## Source Rock Evaluation of the Late Triassic – Jurassic Sediments at Wadi Bih and Wadi Milaha, UAE

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Abstract: Sedimentary rock samples from Late Triassic – Jurassic Formations at Wadi El Bih and Wadi Milaha in the northern part of the UAE have been analyzed using various geochemical methods in order to decipher their organic signature. Examination of the distribution of total organic carbon (TOC) at Milaha Formation (0.07wt% – 2.60 wt%) with average 0.82 wt%, Ghalilah formation (0.04wt% - 0.22 wt%) with average 0.11 wt%, and Musundam Formation (0.05 wt% - 7.70wt%) with average 0.73 suggests that the petroleum potential of the Late Triassic - Jurassic Formations should be taken into consideration. The Late Triassic - Jurassic episodes permitted the accumulation of organic matter, which is typically shallow carbonate plateform as indicated by the unimodal distribution of N-alkane. It is concluded that the organic matter of the Late Triassic - Jurassic is marginally mature, as indicated by the high content of (0.01% - 0.1%) in bitumen, suggesting that the organic matter has been maturedat the beginning of catagenesis. These new results testify to the establishment of suboxic conditions that led to the accumulation and preservation of good quantities of organic matter in the northern part of UAE. However, the results of pyrolysis-gas chromatographic analyses showed that the organic matter of the Late Triassic - Jurassic Formations is rich in sulphur compounds. The presence of sulphur-rich kerogen resulted in the early generation of hydrocarbons from this unit. The results of multi-step Py-GC analyses indicated that the composition of hydrocarbons generated in these two carbonate source rocks will be different, particularly during the early stages of maturation. The Late Triassic – Jurassic sediments could generate mature oil (effective source rock) whereas the Jurassic deposites could only generate oil if subjected to high thermal maturity (relic effective source rock). Based on the obtained results, the Late Triassic – Jurassic sequence has a source organic facies in the northern part of UAE.

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### 1. Introduction

This geochemical study was focused on a Late Triassic - Jurassic, known in the northern part of the UAE as the Milaha, Ghalilah, and Musandam Formations. This Formations represents shallow carbonate platform covered the northern part of the UAE. This platform generated significant volumes of sediments mainly comprising dolomitic limestones to stromatolites algal limestone and oolitic peloidal lime-grainstone (Fig. 1). The aim of the present study was to decipher the geochemical signature of the Late Triassic - Jurassic organic-rich facies localized in the northern part of the UAE (Fig. 2). This work is based on N- alkane distribution as a method used widely for screening the petroleum generative potential of sedimentary rocks. It is rapid and requires only small amounts of material, and generally produces reliable data (Espitalié et al., 1977, 1985; Bordenave et al., 1993). In combination with gas chromatography, liquid chromatography, Pyrolysis gas chromatography, and Total organic carbon study appropriate methods for remain good а characterization of organic matter type and

depositional environment (Tissot et al., 1971; Tissot & Welte, 1984; Hunt, 1996).

# 2-Geological setting

The Late Triassic - Jurassic outcrops are located in the northern part of the UAE in Wadi Bih. These outcrops represented by Milaha Formation which can be broadly divided into three intervals. The lowest 60 m comprise grey and Khaki weathering, thin and medium-bedded, bioclastic dolomitic limestones with beds of pale grey weathering stromatolites algal limestone horizons with fenestral textures Limestones and thin packstone with lithic sand grains. Spectacular dome-shaped stromatolites, up to 1m across, and occur about 46 m above the base of the succession in Wadi Bih. The middle part of the succession consists of crag-forming, thicker bedded dark grey and gravish - brown limestones. These include beds of fine-grained, dolomitic, peloidal lime-grainstone, some of them oolitic. Large megalodontid bivalve shells are characteristically abundant at some horizons. Interbedded with the limestones some nodular limestones and occasional

conglomeratic horizons. Near the top of the formation, there are several bright orange and pinkweathering sandy limestones with cross and planar lamination (Fig. 2). The Ghialilah is lithologically the most distinctive unit of the carbonate platform succession. It comprises predominantly orange and red limestones and dolomitic limestones. The base of the formation is taken at the upward change from the lime rich Milaha Formation to a succession dominated by interbedded nodular limestone. The top of the Ghalilah Formation is marked by a generally sharp colour change from orange weathering limestones to grey limestones of the Musandam Formation (Fig. 2). Three important marker intervals have been mapped in the north of the area from base to top the lowest 60 in of the Ghalilah Formation contain nodular limestones. Sandy limestones with significant amounts of sub very fine sand detrital quartz, and lime. Prominent beds of strongly parallel laminated sandstone also occur in the lowest 60 in of the Ghalilah Formation in Wadi Milaha and Wadi Ghalilah. The Musandam Formation can be broadly divided into three intervals. The Musandam 3 Formation is dominated by a sequence of crossbedded, bioclastic, peloidal lime-grainstones, many coral fragments and medium grey weathered. Chert nodules and discontinuous bands of chert occur towards the top of the formation, and partial silicilication of bioclastic fragments, particularly corals, is a distinctive feature for replacement, may

be occurred during the slow or discontinuous deposition of the limestones (Alsharhan, A.S. and Kendall, C.G. St.C 1994; Alsharhan, A.S. and Whittle, G.L. 1995) and typically takes the form of an orange brown weathering crust that replicates the fossil morphology. In exposures above adjacent Ghalilah the succession comprises thin-to mediumbedded bioclastic, peloiclal and oncoid limegrainstoncs, with pebble-conglomerates containing intraformational clays. The environment of deposition of the Musandam 3 Formation is interpreted as relatively high energy; the combination of coral debris, cross-bedded grainstones and minor intrafonnational conglomerates suggests deposition at or close to the carbonate platform margin. The Musandam 2 Formation Consists of cross-bedded peloidal grainstones, oncolitic packstones and bioclastic packstones containing corals (including solitary and colonial species), inferred to have been deposited relatively close to the platform margin. Towards the top of the Musandam I Formation there is an overall increase in the lime-grainstone facics and decrease in the occurrence of lime-mudstone and lime-wackestone. It is bedded sequence records a regular fluctuation of depositional environment from protected lagoons (oncoid-hearing limestones) to high-energy shoals (cross-bedded grainstones). Through to an open marine shelf (bioclaslic limepackstones and bioclastic lime-wackestones) (Fig. 2).



Fig.1. View of the Milaha, Ghalilah, and Musandam Formations at Wadi Bih and Wadi Milaha.



**Milaha Formation** 

tion Ghalilah Formation

Musandam Formation

Fig.2. Schematic geological section in the Milaha, Ghalilah, and Musandam Formations based on section measured in Wadi Bih and Wadi Milaha.

### 3. Methods

### 3.1. Sampling

This study is based on 38 outcrop samples collected from Milaha, Ghalilah, and Musundam Formations at Wadi Bih northern part of the UAE, in average amount of 500–1000 g per sample. All these samples were selected on account of their organic matter richness (dark grey limestones). Immediately after collection, all samples were dried at 40°C for a few days. Then the samples were finely powdered prior to analysis.

### **3.2.** Analytical procedure

# 3.2.1. Bitumen extraction and liquid-column chromatography

Bitumen, from powdered sample (30-40 g), was extracted with dichloromethane as solvent  $(300-400 \text{ cm}^3)$  for 12 h at 40°C. After filtration the solvent was evaporated (rotary evaporator with water aspirator, evaporation temperature 40°C). Then, the extracts ("free oils" or bitumen) were concentrated by allowing the oil–solvent solution to stand at room temperature until the CH<sub>2</sub> Cl<sub>2</sub> was removed. The bitumen was fractionated by column chromatography on alumina over silica gel. A variety of fractions, including aliphatics (F1), aromatics (F2), and polar compounds (F3), were obtained. F1 and F2 were eluted by n-hexane and n-hexane: dichloromethane (65:35 v/v), respectively. The polar compounds were obtained by mixture of Bezene: Ethanole 2:1.

# 3.2.2. Aliphatic hydrocarbons analysis

Saturated hydrocarbons were analyzed using gas chromatography, the GC was used with a 30-m fused-silica column (0.25 mm i.d.) coated with 5% phenyl methyl siloxane and flame ionization detector (FID). Helium was used as the carrier gas at a flow rate of 1.4 mL/min. The following temperature program was used: 25–325°C with ramping at 4°C/min. The relative contents of particular compounds were calculated from peak areas.

# 3.2.3. Kerogen type

Powdered samples (0.5g) were analyzed using pyrolysis gas chromatography (Py-GC); the following temperature programe was used 100-750°C with ramping at 4°C/min. The relative contents of particular compounds were calculated from peak areas and the type of kerogen will be defined.

# 3.2.4. Total organic carbon content (TOC)

Five grams of powdered, dried and sieved sediment sample were placed in beaker. After that 10 % HCl were added to remove all the inorganic carbon and heat to complete removal of the inorganic carbon. Then take 0.25 gram of sample after HCl and analyze by Leco- carbon analyzer (CS-200) by ignition the sample in the presence of O2. All Co2 released from the ignition of organic carbon will be collected by CO2 trap, then detected by CO2 detector and recorded by digital voltammeter record.

# 4. Results and discussion

# 4.1. Bitumen extraction data

The results of the bitumen extraction and the total organic carbon content (TOC) are given in Table 1. The quantities of the dichloromethane extracts are low, ranging from 0.01 (Ms39) to 0.15 (Gl48) mg/g dry weight for the analyzed samples. The extracts from the Late Triassic Jurassic formations are dominated by higher molecular weight compounds in the range of  $n-C_{23}$  to  $n-C_{30}$ . The low concentrations probably result from the low thermal maturity of organic matter (Tissot & Welte, 1984; Durand, 1993; Waples, 1985; Vandenbroucke *et al.*, 1993; Peter *et al.*, 1999).

# 4.2. Aliphatic hydrocarbons analysis data

As indicated in Fig. 3, the sediments at Wadi Bih have carbon numbers ranging from 13 through 28. It is known that the lower-molecular-weight *N*-alkanes (<C21) are derived from algae and bacteria (Wakeham, 1990), while the high-molecular-weight homologs (>C22) mainly originate from higher plants

wax (Huang *et al.*, 1999). As shown in Fig. 5, gas chromatograms show a unimodal hydrocarbon distribution with a major mode at *n*- C<sub>26</sub>. This result suggests the presence of type-II organic matter in the Wadi Bih area (Peters & Moldwan, 1993). Pristane and phytane occur in very high concentrations in the sample extracts (Fig. 3; Table 1). The Late Triassic – Jurassic source rock show in general a low n-C<sub>17</sub> /(n-C<sub>17</sub> + n-C<sub>27</sub>) ratio. The presence of high molecular weight n-alkanes in the Musandam Formation can be attributed to terrestrial plant input (Tissot and Welte, 1984.), the short chain n-alkanes are reported to be of algae (Gelpi *et al.*, 1970). The dominance of high molecular weight compounds is more pronounced in the Musandam Formation.

## 4.3. Palynofacies and hydrocarbon products

Qualitative analysis of the dispersed organic matter of the studied samples from Wadi Bih and Wadi Milaha shows that, they mainly of marine palynomorphs amorphous organic matter (MAOM) (such as dinoflagellate microforamenifiral test lining) are present in greater quantities than the terrestrial palynomorph amorphous organic matter (TAOM), black wood, and plant tissue. Ultimately, the palvnofacies both terrestrial (such as spore, pollen, algae and fungi) are present in very smaller quantities, and The hydrocarbon products are mainly based on the nature of organic matter, they are classified into gas prone organic matter such as terrestrial amorphous organic matter, plant tissues and brown wood or they are oil prone such as palynomorphous (terrestrial and marine), and marine amorphous organic matter (MAOM) (Fig. 4).

# 4.4. Depositional environment

The measurements of TOC were performed using Leco carbon analyzer (CS-200). Table 1 shows TOC distribution of the studied outcrop samples. This shows that the sediments in the Wadi Bih area contain visible carbonaceous matter with TOC values ranging from (0.07wt% -2.60 wt%) at Milaha Formation with average 0.82 wt%, Ghalilah formation (0.04wt% - 0.22 wt%) with average 0.11 wt%, and Musandam Formation (0.05 wt% -7.70wt%) with average 0.73 suggests that the petroleum potential of the Late Triassic - Jurassic Formations is not ignored in such area.. The organic content of sediments can be attributed to three factors: primary biological productivity, preservation rate of organic matter, and rate of organic deposition versus mineral deposition. Moreover, it is known that the decomposition rate of biomolecules is controlled mainly by the composition of source biomass and by the redox conditions. Nevertheless, the less oxic environment promoted better organic preservation in the depositional environment (Tissot & Welte, 1984). Thus, our results suggest that the Late Triassic -

Jurassic episodes are generally conductive for preservation/accumulation of a relatively high

amount of organic matter in a suboxic depositional environment.





Fig.3. Gas Chromatograms of representative samples from Wadi Bih and Wadi Milaha.

# 4.5. Post-depositional modifications

The variations in redox conditions during the deposition of the Late Triassic - Jurassic organic matter and the oxidation may also be linked to outcropping conditions. This trend is commonly interpreted as а result of increasing degradation/oxidation of type-II organic material. The lower abundances of aliphatic hydrocarbons (Fig.3; Table 1) in the Late Triassic - Jurassic sediments are attributed possibly to a removal of these compounds by combination of post-generation processes such as weathering and biodegradation (Yamanaka et al., 1999). In addition, pristane/n-C<sub>17</sub>  $(Pr/n-C_{17})$  and phytane $/n-C_{18}$   $(Ph/n-C_{18})$  indices have been widely used as indicators of oil biodegradation (Overton et al., 1981; Kennicutt, 1988; Didvk & Simoneit, 1989). As the easily degraded normal hydrocarbons (n-C<sub>17</sub> and n-C<sub>18</sub>) are lost, the more degradation-resistant isoprenoids (pristane and phytane) are conserved, resulting in a relative increase of the ratios of pristane /n-C<sub>17</sub> and phytane /n-C<sub>18</sub> in outcrop samples. The results presented in Table 1 indicate that these samples displayed relative change in the ratios of Pr/n-C<sub>17</sub> and Ph/n-C<sub>18</sub>, with

values in the range of 0.76–6.72 and 1.06–5.69, respectively. These characteristics correspond to moderate degrees of biodegradation (Peters & Moldowan, 1993). Generally all samples were biodegraded (and/or weathered) to such a degree that alkanes (n-C<sub>17</sub> and n-C<sub>18</sub>) have much lower concentrations. The preferential degradation of short-chain *N*-alkanes over isoprenoids is illustrated in (Figs. 5 & 6). The absolute concentrations of pristane and phytane are relatively constant for most of the samples, which may suggest a selective removal of *N*-alkanes over isoprenoids in biodegraded samples.

# 5. Conclusions

Geochemical analyses allow us to characterize the Late Triassic – Jurassic Horizons organic matter at Wadi Bih northern part of the UAE. According to liquid chromatography and *N*-alkanes distribution, it is concluded that the Late Triassic – Jurassic Horizons organic matter is clearly related to type-II kerogen, and is located towards the end of diagenesis and beginning of catagenesis. The Late Triassic – Jurassic Horizons corresponds to a suboxic event that led to the accumulation and preservation of good quantities of organic matter. Biodegradation, weathering and oxidation of the Late Triassic - Jurassic Horizons organic matter are detected and probably linked to outcropping conditions. These geochemical characteristics suggest that the Late Triassic -Jurassic Horizons could be a promising area for hydrocarbons exploration in the subsurface of the UAE.

Table 1. TOC, Sulfur, Bitumen, Gas Chromatograms analyses of representative samples from Wadi Bih and Wadi Milaha.

Sample Name	TOC wt%	Sulfur%	Bitumen %	Pr./ ph.	Pr./ nc17	Ph./ nc18	СРІ	C max.	Waxines
MDTOP4	0.12	0.10	-	0.33	5.27	3.92	0.66	26	0.18
MDTOP9	0.20	0.10	-	-	-	2.18	0.44	26	0.00
MS6	0.05	0.07	_	0.58	-	3.28	1.10	25	0.00
MS7	0.13	0.21	_	0.38	1.06	1.11	1.93	25	0.52
MS8	0.14	0.08	0.03	0.29	-	5.44	0.67	26	0.00
MS14	2.60	0.13	-	0.22	3.03	2.47	0.47	26	0.05
MS15	0.44	0.18	0.11	0.42	-	3.26	0.63	26	0.00
MS21	0.07	0.09	-	0.34	1.83	3.24	0.60	26	0.20
MS22	1.90	0.14	-	0.14	2.26	4.46	0.58	26	0.08
MS39	0.12	0.10	-	0.26	1.26	3.18	1.83	25	0.93
MS44	0.83	0.17	0.01	0.43	-	6.76	0.41	24	-
MS48	0.20	0.10	-	0.43	-	0.46	0.40	26	0.24
MS50	0.05	0.07	-	0.16	-	10.53	0.30	26	0.00
GL9	0.24	0.11	-	0.34	-	5.00	0.68	26	0.00
GL15	0.19	0.14	0.05	0.36	1.49	4.33	1.67	25	0.24
GL17	0.40	0.17	-	0.24	-	6.00	0.62	26	0.00
GL19	0.04	0.07	-	0.20	0.86	5.77	0.31	26	0.24
GL20	0.20	0.07	0.10	0.21	-	4.78	0.61	26	0.00
GL29	0.10	0.11	-	0.31	-	4.70	0.66	26	0.00
GL31	0.14	0.08	0.03	-	1.59	-	0.43	26	0.74
GL33	0.17	0.03	-	0.15	-	16.84	0.34	26	0.00
GL34	0.09	0.08	-	0.39	3.26	3.80	1.89	25	0.02
GL35	0.17	0.13	-	0.31	-	4.93	0.66	26	0.09
GL36	0.06	0.09	-	0.41	-	5.90	0.64	26	0.00
GL37	0.10	0.13	-	0.24	-	8.31	0.36	26	0.00
GL39	0.22	0.08	0.08	0.44	6.72	9.27	0.75	26	0.02
GL40	0.08	0.07	-	0.20	-	7.68	0.36	26	0.00
GL41	0.10	0.11	-	0.27	-	4.69	3.60	25	0.00
GL42	0.09	0.10	0.03	0.27	-	6.16	0.38	26	0.00
GL47	0.06	0.08	0.05	0.36	-	3.38	0.66	26	0.00
GL48	0.14	0.10	-	0.33	-	-	2.04	25	0.00
GL55	0.07	0.10	-	0.39	-	6.44	0.32	26	0.00
ML2	0.16	0.09	0.15	1.00	-	3.68	1.24	25	0.00
ML3	0.11	0.08	-	0.34	-	3.40	0.34	26	0.00
ML8	0.09	0.11	-	0.64	-	5.23	1.47	25	0.00
ML12	0.07	0.07	-	0.63	-	2.45	1.67	25	0.00
ML10	0.12	0.14	-	0.48	-	6.03	0.76	26	0.00
ML18	0.23	0.09	-	0.15	-	7.98	0.38	26	0.00



Fig. 4: Photomicrograph showing spores, pollen, dinoflagellates cysts, black to brown wood remains, plant tissues, fungal spores, and undetermined palynomorphs



Fig.5. Plotting Pr/n-C17 versus Ph/n-C18 showing source type of Late Triassic – Jurassic Formations (GC) (after Lijmbach, 1975)



Fig.6. Plotting Pr/n-C17 versus Ph/n-C18 showing source type of Late Triassic – Jurassic Formations (PY-GC) (after Lijmbach, 1975)

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