have been extensively used as pointers of source types, depositional environments [13,14]. All samples placed in mixed organic matter sector with direction up to non-marine organic matter where fallen E1-NC 101 oil, suggesting sources of terrestrial organic matter contribution (Fig. 3). Carbon Preference Index (CPI) is maturity indicator [14]. The studied oils were > 1, consistent with their oil-window maturities listed in Table 2.

3.3 Tricyclic Terpanes, Hopanes and Steranes

Fractional mass chromatograms are viewing distributions of tricyclic and tetracyclic terpanes and hopanes (m/z 191) and steranes (m/z 217) for various oils (Fig. 4). The hopane, tricyclic terpane and sterane distributions of the oils are far from constant, appearing variances in the origin of their organic matter. In the E1-NC1010, There a relative abundance of C$_{27}$, C$_{28}$ and C$_{29}$ regular steranes and tetracyclic terpanes and
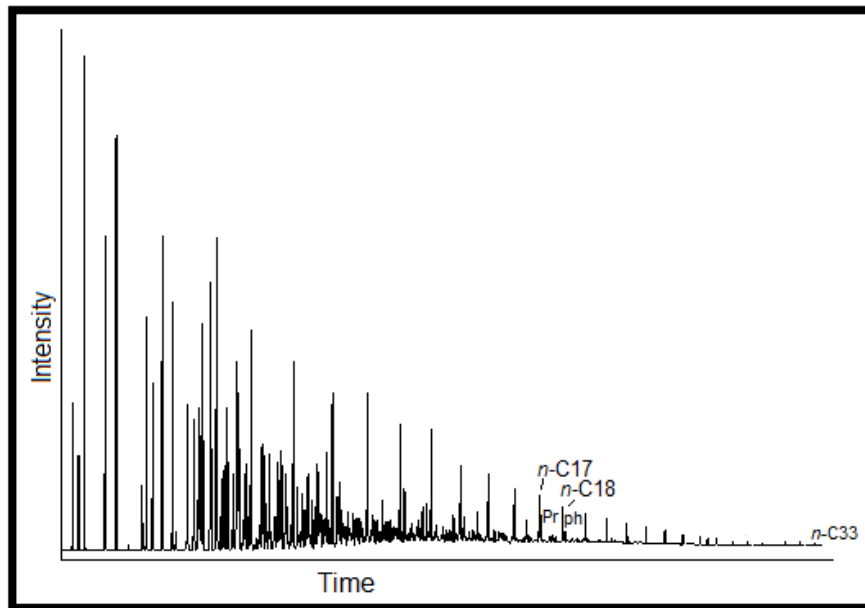

Fig. 3. Gas chromatogram of saturated fraction from A1-NC186 well
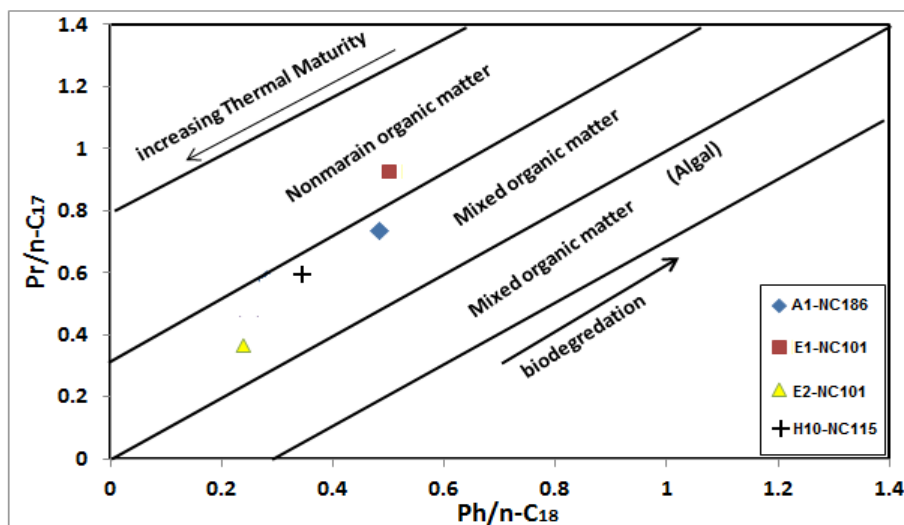

Fig. 4. A plot of Pr/n-C17 against Ph/n-C18 display source and depositional environments [17]

Table 1. Data of physical properties and bulk composition of oil samples

Well	C %	H %	N %	S %	Wax%	API	Viscosity		
							25ºC	40ºC	60ºC
A1-NC186	86.29	13.16	0.24	0.31	1.8	39.5	2.8cst	2.4cst	1.9cst
E1-NC101	86.01	13.55	0.10	0.34	6.7	33.8	16.9cst	9.7cst	6.4cst
E2-NC101	85.72	13.73	0.14	0.41	6.1	36.5	7.0cst	4.7cst	3.4cst
H10-NC115	85.85	13.33	0.27	0.45	1.2	40.3	3.0cst	2.2cst	1.9cst

Table 2. N-alkanes and isoprenoids parameters computed from GC data

Well Name	Pris/Phyt	Pris/n-C_{17}	Phyt/n-C_{18}	n-C_{17}/n-C_{27}	CPI
A1-NC186	2.22	0.63	0.45	14.69	0.99
E1-NC101	1.98	0.67	0.41	5.49	1.02
E2-NC101	1.61	0.33	0.26	6.93	1.02
H10-NC115	2.27	0.55	0.37	10.80	1.00
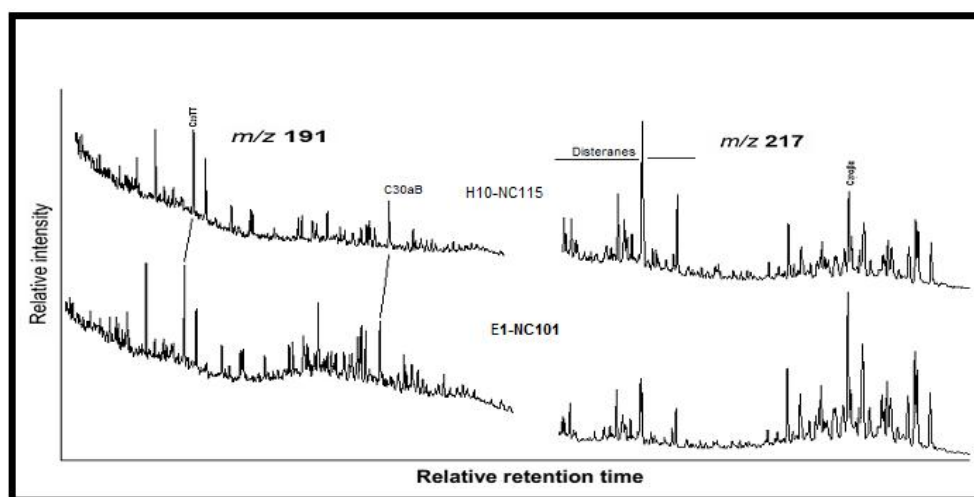
Fig. 5. Distributions of tetracyclic terpanes and hopanes (m/z 191) and steranes (m/z 217) for H10-NC115 and E1-NC101

Hopanes vary depending on the contributions of marine or lacustrine phytoplankton, green algae and/or land plants to their oil sources [15,16]. The different chromatograms of these biomarkers are in agreement with the findings of the above parameters in terms of the original organic matter source variation.

4. CONCLUSION

The determined CHNS, API gravity, sulfur percent, wax, and viscosities were classified all the oils as light crude oils, derived from a marine with trending to notable raise of wax % in studied oils obtained from NC101 wells, as an indication of mixed organic sources to the dominance of lacustrine sources. Normal alkane distribution and isoprenoids confirmed that the crude oils derived from mainly marine, mixed and terrestrial origin. The hopane, tricyclic terpane and sterane distributions of the oils are inconsistent, confirming variances in the origin of their organic matter sediments. The results of this study support the conclusions of the series of research published over the last few years around this region. Narration results and discussion have confirmed a strong variation within previous studies in terms of different sources of sediment, involved the marine organic matter, non-marine organic matter and mixed organic matter that extensively distinguished in the series of research published around the basin.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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