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Petroleum Geochemistry Regional Study of Murzuq Basin: Insights from Biomarkers Characteristic, Stable Carbon Isotope and Environmental Characterization

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Abstract

This search aims to apply developed geochemical methods to a number of oils and source rock extracts to better establish the features of ancient environments that occurred in the Murzuq basin. Geochemical and geophysical approaches were used to confirm further a source contribution from other Paleozoic formations to hydrocarbon accumulations in the basin. One hundred and forty rock units were collected from B1-NC151, D1-NC174, A1-NC 76, D1-NC 151, F1-NC58, A1-NC 186, P1-NC 101, D1-NC 58, H1-NC58 and A1-NC58 wells. Seven crude oils were collocated A1-NC186, B1-NC186, E2-NC101, F3-NC174, A10-NC115, B10-NC115 and H10-NC115 wells. A geochemical assessment of the studied rocks and oils was done by means of geochemical parameters of total organic carbon (TOC), Rock-Eval analysis, detailed-various biomarkers and stable carbon isotope. The TOC values from B1-NC151 range 0.40% to 8.5%, A1-NC186 0.3% and 1.45, A1-NC76 0.39% to 0.74%, D1-NC151 0.40% to 2.00% to F1-NC58 0.40% to 1.12%. D1_NC174 0.30% to 10 %, P1-NC101 0.80% to 1.35%, D1-NC58 0.5% to 1.10%, H1-NC58 0.20% to 3.50%, A1-NC58 0.40% to 1.60%. The categories of organic matter from rock-eval pyrolysis statistics point to that type II kerogen is the main type, in association with type III, and no of type I kerogen recognized. Vitrinite reflectance (%Ro), Tmax and Spore colour index (SCI) as thermal maturity parameters reflect that the measured rock units are have different maturation levels, ranging from immature to mature sources. acritarchs distribution for most samples could be recognized and Palynomorphs are uncommon. Pristane to phytane ratios (> 1) revealed marine shale to lacustrine of environmental deposition. The Stable carbon isotope ($\delta^{13}C$) values of seven rock-extract samples are -30.98‰ and -29.14‰ of saturates and -29.86‰ to -28.37‰ aromatic fractions. The oil saturate hydrocarbon fractions range between -29.36‰ to -28.67‰ and aromatic are among -29.98 ‰ to -29.55 ‰. The $\delta^{13}C$ data in both rock extractions and crude oils are closer to each other, typical in sign of Paleozoic age. It is clear that the base of Tanezzuft Formation (Hot shale) is considered the main source rocks. The Devonian Awaynat Wanin Formation as well locally holds sufficient oil prone kerogen to consider as potential source rocks. Ordovician Mamuniyat Formation shales may poorly contain oil prone kerogen to be addressed in future studies. An assessment of the correlations between the oils and potential source rocks and between the oils themselves indicated that most of the rocks extracts were broadly similar to most of the oils and supported by carbon stable isotope analysis results.

Keywords: Murzuq Basin; Biomarkers; Crude Oils; Source Rocks; Hot Shale

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Introduction

Oil exploration in Murzuq basin began in 1957 and has recently became the focus of petroleum exploration efforts in the most of region. While numerous discoveries were completed in many portions of the basin however the rest of the basin remains typically needs more studies. Such as, lack in information on the basin-wide parameters of the petroleum systems acting in the area by Hallett D [1]. The basin-wide understanding in relation to improvement of knowledge on the provincial aspects of the petroleum geochemistry of Murzuq Basin, in particular the assessment of petroleum systems, the potential and distribution source rocks characteristics. Thermal maturity and source quality in selected oil wells from Murzuq Basin described in study by Archer R [2]. Stratigraphic report and hydrocarbon potential of the of Silurian shale of the Paleozoic Tanezzuft Formation reported by Aziz A [3] as well the geological aspect and hydrocarbon occurrences in the Basin was published [4]. In study of geochemical analysis and thermal history modeling of concession NC174 in Murzuq Basin illustrated that the hot shale facies at the base of the Silurian Tanezzuft Formation as the principal source rock [5]. The hot shale is distinguishing in the subsurface data by Aboglila S, et al. [6], the most rock Kerogen is type II, the Hot Shale Member (Lower Silurian) at the base of the Tanezzuft Formation is a high quality, oil source rock which is currently at oil maturity and has not yet gone in the gas window in addition to Vitrinite Reflectance (% Ro) and Spore Coloration Index (SCI) of the Hot Shale Member, indicted that the hot shale is higher maturity than other sediments. Trailed by oil geochemical search published by Aboglila S, et al. [7], revealed non-biodegradation in all examined crude oils, alkane n-C19 peak, a dominance of C29 over C27 and C28 steranes and light carbon isotope that studied oils are sourced from Lower Palaeozoic facies. This study presented that the depositional environment of studied oils is marine shale deposited under sub-oxic conditions. Studies by Aboglila S, et al. [7] in NC115, confirmed that the Tanezzuft formation includes organic–rich shale facies (Hot Shale) have fair to very good source potential. However, in the region possible hydrocarbon contribution from the Upper Devonian Awaynat Wanin Formation and the Lower Carboniferous Mrar Formation to organic matter accumulations in Murzuq basin, due to high values of maturity parameters such Tmax, Ro%, SCI and elevated values of TOC in addition to Dark-grey shale lithology were established [6]. The present paper is petroleum geochemistry regional study involves numbers of concessions in the Murzuq Basin. This search aims to apply developed geochemical methods to a number of oils and source rock extracts to better establish the features of ancient environments that occurred in the basin. Both individual components and their relative contributions to the overall composition of the oils and rocks will be established. Geochemical parameters of TOC, Rock-Eval analysis, detailed-various biomarkers and stable carbon isotope of source rock and crude oils will be delineated to confirm further contributions from another Paleozoic formations to hydrocarbon accumulations in the basin and to improve understanding on the regional characteristics of the petroleum geochemistry in particular source rocks assessment, distribution, quality, modeled maturity and oil-source rocks correlations.

Geological Setting

The Murzuk Basin is an intra-cratonic sag basin located inside East Saharan Craton on the Saharan Platform of North Africa and also is one of the three major Libyan basins (Figure 1). The stratigraphic column in the Murzuq Basin comprises deposits range from the Precambrian to the Quaternary age. A basement comprises Precambrian metasediments, overlain by Cambrian fluvial and braid plain quartzite of the Hasawnah Formation [8]. The overlying Lower Ordovician Ash Shabiyat Formation. is represented via similar facies however the conformable Middle Ordovician, Hawaz Formation is characterized by sandy, transgressive-regressive marine sequences through intense bioturbation. The Middle Ordovician is extremely incised due to corrosion, strong low stand. The Upper Ordovician, MelezShuqran and Mamuniyat Formation, fillet the incised valleys and rest on the Hawaz Formation, represented by diamictite and slumped delta front shales in locally present, overstepped by cut cycle of coarsening up marine and fluviodeltaic sediments of the Mamuniyat Formation [1]. The Ordovician unit is truncated at the Taconian, which exhibits paleorelief under transgressed sequence comprising the Lower Silurian Tanezzuft Formation. These sediments deposited in restricted to open marine conditions present organic rich shale levels at the base termed. The Tanezzuft Formation marks up into the overlying Acacus Formation, a regressive unit of fine-grained sandstone that forms a prominent escarpment in outcrop at the western margin of the basin [3]. Above this rock, the Devonian is represented by sequences of shale minor, and carbonates sandstones. Two units termed the Basal Devonian Sands, have been recognized as secondary reservoir objective and separated by regional extensive shale. The Basal Devonian Sands section is overlain and be in part laterally equivalent to the Awaynat Wanin Formation. The latest Devonian (Strunian) Tahara Formation. Lower Carboniferous (Marar Formation), comprising deltaic and shallow marine shales with inter bedded sandstones, likely minor reservoirs at the northern border of the basin [9]. The Marara Formation overlain by inlet mudstones and algal limestone of the Collenia Beds, in turn by the Assedjefar and Dembaba Formations. The over lying continental red-bed sequence contain Upper Carboniferous at the base then mainly Triassic, Jurassic and Lower Cretaceous sediments. Quaternary - Recent Aeolian dune as sands and alluvium cover large parts of the basin [10].
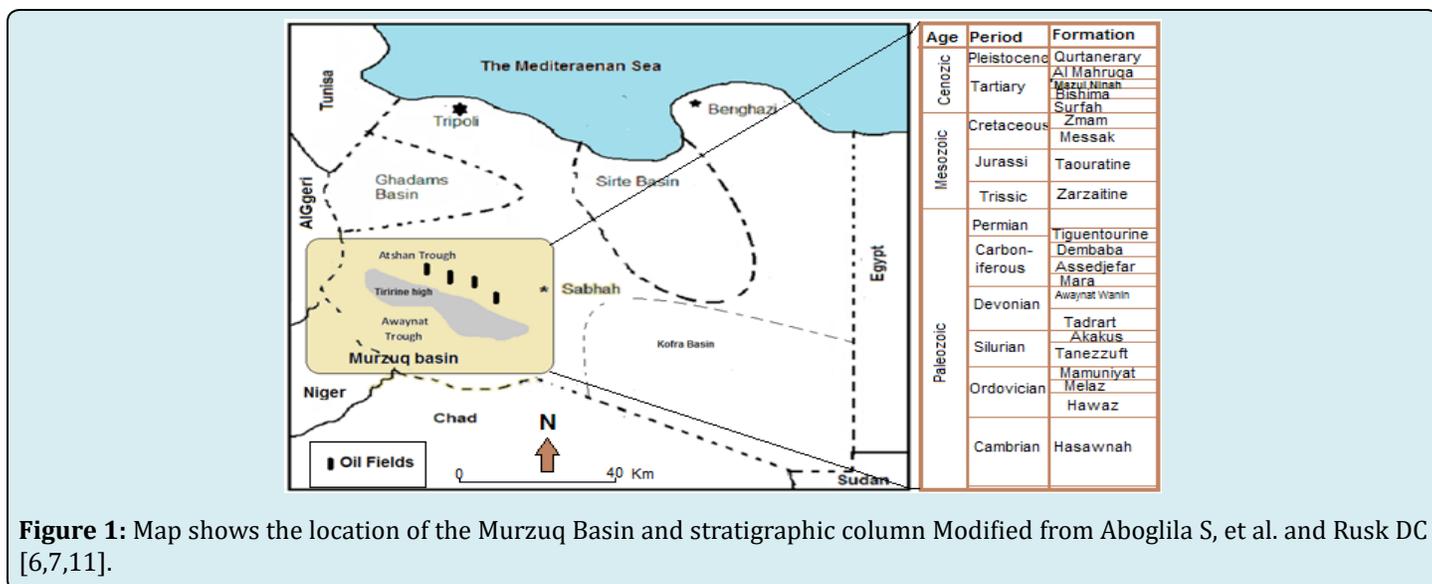
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Figure 1: Map shows the location of the Murzuq Basin and stratigraphic column Modified from Aboglila S, et al. and Rusk DC [6,7,11].

Materials and Methods

Rock Samples

One hundred and forty sediment samples from ten wells in different concessions were collected from Murzuq Basin for total organic carbon (TOC) and Rock - Eval Pyrolysis analyses. Pyrolysis analysis was carried out on samples with total organic carbon (TOC) more than 1 %.

Preparation of Cutting Samples

The cutting samples were thoroughly washed with doubly distilled water and dried at room temperature prior to analysis. Next Rock-Eval pyrolysis and TOC analysis (see below), a suite of representative samples was selected for more detailed organic geochemical analysis. These samples were ground to a fine powder (particle size of <150 μm) using a ring-mill (Rocklabs). Ground samples passed through the sieves were used for analysis.

Microscopy Assessment

Microscopy was used for kerogen typing by palynofacies analysis and spore color index (and acritarchs) measurements. Acritarch color was converted to the spore color equivalents then the Spore Color Index reference slides used in this investigation were labeled based on chart of Collins A [12].

Rock-Eval Pyrolysis and Total Organic Carbon (TOC) Measurements

Rock-Eval pyrolysis of ground cutting (10 - 50 mg) was carried out on a Girdel Rock-Eval instrument, although the TOC was measured on a Leco device. Samples with low TOC values <1.0% were considered unsuitable for Rock-Eval

pyrolysis and therefore not subjected to further analyses.

Solvent Extraction and Isolation of the Maltenes

Seven cuttings samples from representative sediments were selected for solvent extraction based on TOC values. Approximately 10 - 20 g of ground sediment was extracted in an ultrasonic bath for two hours using a 9:1 mixture of dichloromethane (DCM) and methanol (MeOH). The solvent extract was then filtered and extra solvent removed by carefully heating on a sand bath (60 °C) to obtain the bitumen. In brief, about 10 - 20 mg was applied to the top of a small column (5.5 cm × 0.5 cm i.e.) of activated silica gel (120 °C, 8 h) [13]. The aliphatic hydrocarbon (saturated) fraction was eluted with *n*-pentane (2 mL); the aromatic hydrocarbon fraction with a 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).

Gas Chromatography-Mass Spectrometry (GC-MS)

Aliphatic and aromatic fractions were analysed by GC-MS using a Hewlett Packard (HP) 5973 mass-selective detector (MSD) interfaced to a HP6890 gas chromatograph (GC). A HP-5MS (J and W Scientific) GC column (5% phenylmethylsiloxane stationary phase) was used with helium as the carrier gas. In brief, the GC oven was programmed from 40 °C to 310 °C at 3°C/min, after which it was held isothermal for 30 min. Samples were dissolved in *n*-hexane and introduced by the HP6890 auto-sampler into a split-splitless injector operated in the pulsed-splitless mode. Biomarker data were acquired in a full-scan mode (m/z 50 - 500).

GC–Isotope Ratio Mass Spectrometry (GC–IR–MS)

For carbon isotope measurements, a Hewlett Packard

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(HP) 5890 gas chromatograph (GC) with auto sampler was used in tandem with a Micromass isotope ratio mass spectrometer (IR–MS). The $\delta^{13}C$ 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.

Separation–Analysis of Crude Oils

Seven crude oils were collocated and separated into three fractions using a column chromatographic method [13]. 10 to 20 mgs 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 (120ºC, 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 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). The rest steps of oil geochemistry analysis were similar technique above, used with source rocks (sections 3.5, 3.6 and 3.7).

Results and Discussion

The main source rocks in NC 115 and over all Murzuq Basin is the Hot Shale Member (Lower Silurian) at the base of the Tanezzuft Formation is a high level source rock [6,14]. The Tmax of most Carboniferous and Devonian samples dropped in mature side and potential yields exceed 2000 ppm and aromatic hydrocarbon ratios revealed that the Hot shale member high aromatic content at phase of mature whereas rest formations ranged from immature to mature. Furthermore, investigate crude oils samples from same concession, the conclusion revealed the studied oils sourced from Lower Paleozoic facies [7,14]. Based on the dominance of C_{29} over C_{27} and C_{28} steranes and light carbon isotope, all oils sourced from a mature source rock with the exception of the B Field oil, showed the lower source maturity. This pushed up to think for more investigation in further concessions.

Source Rocks

TOC Analyses: One hundred and forty interval samples were analyzed for TOC contents (Table 1). The TOC values from B1-NC151 rocks variety between 0.40 to 8.5 %, A1-NC186 sediments range between 0.3% and 1.45%, A1-NC76 range between 0.39% and 0.74%, D1-NC151 samples have TOC values ranging from 0.40% to 2.00% and F1-NC58 have TOC values ranging from 0.40% to 1.12%. The another wells, D1_NC174 has a TOC ranging from 0.30% to 10 %, P1-NC101 samples range between 0.80% to 1.35%, D1-NC58 samples have TOC range between 0.5% to 1.10% and H1-NC58 sediments have range between 0.20% and 3.50%, while TOC values obtained from the A1-NC58 range between 0.40% to 1.60%. TOC reflects an organic matter riches of sediments estimated typically using the TOC wt%. The TOC value of 1.0% suggested as the lower bound for an effective source sediment, less than 1.0% cannot produce enough oil and commence key migration, while 0.4% point to low source rock potential [15]. Hence, the analytical TOC data indicated the occurrence of a major source rock kitchen is Silurian Tanezzuft Formation particularly hot shale member at the base this formation as the principal source rock for wholly studied fields. Other organic source organic matter occurs in the Tanezzuft shales, the inter bedded Devonian shales (Awaynat Wanin Formation) and Carboniferous shales (Mrar Formation) as a result contain sufficient oil prone kerogen to consider as source rock for hydrocarbon [6,7]. Integrated the TOC values and depth of selected source rock from studied basin fields (Figure 2), showed model construction of the basin and topically point to that the rock kitchens (Silurian Tanezzufdt Formation) were occurred in diverse depths, reflecting line of slop into the basin center. The TOC values for assessing richness of organic matter reveled oil generation potential of studied fields range between poor to excellent (Figure 2).
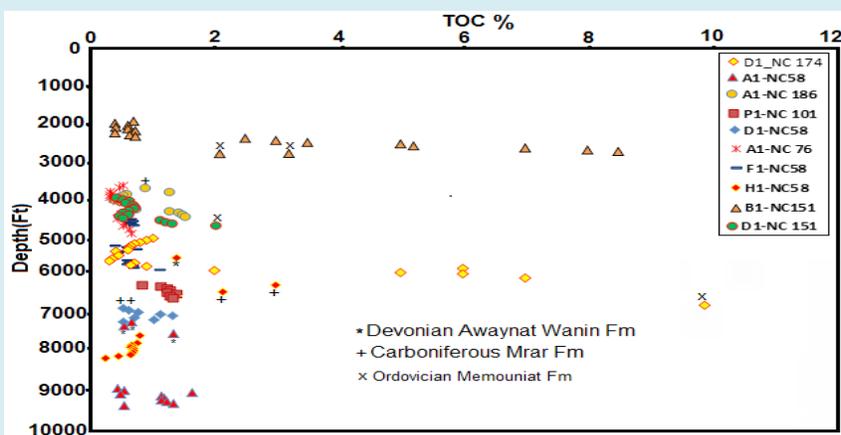

Figure 2: Plot of TOC versus depth for selected source rock collected from the Murzuq Basin.

F1-NC58		D1-NC 151		A1-NC 76		D1-NC174		B1-NC151	
TOC	Depth	TOC	Depth	TOC	Depth	TOC	Depth	TOC	Depth
0.65	4500	0.4	3900	0.6	3550	0.9	5100	0.7	1900
0.68	4550	0.5	3950	0.55	3600	0.8	5150	0.4	1950
0.66	4600	0.61	4000	0.4	3700	0.7	5200	0.61	2000
0.7	4650	0.55	4050	0.42	3750	0.65	5250	0.42	2050
0.4	5200	0.67	4100	0.4	3800	0.62	5300	0.62	2100
0.6	5250	0.7	4150	0.39	3850	0.6	5350	0.73	2150
0.75	5300	0.69	4200	0.45	3900	0.4	5400	0.41	2200
0.46	5350	0.6	4250	0.51	3950	0.45	5500	0.64	2250
0.45	5400	0.5	4300	0.62	4000	0.35	5600	0.73	2300
0.6	5600	0.6	4350	0.67	4100	0.3	5650	2.5	2350
0.63	5650	0.45	4400	0.71	4200	0.7	5700	3	2400
0.6	5700	0.5	4450	0.57	4300	0.65	5750	3.5	2450
0.68	5750	1.1	4500	0.51	4400	0.9	5800	5	2500
0.7	5800	1.2	4550	0.63	4500	6	5850	5.2	2550
1.12	5850	1.3	4600	0.65	4550	2	5900	7	2600
		2	4650	0.6	4600	5	5950	8	2650
				0.7	4700	6	6000	8.5	2700
				0.74	4800	7	6050	3.2	2750[x]
						10	6100[x]	2	2800[x]

A1-NC58		H1-NC58		D1-NC 58		P1-NC 101		A1-NC 186	
TOC	Depth	TOC	Depth	TOC	Depth	TOC	Depth	TOC	Depth
0.75	7200*M	0.8	5750*	0.5	6900[+]	0.8	6250	0.8	3700[+]
0.5	7300*	3.5	6400[+]	0.6	6950[+]	1.1	6300	1.2	3750
1.5	7500*	2	6450[+]	0.75	7000	1.2	6350	0.5	3800
0.4	8950	0.7	7800	1.1	7050	1.25	6400	0.45	3850
0.5	9000	0.61	7850	1.3	7100	1.2	6450	0.4	3900
1.6	9050	0.6	7900	0.68	7150	1.35	6500	0.3	3950
0.44	9100	0.64	7950	1	7200	1.25	6550	0.4	4000
1.1	9150	0.65	8000	0.5	7250	1.3	6600	0.55	4050
1.15	9200	0.63	8050					0.6	4100
1.1	9250	0.6	8100					0.62	4150
		0.4	8150					0.65	4200
		0.2	8200					1.2	4250
								1.35	4300
								1.4	4350
								1.45	4400

Table 1: TOC data for studied rocks from the Murzuq Basin.

Kerogen Type and Environment Description: Data of OI and HI as kerogen parameters measured for the intervals by Rock Eval pyrolysis confirmed fairly diverse values among studied fields (Table 2). Cross plots of hydrogen index versus oxygen index on modified of Van Kravelen DW [16] diagrams for many source rock samples Figure 3. Obviously, most of the kerogen as predominantly type II oil prone kerogen. Characteristically, the values of HI and OI in the cross plot are distributed between the type II and type III kerogen. The kerogen elemental analysis for some representative samples based on Van Kravelen DW [16] diagram is in arrangement with this assessment of the pyrolysis data (Table 2). The base of Silurian Tanezzuft Formation (Hot shale member) naturally holds Type II oil prone kerogen accumulated with

over 80% amorphous organic matter (AOM) and minor quantities of phytoclasts and palynomorphs. This is sign of deposition in a restricted distal marine environment removed from active sources of terrestrial organic matter, supporting by Kerogen elemental analysis data (Table 3). The distinguished exception is well P1-NC101 with only 42% amorphous organic matter probably due to increase margin of terrestrial organic matter, sourced from assemblage of a Type II/III kerogen. Low HI less than 100 in group samples from few wells (Figure 3) with reasonable of TOC values, maybe due to kerogen degradation and deposition in an oxic/dysoxic water column which reason of decrease in the amount of hydrogen-rich organic matter.
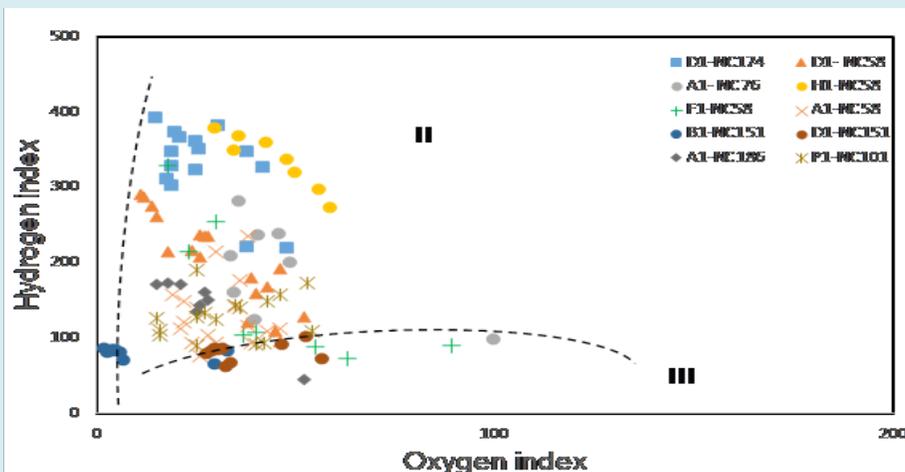

Figure 3: Plot of hydrogen index (HI) versus oxygen index (OI) illustrating the variation of kerogen types in source rocks modified diagrams[16].

D1-NC151		D1-NC174		P1-NC101		D1- NC58		A1-NC58	
OI	HI	OI	HI	OI	HI	OI	HI	OI	HI
28	79	19	301	53	174	46	96	26	77
29	82	18	311	46	158	45	109	24	95
31	84	18	327	43	149	38	122	30	95
30	85	42	325	54	109	52	128	28	105
32	86	25	323	42	95	40	160	21	114
34	67	38	347	40	92	43	169	22	122
33	61	19	347	25	191	39	181	25	140
47	90	26	350	25	91	46	192	22	149
53	101	25	361	15	127	26	209	19	158
57	72	21	366	16	104	24	217	30	215
		20	372	16	111	18	215	43	109
		31	381	25	129	26	238	39	94
		15	391	27	134	27	236	38	116

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A1-NC186		F1-NC58		H1-NC58		B1-NC151		A1- NC76	
				30	126	28	236	46	114
				36	140	12	287	35	143
				35	145	14	276	36	177
						15	262	38	236
						11	291		
OI	**HI**	**OI**	**HI**	**OI**	**HI**	**OI**	**HI**	**OI**	**HI**
25	136	18	330	59	272	5	84	36	281
26	145	30	255	56	297	6	81	41	236
28	152	37	105	50	318	3	82	46	238
27	161	40	108	48	337	4	85	34	209
21	172	63	73	43	359	7	71	49	200
18	173	89	91	35	348	2	87	35	160
15	172	55	89	36	368	4	83	40	123
		23	215	30	377	33	81	50	98
						30	65		

Table 2: Data of OI and HI as kerogen type parameters measured for group of selected intervals by Rock Eval pyrolysis.

Well	%C	%H	%O	% AOM	% Phytoclasts	% Palynomorphs
D1-NC151	18.68	1.25	4.55	88	4.3	7.5
B1-NC151	31.38	1.87	2.92	91.5	8.3	1.7
D1-NC174	24.56	2.62	3.64	93.5	4.8	1.2
P1-NC101	n.d	n.d	n.d	42	22.5	36.3
H1-NC58	35.61	2.58	2.17	82	14	2.2
A1-NC58	12.64	1.27	6.18	92	6.5	4.3

Table 3: Kerogen elemental analysis data and Kerogen group composition showing the main organic matter constituents contributing to the kerogen. AOM= Amorphous organic matter, n.d= not determine.

Thermal Maturity Assessment: The Vitrinite reflectance and Tmax are extensively used thermal maturity indicators of kerogen [17,18]. Data established from laboratory analyses (Table 4). In this study, the consecutive maturity data is wider to determine a thermal and geologic states a recently discussed such Aboglila S, et al. [6,7]. The measured thermal maturity of the Silurian Tanezzuft Formation, particularly hot shale member indicated diversity of maturation stages. The Tmax values are illustrated in Table 4. Commonly organic matter prone definitive source rocks are mature and will produce oil at Tmax temperature range of 430-460 C^o. The Tmax values of studied fields are confirmed and supported recently studies which published that the Silurian Tanezzuft Formation is the main hydrocarbon sources. A distinguished consequence is a Tmax degree in A1-NC58 well at 7500 feet with 435 C^o and 1.5 TOC%, in well D1-NC58 at 6900-6950 feet with 430-435 C^o and 0.5-0.6 TOC% and in H1-NC58 well at 5750 feet with 435 C^o with 0.75 TOC% while in D1-NC174 well at 6100 feet with 438 C^o by 10 TOC% and D1-NC151 well was 446 Co with 2 TOC % at 4650 feet. These notable results derived from Ordovician Mamuniyat Formation, Carboniferous Marar Formation and Devonian Awaynat Wanin (Table 1 & Figure 2, above) to clearly established their contribution as a hydrocarbon sources in the basin, even the Ordovician Mamuniyat Formation is lithologic has been classified as a sandstone reservoir in most basin concessions. Furthermore, the Devonian Awaynat Wanin, the Carboniferous Mrar and the Ordovician and Silurian formations are good to very good generative potential source rocks based on of TOC and S_2 contents in both Ghadames and Illizi Basins [19]. Spore colour index used as parameter of thermal maturity and/or kerogen composition [12] and illustrated difference values (Table 4). Palynomorphs are uncommon in these samples may due to degradation happening next to initial phase of deposition on the other hand acritarchs distribution for most samples showed increase, could be recognized. Based on

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the association of SCI values to a vitrinite reflectance values and Tmax, the region may by covered a variety of margin maturities, between immature to e mature level in constant with study of Aboglila S, et al. [6].

D1NC174

Tmax	$R_o\%$	Spore	Depth
	0.5	2.5	4500
	0.6	2	4700
	0.7	3	4800
	0.65	2.5	4950
	0.8	1.5	5050
	0.9	1.4	5100
	0.6	2.5	5250
	0.7	1.5	5300
	0.6	1.5	5350
	0.6	2.5	5400
430	0.9	1	5850
425	1	2	5900
436	0.85	2	5950
437	1.1	2	6000
439	1	3.5	6050
438	1.14	3.3	6100^x

B1-NC151

Tmax	$R_o\%$	Spore	Depth
445	0.66	2	2300
450	0.65	3	2350
456	1.1	1	2400
458	1.5	3.5	2450
460	1.4	3	2500
459	1.29	3	2550
457	1.2	3	2600
460	1.1	3.5	2650
455	1.22	3	2700
450	1.1	2	2750
	1	2	2800

P1-NC101

Tmax	$R_o\%$	Spore	Depth
420			6250
431			6300
428	0.98	0.5	6350
430	1		6400

A1N76

Tmax	$R_o\%$	Spore	Depth
	0.55	1.7	2950
	0.5	1.5	3550
	0.4	1.2	3600
433	0.7	2	4100
428	0.58	2.2	4200
430	0.55	2.3	4300
436	0.51	2.5	4400
440	0.5	2	4500
441	0.61	1.5	4550
440	0.58	1.2	4600
443	1.2	2.3	4700
444	1.3	2.2	4800

H1- NC58

Tmax	$R_o\%$	Spore	Depth
435	0.58	2	7550*
436	0.62	3	7600
435	0.59	3	7650
439	0.6	1.5	7700
440	0.65	2	7750
441	0.7	2	7800
438	0.66	2	7850
439	0.65	2	7900

A1-NC58

Tmax	$R_o\%$	Spore	Depth
435	0.5	1.5	7500*
		2.5	7550
		2.3	8150
	1.1		8850
445	1.3		8950
441	1.4		9050
431	1.2		9100
430	1.3		9150
461	1.1		9200
428	1.2		9250
430	1.4		9300
432	1,6		9350

D1NC58

Tmax	$R_o\%$	Spore	Depth
430	0.61	1.5	6900^+
435	0.65	1.7	6950^+
436	0.7	2.3	7000
433	0.3	2	7050
435	0.4	2.5	7100
430	0.6	2	7150
431	0.7	2	7200
429	0.4	2	7250

F1NC58

Tmax	$R_o\%$	Spore	Depth
429	0.62		4500
	1.5		5100
435	0.62		5150
427	0.6		5200
426	0.66	1.5	5250
425	0.68		5450
423	0.62		5500
426	0.66		5550
427	0.59		5600
428	0.64	1.4	5650
429	0.61		5700

D1-NC151

Tmax	$R_o\%$	Spore	Depth
445	1.1	2.5	4350
446	1.11	2	4400
448	0.98	2	4450
447	1.2	2.5	4500
446	1.3	3	4550
448	1.2	3	4600
446	105	2	4650^x

A1-NC186

Tmax	$R_o\%$	Spore	Depth
432			3700
433	1.1		3750
	0.8		3900
435	0.6		3950

432	1	2	6450	435	1.3		9400	435	0.7		4000
433	1.1		6500					436	1.1		4100
426	1.15		6550					435	1		4200
433	1.2	3.5	6600					432	0.9		4250
								435	1		4300
								434	1.11		4400

Table 4: Vitrinite reflectance, Tmax and Spore colour index as thermal maturity parameters.

Molecular Composition: The analyzed potential source rock samples contained amounts of extractable organic matter (EOM) range relatively from low to rich. The saturated and aromatic hydrocarbons fraction among EOM some samples demonstrated in Figure 4. The gas chromatograms of the saturated hydrocarbon fractions of the EOM showed smooth n-alkanes distributions from less n-C_{10} to more than n-C_{35} with major common preference (CPI values of around 1.0), consistent with their oil-window maturities indicated by vitrinite reflectance. The pristane to phytane ratios (> 1) with dibenzothiophene to phenanthrene ratio (DBT/P = < 1) clearly reveals marine shale and lacustrine environment deposition [20]. The methyldibenzothiophenes to the methylphenanthrenes (MDBT/MP) ratios of around 0.1 show relatively low concentrations of the aromatic sulfur compounds in the aromatic fractions of both the cores analyzed.
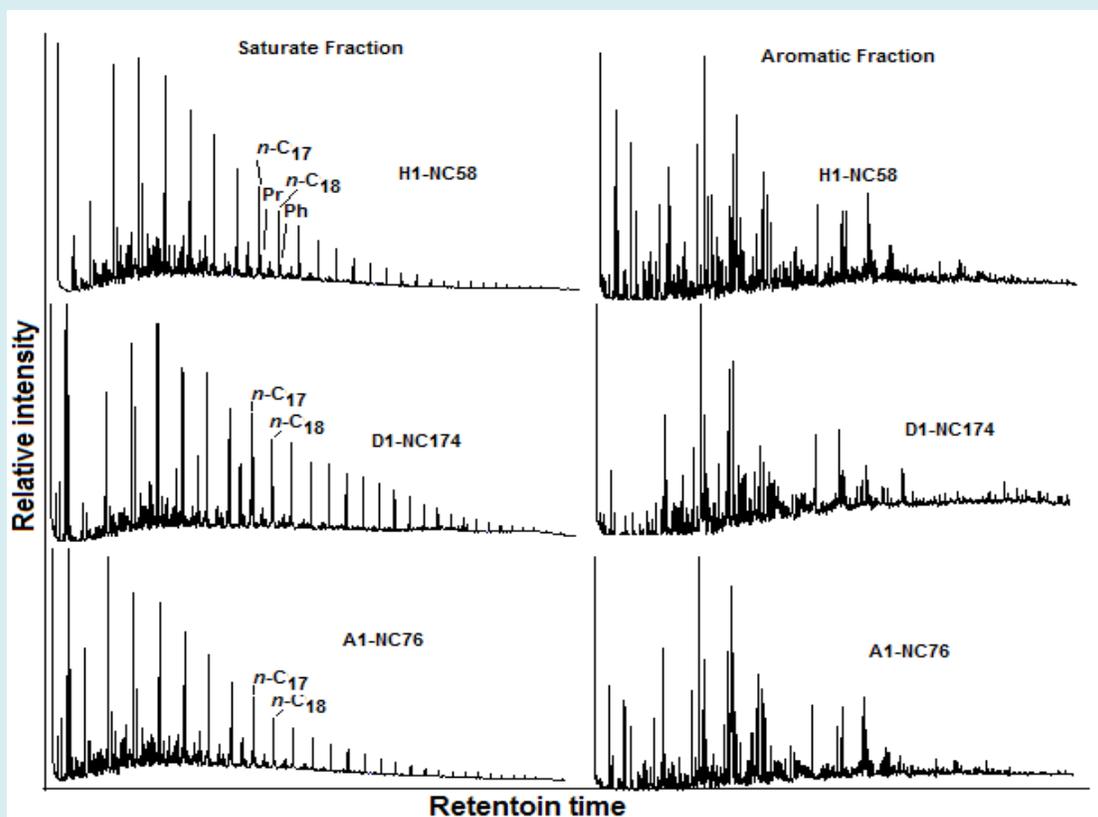

Figure 4: Rock extracts saturated and aromatic hydrocarbon fractions gas chromatograms representing selected samples.

Crude Oils Analysis

Seven crude oils were collocated from A1-NC186, B1-NC186, E2-NC101, F3-NC174, A10-NC115, B10-NC115 and H10-NC115 for geochemistry analysis. Nitrogen, sulfur and wax content in wt. % of the crude oil samples were measured and presented in Table 5. The oil sample from E2-

NC101 illustrated greater wax content among the samples analyzed with low API gravity, to some extent; it indicates a different source comparative to other oils. More detailed in next sections. The low n-C_{17} to n-C_{27} ratio of the E2-NC101 oil indicated it increased waxiness compared with the other oils.

Saturated Hydrocarbon: Gas chromatograms of all oils show an abundance of n-alkanes (> n-C_{30}) such A1-NC186 oil in Figure 5, with exception for the oil of E2-NC101 well, illustrates (< n-C_{27}) alkane. The oil of E2-NC101 well has been certainly subjected to some evaporative losses, compared to further analyzed oils. On the other hand, the difference was also shown between oil of E2-NC101 and the further oils in terms of crude oils wax content (Table 5). It may clear indication to contribution of compounds generated from marginal plants as the source of E2-NC101 oil. The abundance of n-alkanes in the all oils indicates that there have no biodegradation or water washing effects the hydrocarbons. The ratios of pristine/n-C_{17}, phytane/n-C_{18}, pristine/phytane and carbon preference index offered in Table 5 are characteristic as several Paleozoic Type II kerogen expelled oils and again the E2-NC101 oil which has much lower pristine/ n-C_{17} and phytane/ n-C_{18} ratios than the other oils, additional evidence for different it source.
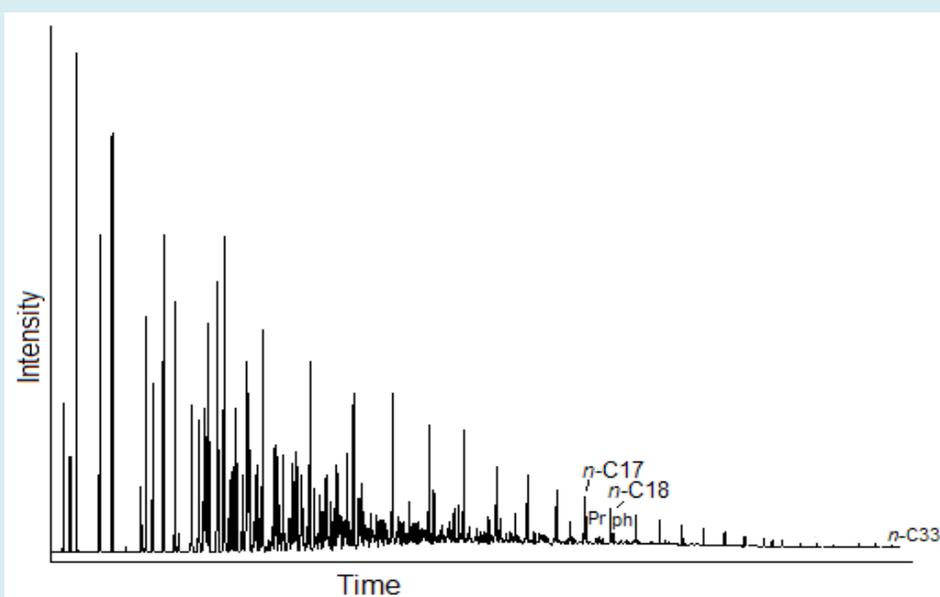

Figure 5: Gas chromatogram of whole oil from A1-NC186 well.

Well	N%	S%	Wax%	Pr/n-C17	Ph/n-C18	Pr/Ph	n-C17/n-C27	CPI	API
A1-NC186	0.34	0.31	1.85	0.63	0.45	2.22	14.69	0.99	39.5
B1-NC186	0.10	0.31	1.41	0.60	0.46	1.86	11.82	0.99	40.1
E2-NC101	0.11	0.30	6.4	0.33	0.26	1.61	6.33	1.02	30.1
F3-NC174	0.31	0.30	1.90	0.69	0.51	1.89	13.23	1.03	39.1
A10-NC115	0.10	0.71	2.60	0.56	0.38	2.08	13.22	1.03	38.6
B10-NC115	0.10	0.40	2.10	0.64	0.52	1.74	10.43	0.94	39.2
H10-NC115	0.29	0.15	1.25	0.57	0.39	2.27	10.80	1.00	40.2

Table 5: Bulk oil composition and saturated hydrocarbon ratios from whole oil chromatographs.

Aromatic Hydrocarbon Fractions: The gas chromatograms of the aromatic hydrocarbon fractions of oil samples showed characteristic mature crude oil distributions dominated by methylnaphthalenes, dimethylnaphthalenes, trimethylnaphthalenes, methylphenanthrenes and dimethylphenanthrenes peaks. The samples displayed aromatic fraction gas chromatograms typical expelled from mature source rocks. The aromatic hydrocarbons are an indication of organic matter maturity. The majority oils sourced from a mature source rock (Hot shale source) with occur of some oil showed the lower maturity than oils porn from hot shale source , certainly sourced form immature

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Type II kerogens possibly other potential formations in
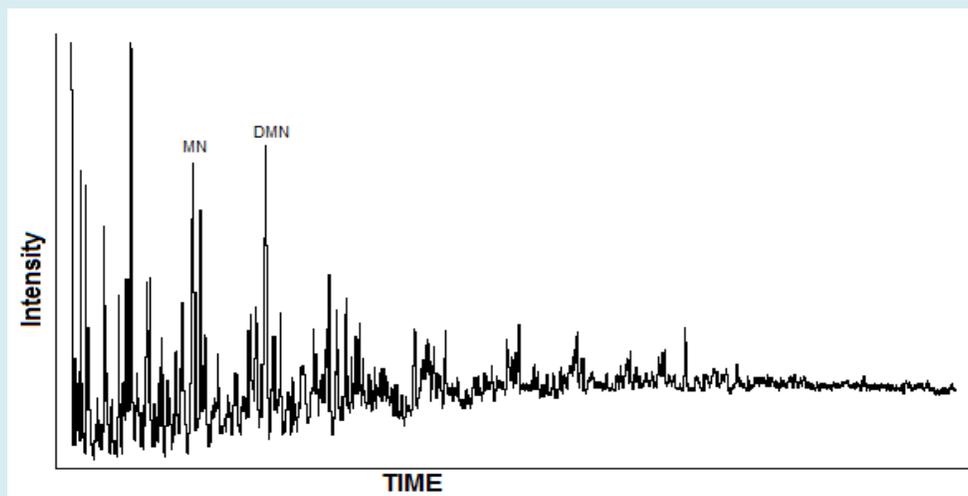
consistent with Aboglila S, et a. [6,7] (Figure 6).

Figure 6: Gas chromatogram of aromatic hydrocarbon fraction from D1-NC174 sample hydrouspyrolysis.

Stable Carbon Isotope (δ^{13}C) of Rocks and Oils

The Stable carbon isotope results of seven rock-extract samples and the eight oils were analyzed and displayed data in Table 6. The δ^{13}C values of the sediments saturates hydrocarbon fractions ley among -30.98‰ and -29.14‰, while the δ^{13}C values of aromatic fractions slightly less negative than those of the saturated hydrocarbon fractions, ranged between -29.86‰ to -28.37‰.

Rocks				Oil			
Saturates	**Aromatics**	**Depth (Ft)**	**Well**	**Saturates**	**Aromatics**	**Whole Oil**	**Well**
-30.98	-29.69	9250	A1-NC58	-29.19	-29.85	-29.9	A1-NC186
-29.84	-29.86	5950	D1-NC174	-29.32	-29.98	-29.82	B1-NC186
-29.37	-28.37	4650	D1-NC151	-28.67	-29.88	-29.97	E2-NC101
-29.15	-28.98	7950	H1-NC58	-29.38	-29.91	-29.97	F3-NC174
-30.33	-29.01	6550	P1-NC 101	-28.68	-29.62	-28.98	A10-NC115
-29.14	-28.92	2350	B1-NC151	-28.92	-29.83	-29.84	B10-NC151
-29.86	-29.84	5750	F1-NC58	-29.02	-29.55	-29.46	H10-NC115
				-29.36	-29.96	-29.85	B10-NC115

Table 6: δ^{13}C‰ of Saturated and aromatic hydrocarbon fraction data of source Rocks and oils.

The δ^{13}C values of the oil saturate hydrocarbon fractions showed range between -29.36‰ to -28.67‰, within about 1‰ of the variety of the oils. The δ^{13}C data of aromatic were among -29.98 ‰ to -29.55 ‰. The Stable carbon isotope results in both rock extractions and crude oils are closer to each other, typical of Paleozoic age.

Oil-Source Rocks Correlations

Oil-Oil Correlation: The correlation of oil and source rock depends on the biomarker composition to find the genetic relationship between them. Similar biological sources will reveal similar biomarker distributions [21]. An evaluation of the correlations between the oils has been distinguished using a visual assessment of chromatograms together with a comparison of quantified data and ratios. These indicated that most of triterpanes and steranes obtained from the oils are broadly similar Figure 7 and Figure 8. This assumption is supported by carbon stable isotope analysis results (Table 6 above), where there no significant variation among oils, due to dominance of hot shale rock as the main source. The m/z 191 mass chromatograms of the oils showed prominent

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peaks due to relatively abundant tricylic terpanes, typically the C_{23} tricylic terpane that was often more abundant than the C_{30} hopane peak. The prominence of tricyclic terpanes relative to hopanes in oils is correspondingly recognized

due increase in maturity [22]. Peaks of disteranes in the m/z 217 mass chromatograms are also more abundant than the chain steranes (C_{27}-C_{29}) in oils, this also can describe as an influence of maturity.
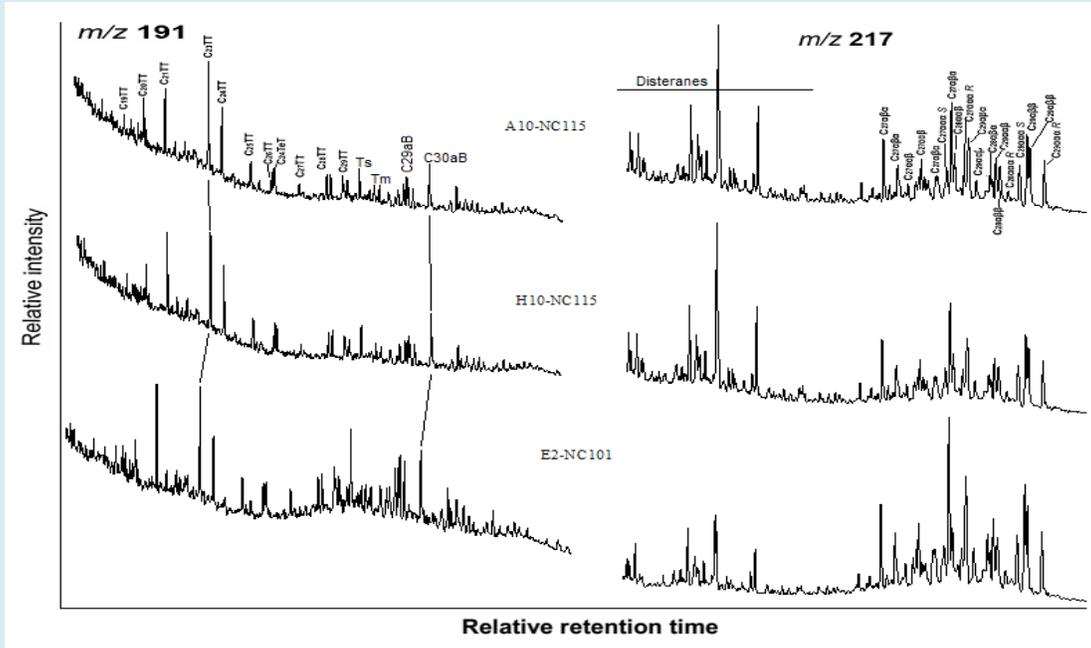

Figure 7: Biomarkers distribution (m/z 191 and 217) of selected oil samples.

Oil-Source Rocks Correlations: The correlations between the studied oils and potential source rocks has been showed in the preceding sections using a visual assessment of chromatograms together with a comparison of quantified data and ratios calculated triterpanes and hopanes peaks

and illustrated in Figure 8. Data indicated that most of the core extracts were broadly similar to most of the oils with some increases in oils data, possible due to development oil maturity and/or a status of mixing in reservoir. The carbon stable isotope results are again confirming this notion.
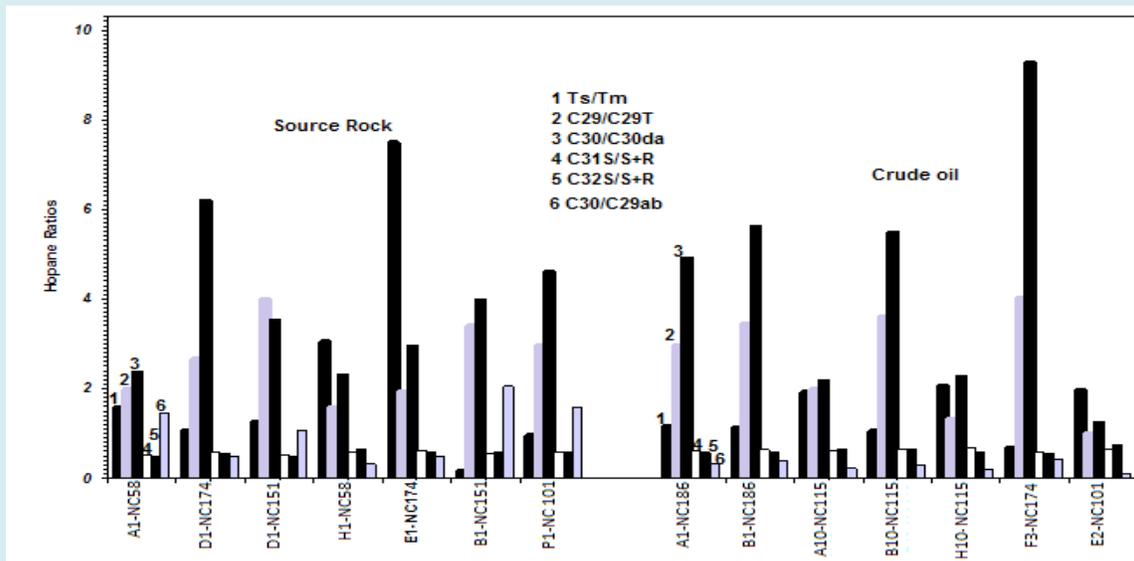

Figure 8: Biomarkers (hopanes ratios) correlation between the crude oils and source rocks samples.

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The Figure 9 display a correlation between saturated, aromatic fractions and whole oil $\delta^{13}C$ fingerprint of the analyzed oil samples. The whole oil samples analyzed are convergent $\delta^{13}C$ values, the $\delta^{13}C$ of saturated hydrocarbon fractions showed flat values and $\delta^{13}C$ data of the aromatic fractions displayed closer to each other (Figure 9). The similarity of the $\delta^{13}C$ values of the oils suggest clear correlation between region hydrocarbons, in terms of era time where light $\delta^{13}C$ data indicate Paleozoic Era and the domination of single source, with exist of other contribution sources. In most cases, the distribution of the d13C value is roughly similar between the crude oil and the organic matter extracted from studied rocks, showed a light values and indication of inheritance of Paleozoic Era. The above clearly indicates a genetic relationship between of both crude oils and the organic matter extracted from studied rocks.
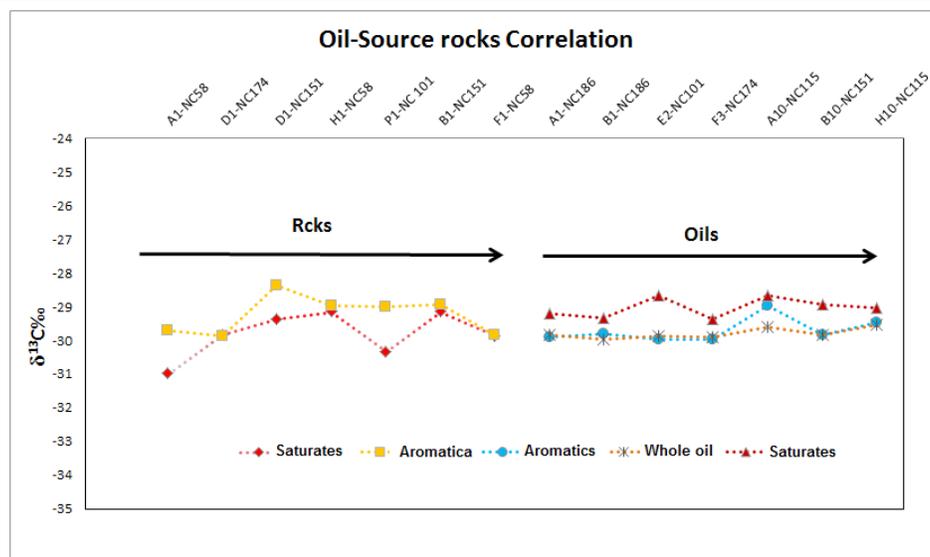

Figure 9: Stable carbon isotope fingerprint of the selected rocks and oils from studied wells in Murzuq Basin.

Conclusion

The data confirmed that the hot shale facies at the base of the Silurian Tanezzuft Formation as the principal source rock for Murzuq Basin. Although other organic rich facies occur in the rest of the Paleozoic Era as well as in the Devonian, and Carboniferous strata their source potential and Ordovician Mamuniyat Formation could be expected. The hot shale typically contains Type II/III oil prone kerogen with high amorphous organic matter and negligible amounts of phytoclasts and palynomorphs, advising deposition in a restricted distal marine environment might remove from active sources of terrestrial organic matter. The hot shale is typically a rich source rock characterized by high TOC content, suggesting its very good initial source potential. Thermal maturity of the hot shale indicated a wide range of maturities between early oil generations to post oil generation base on Ro% values. The oil biomarkers are characterized by low abundances of triterpanes and steranes, with dominance of C_{29} steranes, which is typical of mature Paleozoic oils. The Stable carbon isotope results in both rock extractions and crude oils are closer to each other, typical of Paleozoic age.

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