



Source Rock Characterization of Silurian Tanezzuft and Devonian Awaynat Wanin Formations the Northern Edge of the Murzuq Basin, South West Libya

Albaghdady A, Aboglila S*, Farifr E, Ramadan M and Alburki A

Libyan Academy & Azzytouna University, Libya

*Corresponding author: Salem Aboglila, Science Faculty, Azzaytuna University, Libya, Tel: 00218913700361; Email: salem.aboglila@gmail.com

Research Article

Volume 4 Issue 1

Received Date: January 22, 2020

Published Date: February 21, 2020

DOI: 10.23880/ppej-16000216

Abstract

Drill cutting samples ($n = 92$) from the Devonian Awaynat Wanin Formation and Silurian Tanezzuft Formation, sampled from three wells F1, G1 and H1, locate in the northern edge of the Murzuq basin (approximately 700 kilometers south of Tripoli). The studied samples were analyzed in the objective of their organic geochemical assessment such as the type of organic matter, depositional conditions and thermal maturity level. A bulk geochemical parameters and precise biomarkers were estimated, using chromatography-mass spectrometry (GC-MS) to reveal a diversity of their geochemical characterizations. The rock formations are having varied organic matter contents, ranged from fair to excellent. The total organic carbon (TOC) reached about 9.1 wt%, ranging from 0.6 to 2.93 wt% (Awaynat Wanin), 0.5 to 2.54 wt% (Tanezzuft) and 0.52 to 9.1 wt% (Hot Shale). The cutting samples are ranged oil-prone organic matter (OM) of hydrogen index (HI) ranged between 98 - 396 mg HC/g TOC, related kerogen types are type II and II/III, with oxygen index (OI): 6 - 190 with one sample have value of 366 mg CO₂/g. Thermal maturity of these source rocks is different, ranging from immature to mature and oil window in the most of Tanezzuft Formation and Hot Shale samples, as reflected from the production index data (PI: 0.08 - 0.34). Tmax and vitrinite reflectance Ro% data (Tmax: 435 - 454 & Ro%: 0.46 - 1.38) for the Awaynat Wanin. Biomarker ratios of specific hydrocarbons extracted from represented samples ($n = 9$), were moreover used to study thermal maturity level and depositional environments. Pristine/Phytane (Pr/Ph) ratios of 1.65 - 2.23 indicated anoxic to suboxic conditions of depositional marine shale and lacustrine source rock.

Keywords: Murzuq basin; Source rock; Silurian Tanezzuft; Devonian Awaynat Wanin

Introduction

Murzuq Basin, located in south-western Libya, is one of Libyan productive petroleum basins, extend southward into Niger. The Libyan regain covers an area of almost 58000 km², has many potential reservoirs largely in the Paleozoic units, together with the Cambrian Mourizidie and Hassaouna formations. The Ordovician such Haouaz and Memouniat formations, with the Silurian Tanezzuft formation [1], and

very minor amounts of early organic matter were probably expelled from the Devonian formations in the center basin [2]. Exploration operations have been realized, resulting in over tens discoveries more than 4,000 million barrels of oil even now. Many Organic geochemistry studies have been issued, reported the petroleum geochemistry of oil-Libyan basins, including search focused on the kerogen types, source rocks potential, oil-oil and oil-source rock correlation [1,3-8]. There several geochemical studies around source rocks

and crude oils of Murzuq basin such as gravities API ranges 36–45° in Hot Shale Member, low partition of Tanezzuft Formation [1]. TOC from concession 58 stated 3.45% with average 1.8% TOC in center basin published by Rusk. Rock pyrolysis, TOC analysis, spore colouration, organic matter reflectivity and aromatic molecular biomarker as geochemical parameters were measured to establish kerogen type, potential yield and thermal maturity in six formations from the Murzuq basin [7]. Biomarker ratios and stable carbon Isotopes also measured to study group samples of crude Oils characteristics, collected from the Murzuq Basin. The origin of organic matter in sedimentary rocks and crude oils has received much attention in recent years. The information contained within the organic matter in source rock has been successfully used for the interpretation of depositional environments and assessment of type and thermal maturity of organic matter [9,10]. It is evident that the components of a particular source rock extract provide valuable information about the organic input and the prevailing depositional environment. This study is to assess organic matter type, and thermal maturity based on geochemical parameters derived Rock Eval data and Gas Chromatography examination of the sediments were collected from northern edge of the Murzuq basin, South West Libya (Figure 1).

Geological Setting

The Muruk Basin is a cratonic sedimentary basin and is located in the south-west of Libya and extends inside Niger, bordered to the north by Gargaf Arch, to the west by Thambouka Uplift and to the east by Tebbisti Complex. It covers an area of approximately 350,000 square kilometers [11]. The basin was formed by many tectonic events that began during the pre-cambrian period, and formed some vertical faults in north-south directions coupled with faults in northeast-southwest directions [12]. The Pan African Orogeny in the pre-cambrian were followed by several tectonic movements, the most important of which were the Caledonian Orogeny during the early Paleozoic Era and the Hercynial Orogeny during the late Paleozoic Era and early Mesozoic Era. These movements caused folding and faults [12]. During the Jurassic period, the eastern part of the basin was uplifted and the Dor Alqussa formation was formed. The basin contains a section of sedimentary rocks with a thickness of 3500 m in its center dating back to the Paleozoic Era and Mesozoic Era [11]. The maximum depth in the center of the basin was determined to pre-Cambrian rocks by 3,500 meters [13]. The sedimentary sequence of the Murzuq basin is characterized by the presence of sandstones and clay stones (Figure 2). The Cambrian and Ordovician rocks consist of sandy rocks. The Cambrian Hasawnah, represented by conglomerates and medium to coarse-grained sandstones deposited in a fluvial environment in its lower part and in shallow marine for the upper part. The Hasawnah Formation is unconformably overlain by Ordovician Hawaz Formation that is also composed of medium and coarse-grained sandstones, as well as siltstone and clay stones deposited in a delta fan environment [14].

In the southwestern part of the basin, the Ash Shabiyat Formation changes laterally to the Hawaz Formation. Ash Shabiyat and Hawaz Formations are overlain by marine shale of Melaz Shuqran formation. Mamuniyat Formation, which is the main oil reservoir in the Murzuq Basin, overlies the Melaz Shuqran Formation. The Mamuniyat Formation and Melaz Shuqran Formation deposited during the ice age in Ordovician period [15]. During the Silurian period, the shale of the Tanezzuft Formation deposited during transgressive time and set with an unconformity surface above the Mamuniyat Formation. This formation is overlain by the Akakus formation, which deposited during the middle and upper Silurian Period in a shallow marine environment. The center of the basin, the Tadrat Formation and Awaynat Wanin Formation is setting on Akakus Formation. Awaynat Wanin Formation is dominated by sandstone rich in iron concentrations of the middle and upper Devonian, deposited in coastal environments and a shallow sea [15]. The Carboniferous rocks were also characterized by marine transgression, where the Marar Formation deposited on

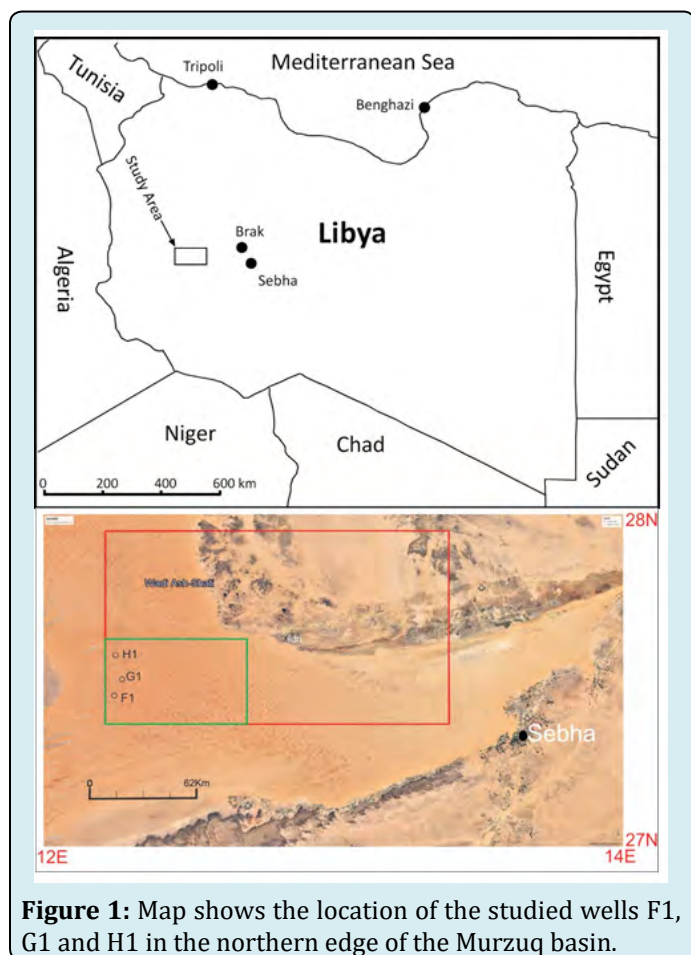


Figure 1: Map shows the location of the studied wells F1, G1 and H1 in the northern edge of the Murzuq basin.

Awaynat Wanin Formation and then Assedjefar Formation above Marar Formation. The Middle carboniferous Dembaba

Formation consists of limestone, sandstone and claystones formed in a marine environment.

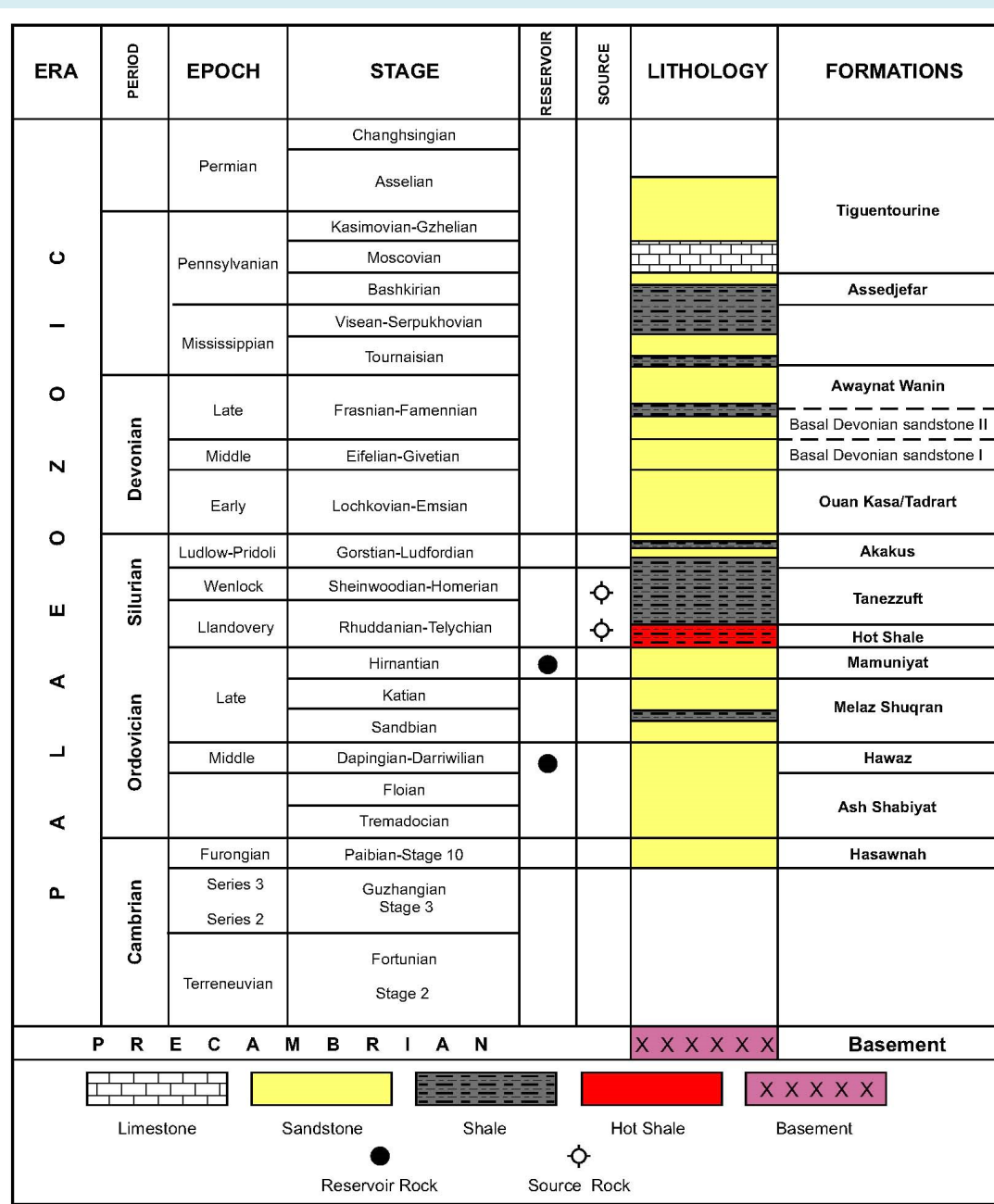


Figure 2: the Stratigraphic column of the Murzuq basin [11] (modified after Echikh and Sola, 2000 and El Diasty et al., 2017).

Experimental Methods

Samples

Ninety-two samples of drill cuttings were collected from three different F1, G1 and H1 wells, located in the northern

edge of the Murzuq basin, South West Libya (Figure 1). The rocks sampled were the Palaeozoic age from Devonian Awaynat Wanin (n=10), Silurian Tanezzuft formations (n= 59) and the Hot shale member (n=23) as the base of Tanezzuft formation. Five samples of Awaynat Wanin from F1 well, depth between 570 to 850 Ft and the rest was from

H1 well (depth among 330 – 690 Ft). Tanezzuft samples were from F1, G1 and H1, divided (n=2, depth 5 from 1100 to 2060 Ft), (n= 12, depth from 700-1680 Ft) and (n=22, depth from 1000 -1850 Ft) respectively. The most Hot shale member samples collected from H1 (n=17, depth from 1860 to 2200 Ft) and 6 samples were G1 well on depth between 1690 to 1740 Ft.

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

Ninety-two samples from three wells northern edge of the Murzuq basin, South West Libya, and representing Devonian Awaynat Wanin and the Silurian Tanezzuft Formations including hot shale unit, were analyzed by Rock-Eval pyrolysis to determine the hydrocarbon generative potential of the organic matter. A Rock-Eval VI Pyrolyser was used to analyze the samples. Crushed samples (100 mg) were pyrolyzed in a helium atmosphere at 325°C for 3 min, followed by temperature programmed pyrolysis at 25°C/min from 300 to 650°C. A flame ionization detector (FID) was used to monitor the evolved hydrocarbons [16]. The first peak (S1 mg HC/g) was obtained from volatilization of free hydrocarbons during isothermal pyrolysis at 300°C. The second peak (S2 mg HC/g) represents hydrocarbons generated by thermal cracking of kerogen during pyrolysis at 300 to 550°C. The third peak (S3) represents the amount of CO₂ in mg generated from one gram of rock during pyrolysis in the temperature interval between 300°C and 390°C and analyzed using an IR detector. Tmax represents the temperature corresponding to the maximum amount of hydrocarbons generated from the cracking of kerogen. The quantity of organic matter or total organic carbon (TOC) was determined using a LECO carbon analyzer for each sample. Samples to be analyzed for vitrinite reflectance are crushed to small fragments and polished using three finer grades of corundum paper to reduce scratches and get smooth surfaces. Reflectance measurements of the polished blocks are obtained under oil immersion using a Zeiss Universal Photo microscope II.

Solvent Extraction

Nine samples were selected for more detailed organic geochemical analysis. For extraction of the source rocks, about 40 g amount of crushed samples were Soxhlet extracted using dichloromethane and methanol with 93:7 ratio. Then extract was transferred to flask and the solvent was removed using a Buchi rotary evaporator. Asphaltenes were removed from the extracts by precipitation with n-pentane. The maltenes were concentrated and separated from the asphaltenes by filtration.

Gas Chromatography

The gas chromatograph (GC) used for analysing the saturate fractions was a DANI 8510 Gas Chromatograph coupled with flame ionization detector (FID) and an OV1 (25m) column. The samples were injected using helium as a carrier gas. The temperature was programmed from 80 to 300°C at 4°C/min and held isothermal for 20 min. For Aromatic hydrocarbon fractions, a Varian 3400 Gas Chromatograph with a 40 m SE 54 capillary column used is for the analysis. The helium is also used as carrier gas and the temperature programmed from 40°C to 290°C at a rate of 4°C/min.

Results

A Variation of organic geochemical analyses were utilized to reveal rocks characteristics, relating to the origin and formation of rock hydrocarbons from three fields located in the Murzuq Basin. On the basis of the determination of this object, the consequences of physical characteristics (Lithology), TOC analysis, rock pyrolysis, organic matter reflectivity and molecular composition have completed (Tables 1-5) to discuss potential yield, kerogen type and thermal maturity for Palaeozoic Devonian Awaynat Wanin, Silurian Tanezzuft formations and the Hot shale member as the base of Tanezzuft formation, collected from three discovered wells in northern edge of the Murzuq basin, South West Libya.

F1 well Feet	TOC	S1	S2	S3	S+S2	Tmax	HI	OI	S2/S3	S1/TOC	PI	Rock
570	2.07	0.23	4.24	0.5	4.47	436	205	24	8.48	0.11	0.05	A.W
660	2.93	0.63	8.68	2.28	9.31	435	296	78	3.81	0.22	0.07	A.W
720	1.39	0.24	4.52	0.81	4.76	440	325	58	5.58	0.17	0.05	A.W
780	0.91	0.12	2.88	1.53	3	441	316	168	1.88	0.13	0.04	A.W
850	1.12	0.28	4.43	0.44	4.71	443	396	39	10.07	0.25	0.06	A.W
1100	0.76	0.21	1.92	1.04	2.13	439	253	137	1.85	0.28	0.10	Tzft
1150	0.66	0.18	2.03	0.53	2.21	441	308	80	3.83	0.27	0.08	Tzft

1200	0.53	0.15	1.5	1.94	1.65	442	283	366	0.77	0.28	0.09	Tzft
1250	0.60	0.17	1.55	0.81	1.72	440	258	135	1.91	0.28	0.10	Tzft
1300	0.59	0.17	1.43	0.6	1.6	441	242	102	2.38	0.29	0.11	Tzft
1350	0.54	0.17	1.42	0.58	1.59	443	263	107	2.45	0.31	0.11	Tzft
1400	0.73	0.22	2.12	0.48	2.34	440	290	66	4.42	0.30	0.09	Tzft
1450	1.14	0.49	3.72	0.4	4.21	439	326	35	9.30	0.43	0.12	Tzft
1500	0.54	0.18	1.12	0.37	1.3	442	207	69	3.03	0.33	0.14	Tzft
1550	0.64	0.21	1.27	0.27	1.48	441	198	42	4.70	0.33	0.14	Tzft
1600	0.59	0.25	1.27	0.31	1.52	441	215	53	4.10	0.42	0.16	Tzft
1750	0.63	0.25	1.5	0.39	1.75	441	238	62	3.85	0.40	0.14	Tzft
1800	0.71	0.32	1.48	0.28	1.8	443	208	39	5.29	0.45	0.18	Tzft
1850	0.65	0.28	1.26	0.42	1.54	442	194	65	3.00	0.43	0.18	Tzft
1900	0.58	0.20	0.88	0.37	1.08	442	152	64	2.38	0.34	0.19	Tzft
1950	0.60	0.21	0.96	0.32	1.17	444	160	53	3.00	0.35	0.18	Tzft
2020	0.77	0.33	1.21	0.34	1.54	445	157	44	3.56	0.43	0.21	Tzft
2040	1.10	0.46	1.77	0.31	2.23	443	161	28	5.71	0.42	0.21	Tzft
2060	1.60	0.72	2.41	0.3	3.13	445	151	19	8.03	0.45	0.23	Tzft

Table 1: Range of rock eval/TOC data for selected rocks from the F1 well. Tzft = Tanezzuft formation, A.W= Awaynat Wanin.

G1 well Feet	TOC	S1	S2	S3	S+S2	Tmax	HI	OI	S2/S3	S1/TOC	PI	Rock
700	0.5	0.11	1.22	0.95	1.33	441	244	190	1.28	0.22	0.08	Tzft
800	0.88	0.3	2.67	0.85	2.97	439	303	97	3.14	0.34	0.10	Tzft
900	0.82	0.33	2.58	0.43	2.91	440	315	52	6.00	0.40	0.11	Tzft
1000	0.56	0.18	1.31	0.48	1.49	443	234	86	2.73	0.32	0.12	Tzft
1100	0.94	0.4	2.2	0.33	2.6	441	234	35	6.67	0.43	0.15	Tzft
1200	0.75	0.32	1.43	0.41	1.75	440	191	55	3.49	0.43	0.18	Tzft
1300	0.64	0.24	1.12	0.31	1.36	444	175	48	3.61	0.38	0.18	Tzft
1350	0.65	0.29	1.15	0.33	1.44	441	177	51	3.48	0.45	0.20	Tzft
1400	0.54	0.24	0.85	0.28	1.09	444	157	52	3.04	0.44	0.22	Tzft
1450	0.81	0.38	1.36	0.28	1.74	443	168	35	4.86	0.47	0.22	Tzft
1500	0.58	0.28	0.87	0.54	1.15	440	150	93	1.61	0.48	0.24	Tzft
1550	0.54	0.22	0.65	0.33	0.87	444	120	61	1.97	0.41	0.25	Tzft
1600	0.86	0.4	1.12	0.32	1.52	447	130	37	3.50	0.47	0.26	Tzft
1650	2.43	1.19	3.37	0.27	4.56	451	139	11	12.48	0.49	0.26	Tzft
1660	2.19	1.16	3.08	0.28	4.24	450	141	13	11.00	0.53	0.27	Tzft
1670	1.72	0.76	2.29	0.35	3.05	452	133	20	6.54	0.44	0.25	Tzft
1680	2.54	1.18	3.3	0.35	4.48	450	130	14	9.43	0.46	0.26	Tzft
1690	3.64	1.71	5.15	0.28	6.86	449	141	8	18.39	0.47	0.25	H.Sh
1700	3.89	1.84	6.07	0.33	7.91	449	156	8	18.39	0.47	0.23	H.Sh
1710	4.26	2.23	6.52	0.38	8.75	447	153	9	17.16	0.52	0.25	H.Sh

1720	3.65	1.95	5.55	0.45	7.5	444	152	12	12.33	0.53	0.26	H.Sh
1730	4.56	1.87	7.34	0.54	9.21	446	161	12	13.59	0.41	0.20	H.Sh
1740	7.25	2.57	10.31	0.5	12.88	447	142	7	20.62	0.35	0.20	H.Sh

Table 2: Range of rock eval/TOC data for selected rocks from the G1 well. Tzft = Tanezzuft formation, A .W= Awaynat Wanin, H.Sh = hot shale.

H1 well Feet	TOC	S1	S2	S3	S+S2	Tmax	HI	OI	S2/S3	S1/TOC	PI	Rock
330	1.86	0.16	2.79	1.21	2.95	440	150	65	2.31	0.09	0.05	A.W
450	1.46	0.25	3.06	0.8	3.31	439	210	55	3.82	0.17	0.08	A.W
570	1.06	0.24	3.4	0.65	3.64	442	321	61	5.23	0.23	0.07	A.W
640	0.98	0.23	3.07	0.45	3.3	441	313	46	6.82	0.23	0.07	A.W
690	0.6	0.08	1.37	0.82	1.45	439	228	137	1.67	0.13	0.06	A.W
1000	0.72	0.25	2.26	0.55	2.51	441	314	76	4.11	0.35	0.10	Tzft
1050	0.6	0.38	1.73	0.44	2.11	440	288	73	3.93	0.63	0.18	Tzft
1100	0.55	0.35	1.31	0.54	1.66	440	238	98	2.43	0.64	0.21	Tzft
1150	0.7	0.32	1.81	0.56	2.13	440	259	80	3.23	0.46	0.15	Tzft
1200	0.58	0.21	1.2	0.61	1.41	440	207	105	1.97	0.36	0.15	Tzft
1250	0.63	0.19	1.32	0.64	1.51	442	210	102	2.06	0.30	0.13	Tzft
1350	0.63	0.27	1.56	0.47	1.83	439	248	75	3.32	0.43	0.15	Tzft
1400	0.67	0.32	1.68	0.41	2	439	251	61	4.10	0.48	0.16	Tzft
1450	0.83	0.4	2.27	0.28	2.67	439	273	34	8.11	0.48	0.15	Tzft
1500	0.78	0.41	2.01	0.5	2.42	439	258	64	4.02	0.53	0.17	Tzft
1550	0.96	0.48	2.22	0.33	2.7	439	231	34	6.73	0.50	0.18	Tzft
1600	1.01	0.62	2.42	0.36	3.04	439	240	36	6.72	0.61	0.20	Tzft
1650	2.22	1.16	4.91	0.32	6.07	440	221	14	15.34	0.52	0.19	Tzft
1700	0.96	0.6	1.77	0.5	2.37	439	184	52	3.54	0.63	0.25	Tzft
1720	1.42	0.72	2.48	0.37	3.2	440	175	26	6.70	0.51	0.23	Tzft
1740	1.87	0.84	3.05	0.43	3.89	437	163	23	7.09	0.45	0.22	Tzft
1760	1.35	0.6	2.2	0.4	2.8	440	163	30	5.50	0.44	0.21	Tzft
1780	1.22	0.52	1.98	0.43	2.5	441	162	35	4.60	0.43	0.21	Tzft
1800	0.77	0.35	1.32	0.47	1.67	442	171	61	2.81	0.45	0.21	Tzft
1820	0.75	0.31	1.16	0.52	1.47	443	155	69	2.23	0.41	0.21	Tzft
1840	0.93	0.52	1.63	0.42	2.15	442	175	45	3.88	0.56	0.24	Tzft
1850	2.53	1.23	4.54	0.3	5.77	444	179	12	15.13	0.49	0.21	Tzft
1860	4.21	1.86	7.32	0.43	9.18	443	174	10	17.02	0.44	0.20	H.Sh
1870	3.69	1.51	6.18	0.51	7.69	437	167	14	12.12	0.41	0.20	H.Sh
1880	3.93	1.85	6.53	0.45	8.38	442	166	11	14.51	0.47	0.22	H.Sh
1890	3.48	1.74	5.48	0.5	7.22	441	157	14	10.96	0.50	0.24	H.Sh
1900	2.9	1.63	4.86	0.48	6.49	440	168	17	10.13	0.56	0.25	H.Sh
1950	0.94	0.5	1.12	0.49	1.62	445	119	52	2.29	0.53	0.31	H.Sh

2000	0.65	0.29	0.72	0.47	1.01	446	111	72	1.53	0.45	0.29	H.Sh
2020	0.52	0.19	0.54	0.42	0.73	447	104	81	1.29	0.37	0.26	H.Sh
2040	0.6	0.29	0.69	0.37	0.98	438	115	62	1.86	0.48	0.30	H.Sh
2060	0.58	0.27	0.61	0.45	0.88	439	105	78	1.36	0.47	0.31	H.Sh
2080	1.46	0.78	1.62	0.35	2.4	451	111	24	4.63	0.53	0.32	H.Sh
2100	0.94	0.53	0.98	0.37	1.51	444	104	39	2.65	0.56	0.35	H.Sh
2120	2	1.12	2.29	0.35	3.41	451	115	18	6.54	0.56	0.33	H.Sh
2140	1.83	0.98	1.9	0.31	2.88	450	104	17	6.13	0.54	0.34	H.Sh
2160	2.65	1.16	3.16	0.26	4.32	450	119	10	12.15	0.44	0.27	H.Sh
2180	1.22	0.55	1.2	0.44	1.75	449	98	36	2.73	0.45	0.31	H.Sh
2200	9.1	2.35	10.27	0.52	12.62	454	113	6	19.75	0.26	0.19	H.Sh

Table 3: Range of rock eval/TOC data for selected rocks from the H1 well. Tzft = Tanezzuft formation, A.W= Awaynat Wanin, H.Sh = hot shale.

Physical Characteristics of samples

The lithologies of the studied formations display different physical appearances in terms of colour and texture. An assessment of the physical characteristics the Awaynat Wanin Formation showed verity between studied formations itself in the concession wells. This formation performed mainly brown grey shales in the well F1 together with dominated sandstones in the top part of formation. In H1 well, it was more rich of sandstones distinguished and dark brown grey to brown black shales were remarkable. The Tanezzuft Formation in studied wells is composed of light brown-grey to dark brown grey and dark grey shales and generally lower amounts of sandstones immediate the upper part of formation. The hot shale member (the base of Tanezzuft Formation) is consisting of pyrite-rich brown black shales in both G1 and H1wells.

Total Organic Carbon and Rock-Eval Pyrolysis

TOC (%) and Rock-Eval pyrolysis measurements for the studied samples show quite varied values (Tables 1, 2 & 3). TOC values from Awaynat Wanin Formation range 0.60% to 2.93%, Tanezzuft Formation range between 0.53 to 2.55%.

The most of basal hot shale samples have a rich TOC content. The values range from 0.52 to 9.1% with the majority of them having values of more than 1%. Rock-Eval pyrolysis data measured for the rocks based on parameters of S1, S2,, Tmax, HI, OI, , and PI in addition to their derivatives demonstrate fairly varied values between studied samples (Tables 1, 2 & 3). Figure 3 of rock-eval (S1+S2mg HC/g rock) versus total organic carbon TOC, wt% illustrating the variation of organic richness and petroleum generation potential in source rocks. The plot of hydrogen index (HI) vs. oxygen index (OI) shows a similarity of kerogen type II (Figure 4).

Thermal Maturity Parameters

Vitrinite reflectance is the widely used as thermal maturity parameter of kerogen [16], and used to assess the studied samples maturity. The Vitrinite reflectance values of illustrative rocks from the Awaynat Wanin Formation range from 0.40 to 0.65, the samples of Tanezzuft Formation %Ro values ranging 0.50 to 0.77. Hot Shale samples have %Ro values range of 0.70 to 1.10 (Table 4). Level of thermal maturity also was estimated from data of Tmax and PI in Tables 1,2 &3, plotted in Figure. 5.

F1 well			G1 well			H1 well		
Dep(ft)	Ro	Fm	Dep(ft)	Ro	Fm	Dep(ft)	Ro	Fm
660	0.46	AW	700	0.52	Tezft	330	0.52	AW
720	0.47	AW	800	0.45	Tezft	450	0.58	AW
850	0.47	AW	900	0.46	Tezft	570	0.58	AW
1100	0.54	Tezft	1000	0.50	Tezft	690	0.65	AW
1250	0.54	Tezft	1100	0.68	Tezft	1000	0.71	Tezft
1400	0.60	Tezft	1200	0.69	Tezft	1250	0.62	Tezft

1550	0.58	Tezft	1300	0.61	Tezft	1400	0.69	Tezft
1850	0.65	Tezft	1400	0.68	Tezft	1550	0.68	Tezft
2000	0.77	Tezft	1500	0.70	Tezft	1700	0.73	Tezft
			1600	0.75	Tezft	1740	0.77	Tezft
			1670	0.77	Tezft	1870	0.85	H Sh
			1700	0.81	H Sh	2000	0.88	H Sh
			1790	0.72	H Sh	2060	0.84	H Sh
			1860	0.70	H Sh	2160	1.10	H Sh
						2200	1.10	H Sh

Table 4: Vitrinite reflectance values of illustrative rocks from group of studied samples. Tzft = Tanezzuft formation, A .W= Awaynat Wanin, H.Sh = hot shale.

Molecular Composition

Biomarker established by Peters and J. Moldowan [9], used as geochemical parameters of thermal Maturity and depositional environment estimated from the abundance and distribution of organic matter fractionation, were extracted of representative samples (n = 9). The values of extractable organic matter (EOM, ppm) show fairly diversity between studied formations and aliphatic and aromatic biomarkers also were chromatography measured and

illustrated in Table 5. A total nitrogen, silver and oxygen (NSO) and asphaltene (Asph) content in ppm of the EOM samples, show rudimentary difference among the samples analyzed. Low ratios of Pr/nC₁₇ and Ph/nC₁₈ (0.26 to 0.58 and 0.16 to 0.36, respectively), used to indicate types of organic matter and cross plot of phytane/nC₁₈ versus pristane/nC₁₇ to indicate types of organic matter (Figure 6). The pristane to phytane (Ph/Ph) values range. The Pr/Ph, CPI, MPI1 and %Rc data calculated and demonstrated in Table 5.

Well	Ft	Fo	EOM (ppm)	Sat (ppm)	Aro (ppm)	NSO (ppm)	Asph (ppm)	Pr/nC ₁₇	Ph/nC ₁₈	Pr/Ph	CPI	MPI1	%Rc
F1	660	A.W	1990.911	627.27	500	500	363.64	0.58	0.28	2.05	1.14	0.6	0.76
	850	A.W	1423.08	511.54	330.77	542.31	38.46	0.46	0.36	1.65	1.11	0.51	0.71
	2080	Tzft	1490.57	735.85	339.62	339.62	75.472	0.42	0.23	1.89	1.14	0.72	0.83
G1	1100	Tzft	1789.47	728.07	428.07	577.19	56.14	0.40	0.22	1.94	1.08	0.59	0.75
	1690	H.Sh	4560.87	2339.13	1039.13	908.70	273.91	0.41	0.25	2.23	1.18	0.78	0.87
	1740	H.Sh	4175	1712.50	1190	855	417.50	0.43	0.25	2.2	1.17	0.9	0.94
H1	1650	Tzft t	2871.83	1346.48	701.41	673.24	150.7	0.26	0.16	1.86	1.09	0.61	0.77
	1880	H.Sh	4576.56	2270.31	1243.75	870.31	192.19	0.42	0.25	2.09	1.1	0.76	0.86
	2200	H.Sh	3421.05	1540.35	966.67	573.68	340.35	0.28	0.21	1.69	1.15	1.05	1.03

Table 5: Geochemical parameters of biomarker established calculated from the distribution and abundance of aliphatic.

Discussion

Bulk Geochemical Parameters

The organic matter richness of sediments is considered using the total organic carbon content (TOC wt. %) and S2 + S1 mg HC/g rock parameters (Figure 3). TOC value of 1.0% is an indication for a good source rock, as a source rock by less than 1.0% of TOC may not be able to produce significant amount of hydrocarbon to start the main oil migration. However, TOC values < 0.5% point to very low potential of the source rock.

Peters, pointed out that the TOC values among 0.5 and 1.0% indicate a fair source-rock reproductive potential, TOC values between 1.0 to 2.0% reflect a good generative potential, and TOC values more than 2.0% mention to a very good generative potential [17]. Rendering to this standard, the most samples of hot shale have rich TOC content, range from 0.52 to 9.1% with majority values more than 1%. Most of the hot shale samples reveal mainly good source, associated with some good and fair source. The samples of Awaynat Wanin formation have fair to rich TOC contents, ranging from 0.60% to 2.93%. For the Tanezzuft Formation, the TOC content is

mainly fair, ranging from 0.53 to 2.55% and the majority of samples are having value less than 1. As shown in Figure 3, the rock-eval S2 +S1 mg HC/g rock versus TOC wt% show the variation of organic richness and petroleum generation potential. The distribution of generation potential of studied rocks obtained from northern edge of the Murzuq basin is shown in figure 2. The majority of the studied samples have

fair to good generation potential, supported by the presence of content of type II kerogen present also at the peak of oil generation and as reflected from the Tmax data, production index (PI) and vitrinite reflectance. Low PI in some samples appears to suggest that the most of the hydrocarbons have expelled and migrated from the resident rocks.

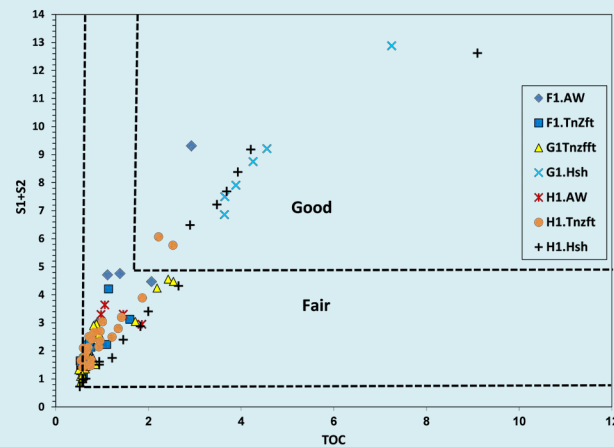


Figure 3: The rock-eval S2 +S1 mg HC/g rock versus TOC, wt% show the variation of organic richness and petroleum generation potential.

Organic Matter Type

Kerogen type is a significant characteristic in assessing interval rock potential and has main effect on the environment of the organic matter harvests [16,18]. As recognized, the gas-prone organic matter has hydrogen index HI values less than 200, mixed-oil and gas-prone has HI values between 200 and 350 and the oil-prone kerogen has

HI of 350 to more than 1000. Peters, 1986 suggested that the HI values less than 150 pointed to gas-prone organic matter from mature source rock, HI values between 150 and 300 are gas-oil-prone organic matter and HI data more than 300 is an indication of oil-prone organic matter. Thus, determination of the kerogen types is an important-geochemical side of hydrocarbon products.

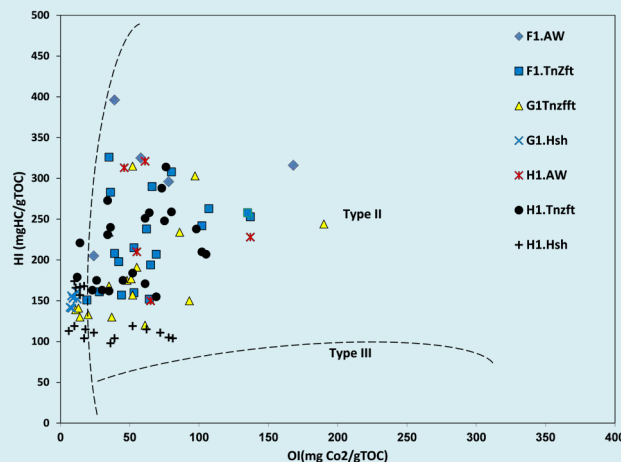


Figure 4: Plot of hydrogen index (HI) versus oxygen index (OI) illustrating the similarity of kerogen type II in studied source rocks.

The plot of HI versus OI illustration exposed in Figure 4 for the studied formations from studied wells shows that the kerogen is type II. The HI dropped in range of 100 – 350 to reflect gas and oil producing organic matter, with low OI values, less than 100 for the majority as indication of marine deposition.

Source Rock Maturity

Vitrinite reflectance and Rock-Eval T_{max}°C are extensively used as indicators of the thermal maturity of organic matter [16,17,18]. Vitrinite reflectance values less than 0.50% R_o % are immature level and values > 0.50 R_o % oil window while the values of vitrinite reflectance greater than 1.3% are post-mature, at the gas generation window [16]. Peters [17], confirmed that, numerous maturity parameters, particularly T_{max} depend on the kind of kerogen and production index (PI) whereas Tissot & Welte [16] published that, the T_{max} is a suitable maturation pointer amid 420 and 460°C for organic matter type II kerogen also T_{max} between 400 and 600°C for type III kerogen derived from terrestrial. Based on the above, thermal maturity of the

studied rocks are esteemed from vitrinite reflectance (R_o %) measurements (Table 4). The Samples of Awaynat Wanin Formation have variable maturity with values of R_o % range from 0.40 to 0.65. This, reflect that the kerogen of Awaynat Wanin Formation is in attendance of immature to marginal of mature platform. Samples of Tanezzuft Formation have 0.50 to 0.77 R_o % laid in the oil generation window. Hot Shale samples have the highest Ro values ranging from 0.70 to 1.10; typical mature source rock reached the peak of oil generation. Rock eval pyrolysis data for the studied formations, such as production index (PI) vs. T_{max} are built rendering Peters [17] (Figure 4). It is clear that, Awaynat Wanin Formation is mostly present in immature marginal of mature stage. The most of the studied samples of Tanezzuft Formation in the whole studied wells are existed in the mature point mirroring oil generation window. Eventually, all Hot Shale member samples (as the base of Tanezzuft Formation) reached the super phases of hydrocarbon maturation. The notable geochemical characteristic is that the production index (PI) values for all studied samples are < 0.40, indicating no migrated hydrocarbon (Figure 5).

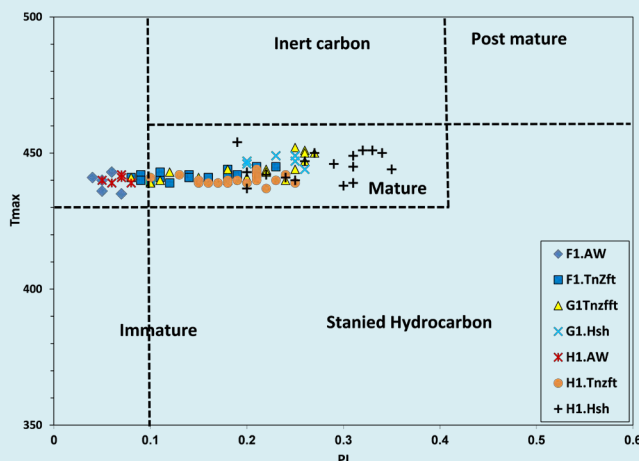


Figure 5: Plots of Production Index (PI) vs. T_{max} showing the level of thermal maturity of the studied samples.

Molecular Composition

Extractable Organic Matter: To show the richness of the formations with organic matter, EOM (ppm), Saturated (ppm), Aromatic (ppm) and Asph (ppm) as well NSO (ppm) were calculated and demonstrated in table 5. The hot shale show the highest values of EOM > 4000 ppm, suggest as super source rock, relate to Awaynat Wanin and Tanezzuft Formations. The results Sat (ppm), Aro (ppm), Asph (ppm) and NSO (ppm) are roughly consistent with content and distribution of EOM between formations.

Depositional Environment: Peters and Moldowan [9] established biomarker to use as geochemical parameters

of thermal Maturity and depositional environment. The carbon preference indices (CPI) have been measured from ratios abnormal number carbon atoms of alkanes. The CPI values < 0.9 proposed quick deposition case into very salty carbonate, evaporate saline an anoxic environments [9,16], however the CPI values > 0.9 is sign of marine sub-oxic to oxic environments. The CPI values of studied rocks are above unity, indicating to marine depositional environment. The saturated chromatograms of Awaynat Wanin and Tanezzuft formations are showing in Figure 6. The n-alkanes of samples from this study range from about nC₁₃ to at least nC₄₀ with maxima between nC₁₆–nC₁₇, in the relative distribution of the C₂₀₊ hydrocarbons shown in The Awaynat Wanin Formation

than the Tanezzuft Formation, which has more than the Hot Shale samples. The Awaynat Wanin Formation samples also show a minor odd n-alkane preference between nC_{23-27} , in comparative with the Tanezzuft and Hot Shale Formation samples. The pristane/phytane ratios with range (1 to < 3) are indicating a comparable source for organ organic matter, recommend generally mild reducing marine shale deposited under sub-anoxic conditions (Table 5). Variations in pristane/phytane within each formation might indicate level of anoxicity during deposition of each source rock type. The low phytane/ nC_{17} versus pristane/ nC_{18} ratios (0.28 to 0.58 and 0.16 to 0.36, respectively) supports a marine of environment [19]. The cross plot of nC_{17} Pr/ nC_{17} and Ph/ nC_{18} data are used to indicate types of organic matter (Figure 7) and the distribution of the samples on this plot support the marine depositional environment for the type II kerogen

within all studied source rocks [20].

Thermal Maturity: Two well-known biomarker parameters [21] used as geochemical parameters of thermal maturity calculated from the distribution and abundance of aromatic biomarkers (Table 5). The methylphenanthrene Index (MPI), calculated as $MPI\ 1 = 1.5 * [3MP + 2MP] / [P + 3MP + 2MP + 9MP + 1MP]$ and suggested by Radke, et al. [21]. It is one of the most widely used aromatic maturity parameters to estimate the level of thermal maturity of hydrocarbon. MPI 1 value of selected samples (Table 5) from both formations is ranging from 0.51 to 1.05 propose that most samples are mature. The calculated vitrinite reflectance (%Rc) from MPI1 ($\%Rc = (0.6 * MPI1) + 0.4$) used as other parameter, representative to R_o (Table 5) and confirm above observation.

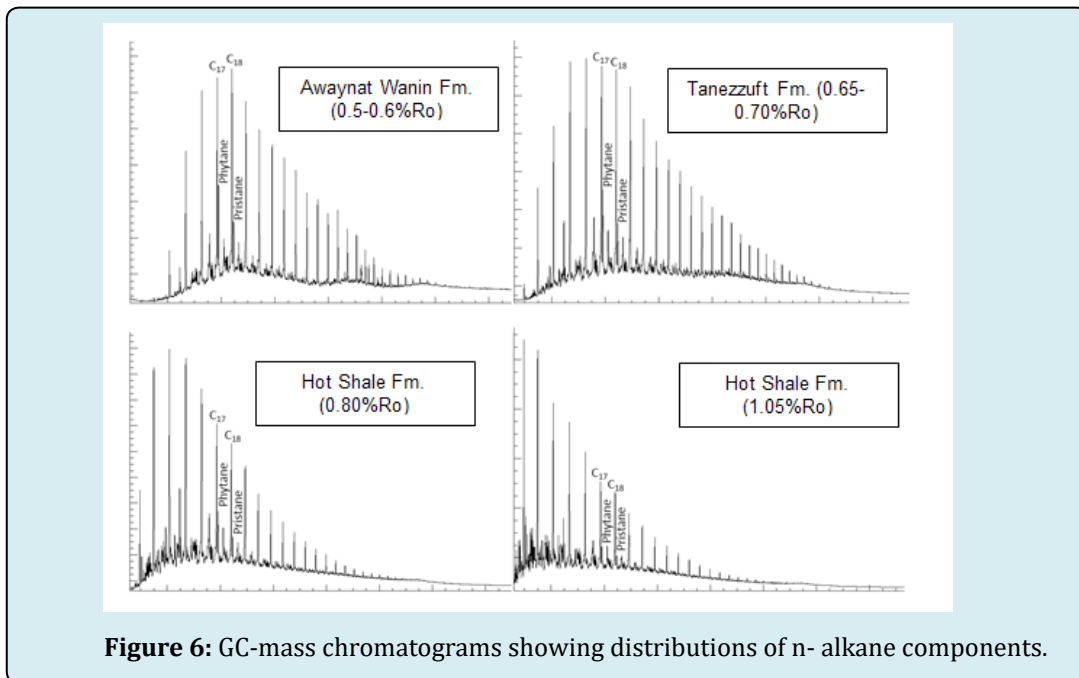


Figure 6: GC-mass chromatograms showing distributions of n-alkane components.

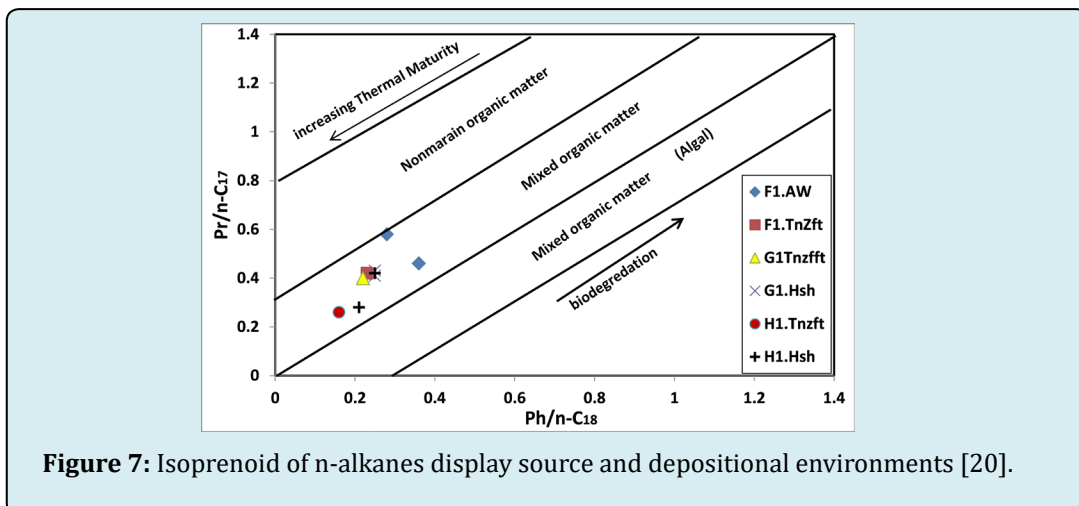


Figure 7: Isoprenoid of n-alkanes display source and depositional environments [20].

Conclusion

1. TOC values for most of source rock samples collected from the Hot Shale are all more than 2%.
2. The Tanezzuft formation samples have fair to excellent oil generation potential. The variation in TOC values may be due to different types of organic matter at different depth.
3. For the Awaynat Wanin formation samples, the TOC values vary from good to excellent for oil generation among the two studied wells.
4. Organic matter type of the investigated rocks is mainly kerogen type II although II/III OM is present.
5. The depositional environment of the organic matter type are generally consistent with marine characteristics.
6. The high abundance of low molecular weight n-alkanes of extracts indicate a high contribution of marine organic matter but these may have been affected by a high level of maturity especially for the Hot Shale samples.
7. These rocks deposited in oxic to suboxic marine conditions as reflected in Pristine/phytane, phytane/ nC_{17} and pristane/ nC_{18} ratios.
8. These rocks are thermally mature with Tmax values between 435 and 454°C and the main phase of generation has been reached.

Competing Interests

Authors have declared that no competing interests exist.

References

1. Hallett D (2002) Petroleum Geology of Libya. 2nd (Edn.), Elsevier Science Limited, Kidlington, pp: 508.
2. Meister EM, Ortiz EF, Pierobon EST, Arruda AA, Olivira AM (1991) The origin and migration fairways of petroleum in the Murzuq Basin, Libya. Volume 7, The Geology of Libya, Elsevier, Amsterdam 7: 2725-2742.
3. Burwood R, Redfern J, Cope M (2003) Geochemical evaluation of East Sirte Basin (Libya) petroleum systems and oil provenance. Geological Society Special Publication, Petroleum Geology of Africa, London 207(1): 203-214.
4. Aboglila S, Grice K, Dawson D, Williford K (2010) Use of biomarker distributions and compound specific isotopes of carbon and hydrogen to delineate hydrocarbon characteristics in the East Sirte Basin (Libya). Organic Geochemistry 41(12): 1249-1258.
5. Aboglila S, Grice K, Trinajstić K, Snape C, Williford D (2011) The significance of 24norcholestanes, 4-methylsteranes and dinosteranes in oils and source-rocks from East Sirte Basin (Libya). Applied Geochemistry 26 (9-10): 1694-1705.
6. Aboglila S, Elchaig M (2013) Organic geochemistry evolution of cretaceous potential source rocks, East Sirte Basin, Libya. Journal of Scientific Research 4(4): 700-710.
7. Aboglila S, Elaalem M, Ezlit Y, Farifir E (2018) Geochemical characteristics of six formations based on organic geochemical parameters. Murzuq Basin, Libya. Advances in Research 15(4): 1 -11.
8. Aboglila S, Abdulgader A, Albaghdady A, Hlal O, Farifir E (2019) Biomarker Ratios and Stablecarbon Isotopes to Describe Crude Oil Characteristics in the Murzuq Basin Libya. Advances in Research 18(3): 1 -12.
9. Peters KE, Moldowan JM (1993) In the biomarker guide interpreting molecular fossils in petroleum and ancient sediments. Englewood Cliffs, NJ: Prentic hall, USA, pp: 363.
10. Philp RP (2007) Formation and geochemistry of oil and gas: In: Mackenzie FT (Ed.), Sediments, diagenesis, and sedimentary rocks. Treatise on Geochemistry.
11. Echikh K, Sola MA (2000) Geology and hydrocarbon occurrences in the Murzuq Basin, SW Libya. In: Murzuq Basin, Sola MA, Worsley V (Eds.), Geological Exploration in Murzuq Basin. Elsevier, Amsterdam, pp: 175-222.
12. Bellini E, Massa D (1980) A stratigraphic contribution to the palaeozoic of the southern basins. The Geology of Libya, Academic Press, London, pp: 3-56.
13. Aziz A (2000) Stratigraphy and hydrocarbon potential of the lower Palaeozoic succession of license NC 115, Murzuq Basin, SW Libya. In: Sola MA, Worsley D (Eds.), Geological Exploration in Murzuq Basin. Elsevier, Amsterdam, pp: 349-368.
14. Vos RG (1981) Sedimentology of an Ordovician fan complex, western Libya. Sediment Geol 29(2-3): 153-170.
15. Davidson L, Beswetherick S, Craig J, Eales M, Fisher A, et al. (2000) The structure, stratigraphy and petroleum geology of the Murzuq Basin, southwest Libya. In: Sola MA, Worsley D (Eds.), Geological Exploration of the Murzuq Basin. Elsevier, Amsterdam, pp: 295-320.
16. Tissot RP, Welte DH (1984) Petroleum formation and occurrence. 2nd (Edn.), Springer-Verlag Berlin Heidelberg, Newyork, pp: 702.
17. Peters KE (1986) Guidelines for evaluating petroleum

- source rocks using programmed pyrolysis. American Association of Petroleum Geologists Bulletin. 70(3): 318-329.
18. Hunt JM, Freeman WH (1996) Petroleum Geochemistry and Geology. 2nd (Edn.), Energy & Fuels, Company New York, pp: 743.
 19. Lijmbach GWM (1975) On the origin of petroleum. Proceedings 9th world Petroleum Congress. Applied Science Publishers, London, pp: 357-369.
 20. Shanmugam G (1985) Significance of coniferous rain forests and related organic matter in generation commercial quantities of oil, Gippsland Basin, Australia. American Association of Petroleum Geologists Bulletin 69(8): 1241-1254.
 21. Radke M, Welte DH, Willsch H (1982a) Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. Geochimica et Cosmochimica Acta 46(1): 1-10.

