## Thermal Maturity and Time of Oil Generation of the Source Rock, Murzuq Basin

## \* Dr. Mohamed Omer Musa

#### Abstract

Two blocks from Murzuqe Basin were selected to examine the thermal maturity of the source rock which is the main factor controlling source rock quality. These blocks are NC-115 and NC-174. Many samples were chosen from the studied blocks and analyzed for thermal maturity as well as time of oil generation. Different techniques were used here including spore colour index (SCI), vetrinite reflectance (VR), and  $T_{max}$  as well as basin modelling to investigate time of oil generation of the source rock. All parameters indicate that the source rock at these blocks is at mature level and the oil was generated during Late Cretaceous to Tertiary periods.

Key words: Thermal maturity, spore colure index, vetrinite reflectance oil generation

#### **INTRODUCTION**

The Murzuq Basin is an intracratonic basin covering an area about 350 000 km<sup>2</sup> with sedimentary sequences about 3500 m thick (Figure,1). The stratigraphy of the basin is mostly comprised Palaeozoic and Mesozoic sediments. The principal hydrocarbon play in the basin consists of preglacil sandstone reservoir of Ordovician age sourced and sealed by overlying Silurian shale(DAVIDSON, 2000). The northern part of the Murzuq Basin represents the most important part for the hydrocarbon discoveries in the basin. The distribution and the depositional conditions of the lower Silurian source rock as well as its maturity and the time of oil generation in this part of the basin need farther investigation. To date the geochemical studies remain rather few, with just a limited number of publications largely based on total organic carbon (TOC), pyrolysis and uranium contents. A combination of organic geochemistry and organic petrology analyses is therefore necessary for a more complete potential assessment of the basin.

This study was focused in this study on the important factors that evaluate the source rock quality which include the source rock maturation as well as time of oil generation. Many techniques are used to evaluate the maturation of the source rock such as T max, spore colour

index, vetrinite reflectance. Two blocks were chosen to select samples from the lower part of Tanazefet shale which is called Hot Shale Member. These blocks are NC 115 and NC 174

#### \* Geophysics Department, Al-Mergab University

mohammed\_mossa@okstate.edu

(Figure 1).



Figure (1): Location Map of the NC 115 and NC 174 Blocks at Murzuq Basin After (YOUSSEF, 2000).

## **GEOLOGY OF STUDIED SHALE**

The Murzuq basin is the stratigraphy of the basin is mostly comprised Palaeozoic and Mesozoic sediments (Figure 2). The Silurian began with major transgression which spread from the north, across much of North Africa margin by melting of the ice led to eustatic sea level rise, culminating in highstand with deposition of the Tanezzuft Formation shales. An unconformity separates the Mamuniyat Formation from the overlying shale of the Silurian Tanezzuft Formation.



Figure (2): Stratigraphic Column of Murzuq Basin (SIJOK, 2006)

The Tanezzuft Formation consists of dark gray claystone usually with shaly lamination, very compact, frequently micaceous and pyretic, sometimes with silty and sandy interlaminae and beds, which become increasingly common upward(AZIZ, 2000). The formation is very rich in graptolites and there are indicate an Early to Middle Landovery age. The Tanezzuft Formation is up to 475 m thick in outcrop in the southwestern Murzuq Basin, while subsurface thickness in concession NC115 wells varies between 117 and 368 m (AZIZ, 2000). The Tanezzuft shale is generally regarded as the main source in the Murzuq Basin. The geochemical results indicate that the hot shale in the Murzuq Basin has generated huge quantities of hydrocarbon, with in NC-115 alone the hot shale interval may have generated approximately 8.3 to 19.4 mmbb1/km<sup>2</sup>, giving the potential for approximate amounts of entrapped hydrocarbons in the Murzuq Basin of around 40 billion barrels (AZIZ, 2000). The anoxic conditions of deposition of the hot shales probably developed as a result of restricted marine circulation in shallow seas broken by numerous islands and peninsulas, the natural result of a low energy marine transgression over an irregular post-glacial topography. The Early Silurian bottom waters were dense and very anoxic which, coupled withvery low sedimentation rates, allowed the preservation of very high concentration of organic matter (DAVIDSON, 2000).

#### **METHODS OF STUDY**

Many methods are used in this study considering source rock maturation which include:

#### **Kerogen isolation**

The first and probably main hindrance when studying the kerogen is to isolate kerogen quantitively without notable alteration of the general structure (Akaegbobi, 2000; Hutton et al., 1994). This preliminary isolation from the inorganic material is required for most physical or chemical analyses. The purpose of this preparation is to crack a concentrate of insoluble organic matter (kerogen) for optical analysis.

Ten samples have been selected from two wells S1-NC115 and EI-NC174 to be studied under microscope with methods as following:

The rock samples have been washed and dried for kerogen preparation for optical analyses, the core only must be crushed to a particle size of approximately 1 mm, then each sample exposed to Hcl in beaker to remove the carbonate from the sample. The beakers containing the sample and the Hcl have been allowed to stand at least 12 hours.

The Hcl must then be decanted from the beaker and the sample washed until neutrality (normal water) has been attained, after that Hydrofluoric acid HF must then be added to the beaker at least 24 hours, or until the silicate material has been dissolved. The sample must be continuously agitated at least during the first 4 hours. The HF must then be decanted from the beaker and the sample washed until neutrality (normal water) has been attained.

Any carbonate released during HF treatment must be removed by a final treatment with HCl. The samples then sieved using very fine sieve, until all suspension was clearly removed. Preparation of kerogen slides by using pipette to remove a little of the rest of the results in tempered solution on a clean slide, this slide which can be covered by cover slide after nearly 24 hour until all fluid evaporated. The purpose of this preparation is to obtain slides containing a thin and statistically homogeneous layer of representative, finely dispersed kerogen for "visual kerogen" analysis in transmitted and fluorescent light.

#### **Spore Color Index (SCI)**

Ten slides of kerogen isolation were used for SCI measurements to determine thermal maturity level of these samples by the color change of the palynnomorphs (spores) (MARSHALL, 1991; Spina et al., 2018).

## Vitrinite Reflectance (VR)

Vitrinite reflectance measurements are made to obtain information on the thermal maturity of kerogen (Botoucharov, 2007; Petersen et al., 2009). The technique is adapted from coal petrology and applicable to the whole range of maturities relevant to petroleum exploration. The purpose of this preparation is to obtain polished particulate mounts of sufficient representatively and surface quality for vitrinite reflectance measurement and incident light organic petrographic analysis.

Seven samples have been selected from two wells S1-NC115 (Four samples) and as EI-NC174 (Three samples) to be studied under reflected microscope. Rock samples must be broken up to a particle size of 1-2 mm, with a minimum of fine material, and mounted in fast-setting synthetic resin. Alternatively, kerogen concentrate may be mounted, the top surface of

the plug must be cleared of excess resin and carefully polished by several polished number until a scratch-free, polished surface is obtained.

#### **Basin Modelling**

The geohistory modelling package, Genex software (Clarke et al., 2004), were used as input of the lithology heat flow, the bottom hole temperature and the burial history for S1-NC115 and E1-NC174 wells.

#### RESULTS

Three types of optical measurements were applied on samples from S1-NC115 and E1-NC174 wells. These measurements are kerogen typing, Spore Color Index (SCI) and vitrinite reflectance (VR<sub>o</sub>). Deferent types of kerogen assemblages were recovered from the studied samples (See Plates I and II). The percentage of amorphous organic matter (AOM), phytoclasts and palynomorphs kerogen components for the analysed samples are given in Table (1). Both samples of the Lower Silurian lower Tanezzuft Formation hot-shale contain great amount of structure less AOM organic matter, whereas samples of the upper Tanezzuft Formation cold shale contain a large amount of AOM kerogen with associated forms of the phytoclasts and palynomorphs. In contrast, the samples of Upper Devonian Awaynat-Wanin Formation contain nearly identical amount of AOM, phytoclasts and palynomorphs organic matter.

Spore colour index (SCI) determinations were made on the same kerogen samples. The results of SCI measurements are shown in Table (2). In the lower Palaeozoic sequence, the samples are dominated by AOM, the land plant and spores are rare or absent, other maturity indicator can be used instead of SCI.Moreover, vitrinite reflectance measurements for seven samples from S1-NC115 and E1-NC174 were made in this study (Table 2). The values of vitrinite reflectance in S1-NC115 range from 0.78% - 0.8% and have an average of 0.79%.

# Table 1: Showing the Percentage of Each Kerogen Group as Remarked Under Transmitted Microscope.

Well name	S.NO	Formation	Depth (ft)	Amorphous %	Palynomorphs %	Phytoclasts %
S1- NC115	1	Awaynat- Wanin	3260	30	31	39
	2	Awaynat- Wanin	3410	29	36	35
	3	Tanazzuft	4670	30	38	32
	4	Tanazzuft	4675	34	36	30
	5	Tanazzuft	4700	56	27	17
E1- NC174	1	Tanazzuft	6350	43	32	25
	2	Tanazzuft	6900	54	32	14
	3	Tanazzuft	7242	97	3	0
	4	Tanazzuft	7254	98	2	0
	5	Tanazzuft	7268	96	4	0
	6	Tanazzuft	7284	97	3	0

## Plate I

Slide (1) at Depth 3260 ft, Well name S1-NC115, Awaynat-Wanin Formation, showing Phytoclasts.

Slide (2) at Depth 3260 ft, Well name S1-NC115, Awaynat-Wanin Formation, showing Palynomorphs Spore.

Slide (3) at Depth 3260 ft, Well name S1-NC115, Awaynat-Wanin Formation, showing Amorphous Organic Matter (AOM).

Slide (4) at Depth 3260 ft, Well name S1-NC115, Awaynat-Wanin Formation, showing Amorphous (AOM) under fluorescent light.

Slide (5) at Depth 3410 ft, Well name S1-NC115, Awaynat-Wanin Formation, showing Palynomorphs Spore.

Slide (6) at Depth 3410 ft, Well name S1-NC115, Awaynat-Wanin Formation, showing Phytoclasts.



Plate I Showing Each Kerogen Group as Remarked Under Microscope. Plate II

Slide (1) at Depth 6350 ft, Well name S1-NC174, Tanezzuft Formation, showing Palynomorphs Spore.

Slide (2) at Depth 6350 ft, Well name S1-NC174, Tanezzuft Formation, showing Kithinozoa.

Slide (3) at Depth 7527 ft, Well name S1-NC174, Tanezzuft Formation, showing Amorphous (AOM).

Slide (4) at Depth 7527 ft, Well name S1-NC174, Tanezzuft Formation, showing Amorphous (AOM) under fluorescent light.

Slide (5) at Depth 6900 ft, Well name S1-NC174, Tanezzuft Formation, showing Graptolites.

Slide (6) at Depth 7284 ft, Well name S1-NC174, Tanezzuft Formation, showing Palynomorphs Spore.



Plate II Showing Each Kerogen Group as Remarked Under Microscope.

 Table 2:. Optical Maturity Data for S1-NC115 and E1-NC174 wells. %Ro = Vitrinite

 Reflectance, SCI = Spore Colour Index, %RE = Vitrinite Reflectance Equivalents, and

 N A = Not Avalible

Well Name	Depth (ft)	Formation	%R₀	%RE	SCI (1-10)
NC-115	3260	Awaynat Wanin	1.022	NA	5.5
	3410	Awaynat Wanin	1.117	NA	6
	4670	Tanezzuft	1.027	0.82	6
	4675	Tanezzuft	1.01	0.8	6
NC-174	4700	Tanezzuft	NA	NA	6.5
	6350	Tanezzuft	NA	NA	5.5
	6900	Tanezzuft	NA	NA	6
	7242	Tanezzuft	0.99	0.79	6
	7254	Tanezzuft	NA	NA	6.5
	7268	Tanezzuft	1.01	0.8	6.5
	7284	Tanezzuft	0.99	0.79	6.5

# DISCUSSION

The assessments of thermal maturity have been done on the Tanezzuft Formation at S1-NC115 and E1-NC174 where the core samples from Tanezzuft Formation have been geochemically analyzed in this study. From the Rock-Eval data, the production index and the Tmax gave an indication of a generally mature source rock due to moderate values of Tmax (439 - 448  $^{\circ}$ C) and moderate values of production index (0.14 – 0.22); most of these values correspond to the oil window. The oil window based on the Rock-Eval parameters is taken to

be  $435 - 470^{\circ}$ C Tmax (early mature  $435 - 445^{\circ}$ C, peak mature  $445 - 450^{\circ}$ C and late mature ~  $470^{\circ}$ C; PETERS, 1993) and 0.1 – 0.4 production index (early mature ~0.1, peak mature ~0.25 and late mature~0.4; PETERS, 1993).

The PI, shows clear trend in maturity increase from the top to the bottom through the study section of wells S1-NC115 and E1-NC174.

Vitrinite reflectance is the most reliable and precise method of assessing thermal maturity in the source rocks (Botoucharov, 2007; Petersen et al., 2009; Bustin *et al.*, 1985). It increases regularly from a minimum of 0.15% to greater than 5.5% at a level equivalent to the lower green schist metamorphic facies. The oil window is defined relying on the vitrinite reflectance value as presented in Table (3).

# Table 3: Vitrinite Reflectance and Rock-Eval Parameters Describing Source RockThermal Maturity from (PETERS, 1993) .

Maturation level	PI	T <sub>max</sub> (C°)	R <sub>o</sub> (%)	SCI (1-10)
Beginning oil	~ 0.1	~ 435 – 445	~ 0.6	3.5-5
window				
Peak oil window	~ 0.25	~ 445 – 450	~ 0.9	5-7
End oil window	~ 0.4	~ 470	~1.4	7-8.5

The marine deposits of pre-Devonian age often contain little or no vitrinite as illustrated under microscope. However, Lower Silurian shales in the Murzuq Basin contain fragments of graptolites and chitinozoans. The graptolites and chitinozoan reflectance values were converted to vitrinite reflectance equivalents (%VR<sub>E</sub>) using Cole's (1994) conversion chart and Tricker's formula [VR<sub>E</sub> = ( $R_{chit}$ -0.08)/1.152] (Tricker *et al.*, 1992) respectively.

The Lower Tanezzuft Formation hot-shale samples at E1-NC174 well are characterized by vitrinite reflectance equivalent values ranges from 0.78% to 0.80% at 7242 – 7284 feet, with an average of 0.79%. These values of vitrinite reflectance suggest a mature source rock with respect to the oil window. Further to the North of well E1-NC174 at well S1-NC115, with thinning of the Palaeozoic strata, the maturity of Lower Silurian Tanezzuft Formation 'hot-shale' remained the same, the average graptolite reflectance (vitrinite equivalent) measured is 0.8%. This indicates that the maturity levels are not the result of present-day burial.

Furthermore, The spore color index (SCI) (MARSHALL, 1991; Spina et al., 2018), suggest that the samples from lower Tanezzuft at wells S1-NC115 and E1-NC174 hot-shale are mature average SCI is 6.0 (see Table 2).

#### **Burial History and Timing of Oil Generation**

Burial history reconstruction performed for wells S1-NC115 and E1-NC174, located in the central part of NC-115 and meddle part of NC-174 Concessions, shows two cycles of subsidence separated by uplift and cooling during Permian-Triassic (Figure 3 and 4). The first cycle occurred during the Palaeozoic and is characterized by continuous and rapid burial until late Carboniferous Hercynian inversion and subsequent uplift and erosion, associated with uplift of the Qarqaf Arch to the North. The pre-Hercynian burial and temperature are largely determined by the amount of eroded section. The burial depth reached by the rocks today is result of the second phase of subsidence that occurred after Triassic-Jurassic rifting.

Maturity data and burial history analyses indicate that the Lower Silurian 'hot shale' generated hydrocarbons, but the latter indicates they reached their highest maturity only relatively recently (i.e., during Late Cretaceous-Tertiary). The level of organic maturity reached prior to the Hercynian uplift and erosion is directly proportional to the depth of burial at that time. The early episode of hydrocarbon generation is shown by the position of the modeled hydrocarbon generation window in (Figure 5 and 6). There is many different suggesting for the time of oil generation. For example Aziz suggest the source entered the oil window in the Carboniferous to Permian, by used input data 2000 m eroded in Hercynian phase, while this study used 250 m.



Figure 3: Burial Curve Geohistory Diagram of the S1-NC115 Well.



Figure 4: Burial Curve Geohistory Diagram of the E1-NC174 Well.



Figure 5: Hydrocarbon Windows Geohistory Diagram of the S1-NC115 Well.



Figure 6: Hydrocarbon Windows Geohistory Diagram of the E1-NC174 Well.

#### CONCLUSION

The spore colour index (SCI) and vitrinite reflectance equivalent suggest that the samples from lower Tanezzuft at wells S1-NC115 and E1-NC174 hot-shale are mature. With thinning of the Palaeozoic strata, at well S1-NC115 compared to E1-NC174 the maturity of Lower Silurian Tanezzuft Formation 'hot-shale' remained the same, the average graptolite reflectance (vitrinite equivalent) measured is 0.8%. This indicates that the maturity levels are not the result of present-day burial. Maturity data and burial history analyses indicate that the Lower Silurian 'hot shale' generated hydrocarbons and reached their highest maturity only relatively recently (i.e., during Late Cretaceous-Tertiary).

النضج الحراري وزمن تولد البترول للصخور المصدرية للنفط بحوض مرزق

د. محمد عمر موسي

. قسم الجيوفيزياء ،جامعة المرقب ،ليبيا

مستخلص الدراسة: لقد تم اختيار اتنين من الامتيازات النفطية في حوض مرزق لاختبار درجة النضج الحراري للصخور المصدرية للنفط الذي يعتبر العامل الرئيسي المتحكم في جودة الصخور المصدرية للنفط. الامتيازات النفطية المختارة هي ان سي 174 و ان سي 115 حيث تم اختيار العديد من العينات من الامتيازين لمعرفة النضج الحراري وكذالك لمعرفة زمن تولد البترول في الحوض. عدة تقنيات استخدمت في هذة الدراسة متمثلة في: درجة لون الابواغ و درجة انعكاس الفترينايت و درجة الحرارة القصوى و كذالك ثم استخداك موديلات الحاسوب لمعرفة زمن تولد البترول في الحوض. جميع المؤشرات دلت بأن الصخور المصدرية للنفط تعتبر في مرحلة نضج حراري وأن النفط تولد في الحوض في الحوض في الفترة من زمني الكريتاسي والثلاثية.

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