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Highlights

1. A wide variation of source richness and quality between Hot Shale and the Tanezzuft Formation is recognized.
2. Immature to early mature kerogen type II/III kerogen for the Hot Shale samples is reported.
3. The Tanezzuft samples are dominated by type III/II kerogen.
4. The Hot Shale and Tanezzuft Formation are of mixed organic matter input and different concentrations.

Hydrocarbon source potential of the Tanezzuft Formation, Murzuq Basin, south-west Libya: An organic geochemical approach

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Abstract

A detailed organic geochemical study of 20 core and cuttings samples collected from the Silurian Tanezzuft Formation, Murzuq Basin, in the south-western part of Libya has demonstrated the advantages of pyrolysis geochemical methods for evaluating the source-rock potential of this geological unit. Rock-Eval pyrolysis results indicate a wide variation in source richness and quality. The basal Hot Shale samples proved to contain abundant immature to early mature kerogen type II/III (oil–gas prone) that had been deposited in a marine environment under terrigenous influence, implying good to excellent source rocks. Strata above the Hot Shale yielded a mixture of terrigenous and marine type III/II kerogen (gas–oil prone) at the same maturity level as the Hot Shale, indicating the presence of only poor to fair source rocks.

Keywords: *Rock-Eval pyrolysis, Hot Shale, Tanezzuft Formation, Silurian, Murzuq Basin, Libya*

1. Introduction

The Murzuq Basin is one of the largest Palaeozoic intracratonic basins in the North African Sahara. It covers an area of about 350,000 square km in south-west Libya (Davidson et al., 2000), extending southwards into Niger. The focus of this study is the Silurian Tanezzuft Formation in three major oilfields, A, B and H within the NC115

Concession in the basin (Fig. 1). The lower part of the formation is referred to as the Hot Shale, a radioactive deposit that has a high gamma ray response in wireline logs, probably as a result of a high content of uranium (Fello et al., 2006). This organic-rich shale is thought to be the main source rock in the Murzuq Basin (Echikh and Sola, 2000; Sikander et al., 2000; Craig et al., 2008), and is estimated to be the origin of 80–90% of all Palaeozoic-sourced hydrocarbons in North Africa. These hydrocarbons have migrated into various reservoirs, ranging from Cambrian to Triassic sandstones that are sealed by shale intercalations. In the Murzuq Basin, Ordovician sandstones are the main reservoir rocks (Lüning et al., 2000).

The NC115 Concession is located in the north-western part of the basin, about 1,330 km south-west of Tripoli. It is about 25,850 square km in areal extent, covering approximately three-quarters of the area between 11° 30' and 12° 30'E, and 26° 8' and 26° 38'N. The B-NC115 Field is the most south-westerly of the fields examined. It is approximately 50 km to the south-west of the A-NC115 Field. This in turn is approximately 10 km west of the H-NC115 Field (Fig. 1).

The application of organic geochemical analyses of samples from the Hot Shale and overlying deposits of the Tanezzuft Formation in the NC115 Concession is reported in this paper in order to characterize the disseminated organic matter and to determine the hydrocarbon generation potential of, and depositional environments reflected by, the succession.

2. Geological background

The Murzuq Basin abuts the borders of Algeria, Niger and Chad. It is bounded to the north by the Al Gargaf Uplift, to the east by the Tibesti High, and to the west by the Tihemboka High (Echikh and Sola 2000). It lies to the south-east of the Ghadamis Basin, from which it is separated by the Atshan Saddle, an anticlinal structure trending approximately ENE–WSW, which leads into the western end of the Al Gargaf Uplift (Fig. 2).

The present structural framework of the basin reflects periods of uplift related to Caledonian (Late Silurian–Early Devonian), Hercynian (Late Carboniferous–Permian) and

Alpine (early Tertiary) events. The regional lineaments, NW–SE, are probably related to late Precambrian Pan-African fault systems (Fig. 3), which largely controlled the early Palaeozoic structural evolution of, and sediment accumulation in, the Murzuq Basin (Klitzsch, 1995).

Deposition of the Silurian succession began after the melting of the Late Ordovician ice sheets, which led to a major marine transgression that spread from the north, culminating in a high-stand with deposition of the Llandovery–Wenlock Tanezzuft Formation (Davidson et al., 2000). The formation was named by Desio (1936) after Wadi Tanezzuft, between Ghat and Awaynat. It includes a thick shale unit that overlies the Hirnantian (Late Ordovician) Mamuniyat Formation and underlies the Ludlow–Pridoli (Late Silurian) Akakus Formation (Fig. 4). The lower part of the Tanezzuft Formation is predominantly dark grey, fissile shale, and the upper part a monotonous argillaceous sequence interbedded with thin sandstone layers. Altogether it is more than 700 m thick in some wells in the NC115 Concession.

The basal part of the Tanezzuft Formation consists of the Hot Shale. It was referred to as Rhuddanian black shale by Hallett (2002), the Rhuddanian being the lowest stage of the Llandovery Epoch (443.8–440.8 Ma; Gradstein et al., 2012). The high level of natural radioactivity in some of the shales is the result of an increase in authigenic uranium, which is readily recognized in well logs by high gamma-ray values (up to 400 API). High gamma-ray intervals can also be related to lithologies other than hot shale, e.g., shale rich in detrital K and Th (Lüning et al., 2000; Armstrong et al., 2005). The Hot Shale consists of black, dark brown and dark grey, splintery, compact, micaceous, pyritic shale (Fig. 4). It is present only in the B42 and H39i wells, where it is up to 45 m thick. The organic matter it contains was probably a result of high algal productivity in a region of oceanic upwelling along the North Gondwanan shelf margin (Finney and Berry, 1997).

3. Samples and analytical procedures

Twenty core and cuttings samples of the Tanezzuft Formation, including the Hot Shale, were selected from seven wells in oilfields A, B and H in the NC-115 Concession

(Fig. 2). These were subjected to total organic carbon (TOC) and Rock-Eval pyrolysis analyses at the StratoChem Laboratory, New Maadi, Cairo (Egypt). The instrument used was a Rock-Eval 6 pyro-analyzer equipped with a TOC module. The samples were heated from 300°C (hold time 3 min) to 850°C (hold time 5 min) at 25°C/min for oxidation.

4. Results and discussion

The TOC/Rock-Eval analytical data on the rock samples are summarized in Table 1 and graphically represented in Figs. 5–8. The cross-plot between TOC and S_2 is reliable for evaluating the organic richness of a source rock (Dembicki, 2009), and the hydrogen index (HI) versus oxygen index (OI) cross-plot defines the type of kerogen present (Espitalié et al., 1977; Peters and Cassa, 1994). The cross-plot of HI versus T_{max} is commonly used to avoid the influence of OI for determining thermal maturity and kerogen type (Hunt, 1996), and the relationship between the pyrolysis T_{max} and production index (PI) is a valuable method for evaluating the thermal maturity of organic matter (Peters and Cassa, 1994).

As shown in Fig. 5 and Table 1, the TOC of the Hot Shale samples ranges from 1.22 to 20.90%, and S_2 values from 0.36 to 59.47 mg HC/g rock, whereas the overlying deposits of the Tanezzuft Formation have TOC values that range from 0.34 to 1.08%, and S_2 values from 0.14 to 2.78 mg HC/g rock. These data indicate the superior petroleum potential of the Hot Shale (good to excellent) by comparison with the rest of the formation (poor to fair). From a statistical point of view, shale with TOC values >3%, as for four of the six samples of the Hot Shale examined, usually contain marine organic matter, and are thus oil-prone (Demaison and Moore, 1980; Tyson, 1995; Batten, 1996).

The HI versus OI cross-plot (Fig. 6) shows that, apart from one sample, the Hot Shale deposits examined yielded Type II/III kerogen (oil/gas-prone), i.e., mixed marine and terrigenous organic matter. The exception is from well B42 at depth 4640 ft (1414 m). This contained Type III (gas-prone) kerogen, which indicates a well-oxygenated (oxic) depositional environment (Peters and Cassa, 1994). On the other hand, again with one exception, the rocks above the Hot Shale yielded Type III to II/III kerogen (gas-prone) to (oil/gas-prone). The exception is a sample from well H40 at a depth 4380 ft (1335 m) that

1 produced an HI value of 375 mg HC/g TOC (Table 1), reflecting Type II kerogen that was
2 probably derived from marine organic matter (Peters and Cassa, 1994).

3 Figs. 5 and 6 clearly separate the organic-rich Hot Shale from the organically lean
4 deposits of the rest of the formation. The difference between the organic content and hence
5 kerogen type in the two parts of the succession is likely to reflect variations in the supply of
6 organic matter, and its preservation and dilution in different depositional environments.

7 The relationship between HI and $T_{\max}$ (Fig. 7) shows that the Hot Shale and
8 overlying deposits have $T_{\max}$ values that range from 432 to 444°C and 433 to 439°C,
9 respectively (Table 1), indicating an early mature stage for the samples analyzed. This is
10 confirmed by the cross-plot of $T_{\max}$ versus PI (Fig. 8), which shows that the majority of the
11 samples lie within the zone of the early oil window.

13 5. Conclusions

14
15 The results of an analysis using TOC/Rock-Eval pyrolysis equipment of 20 cores
16 and cuttings samples taken from the Tanezzuft Formation in the Murzuq Basin of south-
17 west Libya are presented. The basal unit of the formation, known as the Hot Shale, reflects
18 deposition in a marine environment under terrigenous influence. Being close to and within
19 the early mature oil window it has generally good–excellent potential to generate both oil
20 and gas. The rest of the formation, which overlies the Hot Shale, is of similar maturity but
21 has more limited (poor to fair) potential to generate gas and minor oil. However, in places
22 there are thin horizons where the shales are good oil/gas-prone source rocks. These contain
23 kerogen types III to II/III, the organic matter having both marine and terrigenous origins.
24 The differences in geochemical characteristics between most of the Hot Shale and the rest
25 of the Tanezzuft Formation largely reflect differences in organic matter influx, mode of
26 preservation and depositional environments.

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Figure and Table captions

Fig. 1. Location of the A, B and H fields in the NC115 Concession of the Murzuq Basin and of the samples within these fields.

Fig. 2. Map of the tectonic elements in the Murzuq Basin (after Echikh and Sola, 2000).

Fig. 3. Schematic cross-section through the Murzuq Basin showing major structures, three tectonic unconformities and eroded sedimentary sequences: Unc, unconformity (after Davidson et al., 2000).

Fig. 4. Subsurface stratigraphic chart for the Murzuq Basin (substantially modified after Aziz, 2000; Gradstein et al., 2012).

Fig. 5. Organic richness based on TOC content and S_2 values of samples from the Tanezzuft Formation including the Hot Shale, plotted separately.

Fig. 6. HI versus OI of samples from the Tanezzuft Formation including the Hot Shale, plotted separately.

Fig. 7. HI versus T_{max} of samples from the Tanezzuft Formation including the Hot Shale, plotted separately.

Fig. 8. T_{max} versus PI of samples from the Tanezzuft Formation including the Hot Shale, plotted separately.

Table 1. TOC % and Rock-Eval pyrolysis results of samples from the Tanezzuft Formation.

1 Figure 1

Figure 2

Figure 3

Figure 4

ERA	PERIOD	EPOCH	STAGE	AGE (Ma)	RESERVOIR	SOURCE	LITHOLOGY	FORMATIONS
PALAEZOIC	Permian		Changhsingian	254.2				
			Asselian					
	Carboniferous	Pennsylvanian	Kasimovian-Gzhelian	298.9				Tiguentourine
			Moscovian	307.0				Dembaba
			Bashkirian	315.2				Assedjefar
		Mississippian	Visean-Serpukhovian	323.2				Marar
			Tournaisian	346.7				
				358.9				
	Devonian	Late	Frasnian-Famennian					Awaynat Wanin
		Middle	Eifelian-Givetian	382.7				Basal Devonian sandstone
		Early	Lochkovian-Emsian	393.3				Ouan Kasa/ Tadart
	Silurian	Ludlow-Pridoli	Gorstian-Ludfordian	419.2				Akakus
		Wenlock	Sheinwoodian-Homerian	427.0				Tanezzuft
		Llandovery	Rhuddanian-Telychian	433.4				Hot Shale
	Ordovician	Late	Hirnantian	443.8				Mamuniyat
			Katian	445.2				
			Sandbian	453.0				Melaz Shuqran
		Middle	Dapingian-Darriwilian	458.4				Hawaz
		Early	Floian	470.0				Ash Shabiyat
			Tremadocian	477.7				
	Cambrian	Furongian	Paibian-Stage 10	485.4				Hasawnah
		Series 3	Guzhangian	497.0				
		Series 2	Stage 3					
		Terreneuvian	Stage 2	521.0				
	PRECAMBRIAN							XXXXX
<div> <div> <div></div> <div>Not Present in NC115</div> </div> <div> <div></div> <div>Present in NC115</div> </div> <div> <div></div> <div>Sandstone</div> </div> <div> <div></div> <div>Studied formation</div> </div> <div> <div></div> <div>Clay/Shale</div> </div> <div> <div></div> <div>Limestone</div> </div> <div> <div></div> <div>Source rock</div> </div> <div> <div></div> <div>Reservoir rock</div> </div> </div>								

Figure 5

Figure 6

Figure 7

Figure 8

1

2 **Table 1**

Well name	Rock-unit	Sample type	Depth (m)	TOC wt%	S ₁ mg/g	S ₂ mg/g	S ₃ mg/g	T _{max} (°C)	HI mg HC/g TOC	OI mg HC/g TOC	PI	
B31	Tanezzuft Formation	Cores	1409	0.90	0.58	2.35	0.19	437	262	21	0.20	
			1410	1.08	0.67	2.78	0.09	439	257	8	0.19	
A17			1479	0.48	0.15	0.61	0.10	437	128	21	0.20	
			1481	0.57	0.21	0.79	0.13	438	138	23	0.21	
H39i		Cuttings	1213	0.40	0.05	0.60	0.51	436	152	129	0.08	
A37			1298	0.40	0.05	0.31	0.46	433	77	115	0.14	
			1380	0.40	0.07	0.67	0.35	439	169	88	0.09	
			1463	0.48	0.08	0.55	0.39	438	114	81	0.13	
B42			1185	0.73	0.10	1.75	0.38	434	239	52	0.05	
			1286	0.42	0.08	0.67	0.32	436	161	77	0.11	
			1395	0.34	0.09	0.14	0.50	433	42	149	0.39	
H40			1225	0.35	0.05	0.40	0.67	438	114	191	0.11	
			1335	0.68	0.53	2.56	0.21	434	375	31	0.17	
			1438	0.51	0.14	0.99	0.30	439	195	59	0.12	
B42			Hot Shale	1414	1.22	0.13	0.36	0.99	432	30	81	0.27
H39i				1449	9.70	2.58	26.63	0.98	433	275	10	0.09
H29			Cores	1473	4.86	1.96	11.04	0.21	440	227	4	0.15
				1477	8.61	2.98	22.58	0.23	444	262	3	0.12
	1482	20.9		7.42	59.47	0.33	438	285	2	0.11		
	1487	1.71		0.84	3.90	0.17	438	228	10	0.18		

3

4 **TOC** = Total organic carbon as weight percent organic carbon in rock; **S₁** = Free hydrocarbons emitted from
5 rock without cracking of kerogen (mg hydrocarbons per gram of rock); **S₂** = Residual hydrocarbons
6 representing the remaining generative hydrocarbon potential (mg hydrocarbons per gram of rock); **S₃** =
7 Generated carbon dioxide (mg carbon dioxide per gram of rock); **T_{max}** = Temperature reached during
8 maximum generation of hydrocarbons measured via S₂ peak of Rock-Eval pyrolysis (°C); **HI** = Hydrogen
9 index = S₂×100/TOC; **OI** = Oxygen index = S₃×100/TOC; **PI** = Production index = S₁/(S₁+S₂).

10

11

12

13