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Organic Geochemical Evaluation of the Black Shale interbeds Within the Lithological Succession of the Al Aziziyah Formation, NW Libya

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Abstract

The samples under investigation represent the black shale in interbeds within the Al Aziziyah Formation, located in the NW part of Libya and were analysed using geochemical techniques method and a variety of organic geochemical parameters. The aim of this study is to assess the type of organic matter, thermal maturity, and environment of deposition, based on biomarker distributions and Rock-Eval pyrolysis. The Gas chromatograms of the saturated hydrocarbon fractions of the study samples display a smooth high-end member distribution of the n- n-alkanes extending beyond nC_{34}. The sample displayed evidence of biodegradation as suggested by the presence of the loss of some of the lower molecular weight n-alkanes. The predominance of high molecular weight n-alkane in the study sample suggests a significant input of higher land plant organic matter into these sediments. Geochemical (Rock-Eval, Tmax. values ranging from 416-439^{0}C typical of immature range). Another related feature of these rocks extracted is the presence of a high relative abundance of gammacerane, indicating an anoxic marine hypersaline source depositional environment. The relatively high abundance of common land-plant-derived biomarkers, such as oleananes, is a clear indication of major terrigenous input to the source of these extractable organic matters. The high abundance of C_{24} tetracyclic terpanes could be associated with higher land-plant, algae, or microbial sources, thereby suggesting a mixed source input. TOC valued < 0.5 wt.%, in the analyzed samples can be considered as a poor source rock generative potential. Based on this study, it can be said that the interbedded shales of the Al Aziziyah Formation seem to have received substantial amounts of land-derived organic matter that has been transported into an open marine subtidal depositional setting had prevailed and was deposited in a photosynthetic-organisms dominated environment (thereby suggesting a mixed source input).

INTRODUCTION

The area that forms the scope of this paper is situated in Ras al Lifa, and Abu Arqub quarries developed at about 11 km SW of Al Aziziyah town (Figure 1). Previous studies on the Triassic sedimentary rocks of Jabal Nafusah are mostly limited to geological and petrological descriptions with little or no emphasis on the organic geochemical aspects and evaluations of the carbonaceous units in this part of Libya. A detailed organic geochemical study was performed on selected black shale samples collected from two outcrop locations that are representative of the Al Aziziyah Formation.

Kurrsh and Al Aziziyah Formation represent the Triassic rocks, which were grouped later in the Al Mazul Group (Ben Ashour et al., 1991). The name of Al Aziziyah Limestone was introduced by the researcher Parona (1914) for the rocks outcropping around the Al Aziziyah town, south of Tripoli. The strata of the Al Aziziyah Formation are well exposed including the upper contact with Abu Shaybah Formation. The Middle-Late Triassic (Ladinian Carnian) of Al Aziziyah Formation was deposited on a gently sloping carbonate ramp in the Northwest of Libya.

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Lithologically, the limestone is partly siliceous and partly dolomitic. Clay and chart bands are common occurrences, and the upper boundary of the formation is intercalated by phosphatic bands. Facies of the Al Aziziyah Formation are interpreted from shallowest to deepest as a tidal sandstone; pre tidal carbonate; barrier; shallow sub-tidal facies; deep subtidal; and basinal facies (black shale and carbonate mud). The transition from the underlying Kurrush Formation to the Al Aziziyah Formation is marked by a change from fine sand and red clay to carbonate. Whilst the transition from the Al Aziziyah Formation to the overlying Abu Shaybah Formation is marked by an iron-rich and phosphatic band.

The Middle-Late Triassic (Ladinian-Carnian) Al Aziziyah Formation consists of massive grey limestone, dolomite and dolomitic limestone interbedded with shale (Asserto and Benelli, 1971; Magnier 1963). Some black shales and dolomite interbeds with possible hydrocarbon source potential also occur (Hammuda, et al., 2000).

In the Jifarah Basin on the shore of northwest Libya, the Triassic sediments are marine and non-marine deposits, and the Middle-Late Triassic Al Aziziyah Formation is mainly carbonate facies (Desio et al., 1960; Magnier, 1963; Asserto and Benelli, 1971). Other geologists, such as Christie (1955), Desio et al. (1963), El Hinnawy and Cheshitve (1975), Fatmi et al. (1980) and Hammuda et al. (2000), have contributed to the stratigraphy and geological setting of the Al Aziziyah Formation in Jabal Nefusah, NW Libya.

In this paper, the organic geochemical parameters are discussed, based on ten outcrop samples of the Al Aziziyah Formation. The aim of this study is to discuss the use of biomarkers and Rock-Eval pyrolysis data in assessing the type of organic matter, organic matter richness, thermal maturity, and depositional environment for the sediments under investigation.

Figure 1. Location of study area (from Hammuda et al. 2000)

MATERIAL AND METHOD

Ten outcrop black shale samples were collected from two different quarries localities, across the southwest of Al-Aziziyah town, NW Libya. The samples were collected using quarry sampling and handpicked from non-weathered exposures after removing the weathering surface and stored in closed bags. The number of samples from any of these localities was based on the accessibility of the sample area and the extent to which the shale is development at the outcrop (Figures 2 and 3).

The collected samples were crushed into fine powder using a crushing machine to reduce the rock aggregate down to monomineralic particles by vibrating steel disk mills (Herzog, type: Hsm 100A). The studied samples were analyzed by the Rock-Eval pyrolysis technique (as described by Espitalie et al.1977) to determine the hydrocarbon generative potential of the organic matter parameters (S_1,S_2,S_3,Tmax, HI, OI, and total organic carbon (TOC) using a LECO carbon analyzer to estimate the amount of organic matter in each sample. Following pyrolysis analysis, the samples were selected for further geochemical analyses**.**

Bitumen extractions were performed on approximately 123 – 134 g of the powdered samples using a Soxhlet apparatus for 60 h using an isotropic mixture of dichloromethane (DCM) and methanol (CH_3OH) (93:7). They separated into saturated hydrocarbon, aromatic hydrocarbon and NSO compound fractions by liquid column chromatography. A chromatographic column (30×0.72 cm) was packed with silica gel of 60–120 mesh that was activated for 2 h at 120 °C and capped with a few centimeters of alumina. Only the saturated fraction was analyzed in this study.

The saturated fraction of all the analyzed samples was dissolved in petroleum ether and analyzed using gas chromatography (GC), and gas chromatography–mass spectrometry (GC–MS). The GC was performed using an HP-5MS column with a temperature programmed from 40 to 300 °C at a rate of 4 °C/min and then held for 30 min at 300 °C. The GC–MS analysis was performed on an Agilent 5975B inert MSD mass spectrometer with a gas chromatograph attached directly to the ion source (70 eV ionization voltage, 100 m A filament emission current, 230 °C interface temperature).

For the analysis of biomarkers, the fragmentograms for steranes (m/z 217) and triterpenes (m/z 191) were recorded. Individual components were identified by comparison of their retention times and mass spectra with previously published literature, Relative abundances of triterpenes and steranes were calculated by measuring peak heights in the m/z 191 and m/z 217 fragmentograms, respectively.

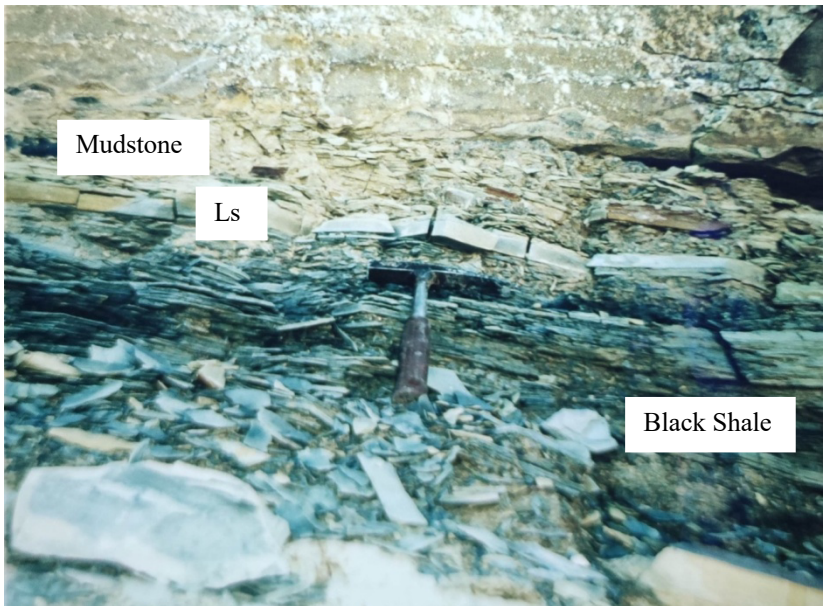

Figure 2. Close view of Al Aziziyah Fm. Showing black Shale & Mudstone units separated by thin limestone bed. Location: Bu Arqub quarry.

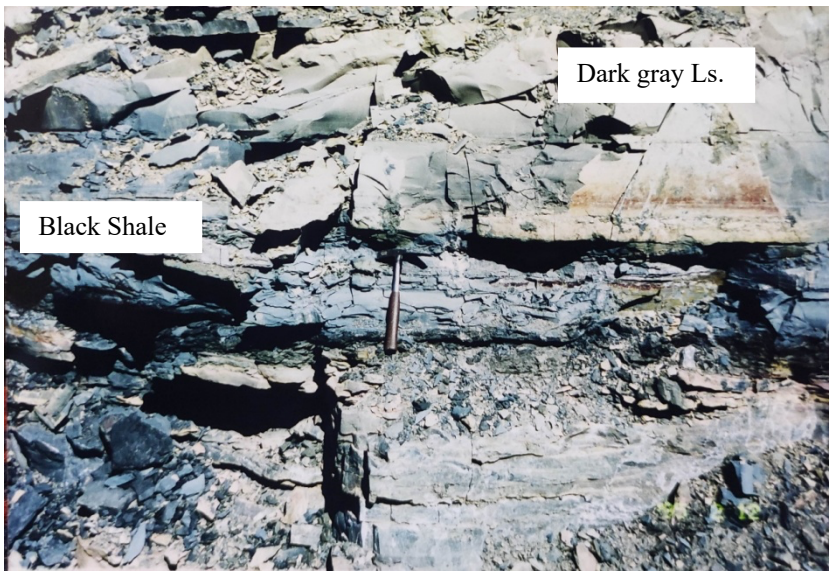

Figure 3. Close view from Al Aziziyah Fm. Showing black shales overlaying by thick dark gray color Limestone bed. Location: Ra's Alifa quarry.

RESULTS AND DISCUSSIONS

Biomarker distributions

Representative gas chromatograms (GC) and mass fragmentograms (m/z 191) and (m/z 217) are shown in Figures 4, 5, and 6 respectively, with peak identification for m/z 191 and m/z 217 in Tables 2 and 3. Diagnostic biomarker ratios and indices are listed in Tables 1, 4 and 5.

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n-Alkanes and isoprenoids

The distribution of saturated hydrocarbons fraction illustrated by capillary gas chromatograms of one representative carbonaceous sediment facies within the Al Aziziyah Formation in this study (Figure 4) clearly displays abundant a skewed unimodal *n*-alkanes distribution of higher molecular weight, with *n*-C_{23} alkane maximum and a moderate waxy appearance.

The distribution is depleted in the *n*-C_{10}–*n*-C_{16} range and shows an odd predominance of the heavier members (*n*-C_{25+}) which gave a high CPI value of 1.4 (Table 1). The distributions support a significant terrestrial higher plant input for these sediments (Powell and Mc Kirdy, 1973; Tissotetal, 1978).

The gas chromatogram displays a smooth homologous series within the higher molecular weight n-alkane extending beyond nC_{30} suggesting significant input of higher land plant organic matter into these sediments. The moderate molecular weight n-alkanes (*n*-C_{10}–*n*-C_{20}) and acyclic isoprenoids, such as pristane and phytane, occur in a low concentration in the analyzed sample, with Pr/Ph ratio < 1.0, suggesting reducing environment (anoxic condition). Pristane concentrations and eluting *n*-alkane (*n*-C_{17}) are generally low compared with phytane and eluting *n*-alkane (*n*-C_{18}) ratio in the analyzed sample, thus giving distinctively low pr/ C_{17} and Ph/ C_{18} ratios of 1.0 & 0.81, respectively (Table1).

The fingerprints also show apparent evidence of slight biodegradation (i.e. partially removal of n-alkanes relative to entire alkane distribution) for the representative analyzed sample, being more affected around *n*-C_{10}–*n*-C_{16} range. The presence of biodegradation could be related to the intrusion of mixing of oxygenated waters within these sediments due to prolonged surface exposures, which is a necessary condition for biodegradation to occur.

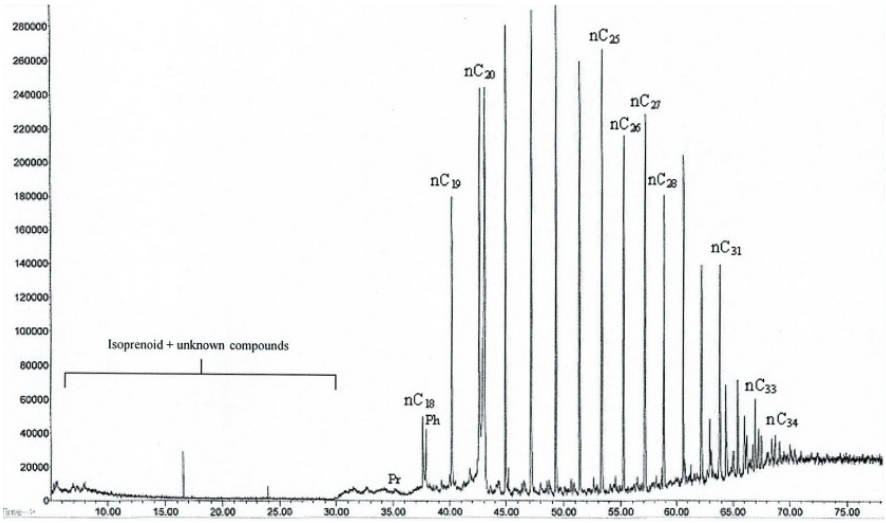

Figure 4. Gas chromatograms of saturated hydrocarbon fraction of black shale in the Al Aziziyah Formation (sample Az8).

Table 1. Biomarkers parameter for rock extracts occurring in the area of study.

Parameters	Al-Azizyah Formation - Sample No AZ 8
Pr/Ph	0.1
Pr/nC_{17}	1.0
Ph/nC_{18}	0.81
n-alkane max.	C_{23}
$CPI_{24\text{-}35}$	1.43

Pr/Ph: Pristane/Phytane; Pr/nC_{17}: Pristane/normal-C_{17}; Ph/nC_{18}: Phytane/normal-C_{18}; $CPI_{24\text{-}35}$: Carbon preference index (after Bray and Evans, 1961).

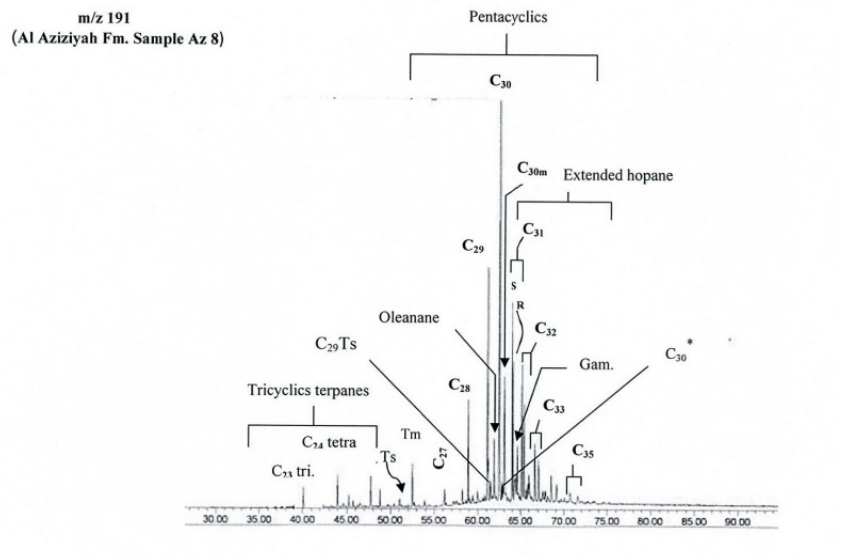

Figure 5. m/z 191 mass fragmentograms of the saturated fractions, showing the relative distribution of tricyclic, tetracyclic terpans and pentacyclic hopane in the shale extracts Al Aziziyah Formation (sample Az8).

Table 2. Peak assignments in the m/z 191 mass fragmentograms.

C_{23} tri.	tricyclic terpane
C_{24} tetra.	tetracyclic terpane
C_{27} Tm	17*α* (H),22,29,30-trisnorhopane
C_{27} Ts	18*α* (H),22,29,30-trisnorneohopane
C_{27}	17α (H),21 *β* (H)- hopane
C_{29}	17α (H),21 *β* (H)- hopane
C_{29} Ts	18α (H)-30-norneohopane
C_{29}m	17 β (H),21 α (H)- moretane
OI	18α (H)-oleanane
C_{30}	17α (H),21*β*(H)- hopane
C_{30}m	17 β (H),21 α (H)- moretane
C_{31}S	17α (H),21*β*(H)-homohopane (22 *S*)
C_{31}R	17α (H),21*β*(H)-homohopane (22 *R*)
Gam.	C_{30}Gammacerane
C_{32} S	17α (H),21*β*(H)-bishomohopane (22 S)
C_{32} R	17α (H),21*β*(H)-bishomohopane (22 *R*)
C_{33} S	17α (H),21*β*(H)-trishomohopane (22 *S*)
C_{33} R	17α (H),21*β*(H)-trishomohopane (22 *R*)
C_{34} S	17α (H),21*β*(H)-tetrakishomohopane (22 *S*)
C_{34} R	17α (H),21*β*(H)-tetrakishomohopane (22 *R*)
C_{35} S	17α (H),21*β*(H)-pentakishomohopane (22 *S*)
C_{35} R	17α (H),21*β*(H)-pentakishomohopane (22 *R*)

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Table 3. Biomarkers parameter for rock extracts occurring in the area of study.

Parameters	Al-Azizyah Formation - Sample No Az8
Tm/Ts	6.0
OI/C_{30}hop	0.15
C_{30}m/C_{30}hop	0.74
C_{29}/C_{30}hopane	0.63
C_{24}tetra/C_{30}hop	0.08
C_{23}tri/C_{30} hop	0.05
C_{24}tetra/C_{23} tri	1.8
C_{32}hopane 22*S*/(22*S*+22*R*)	0.58
C_{31} 22*S*/22*R*	1.50
C_{32} 22*S*/22*R*	1.40
C_{33} 22*S*/22*R*	1.50
C_{30}*/C_{29}Ts	0.14
C_{35} (22*S*+22*R*)/ C_{34} (22*S*+22*R*)	5.0
Gam./ C_{30}hopane	0.14

Tm: 17α (H), 22, 29, 30-trisnorhopane; Ts: 18α (H), 22, 29, 30-trisnorneohopane; OI/C_{30}: Oleanane/C_{30}hopane; C_{30}m/C_{30}hop: C_{30} mortane/C_{30} hopane; C_{24} tetra/C_{30}hop. : C_{24} tetracyclic terpanes/C_{30}hopane; C_{24} tetra/C_{23} tri: C_{24} tetracyclic terpanes/ C_{23} tricyclic terpanes; C_{32} hopane 22*S*/ (22*S*+22*R)*: 17*α* (H), 21*β* (H) - bishomohopane (22 *S*)/ [17*α* (H), 21 *β* (H)- bishomohopane (22 *S*) + 17*α* (H), 21*β* (H) - bishomohopane (22 *R*)] of C_{32}homohopane; C_{23} tri/C_{30}hop. : C_{23} tricyclic terpanes/C_{30}hopane; 22*S*/22*R* of $C_{31\text{-}32\text{-}33}$: 17*α* (H), 21*β* (H)-bishomohopane (22 *S*)/ 17*α* (H), 21*β* (H)-bishomohopane (22 *R*) of $C_{31\text{-}32\text{-}33}$ C_{30}*/C_{29}Ts: 17 *α* (H) diahopane/18α (H)- norneohopane; Gam./ C_{30}hopane: Gammacerane/17*α* (H), 21 *β* (H)- hopane.

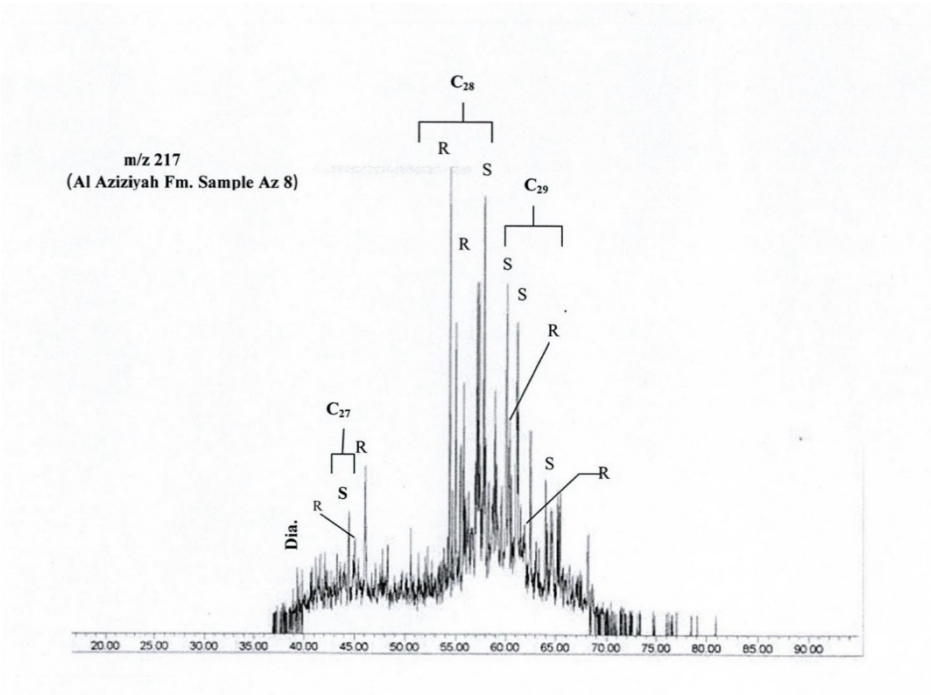

Figure 6. m/z 217 Sterane distributions from rock extracts of Al Aziziyah Fm. demonstrating a predominance of C_{28} over C_{27} and C_{29} regular steranes, indicating synthesised higher plant and marine organism sources.

Table 4. Peak assignments in the m/z 217 mass fragmentograms.

Dia. (Diasterane)	C_{27} 13 β (H), 17 α (H)-)-diacholestane - 20*S*
	C_{27} 13 β (H), 17 α (H)-)-diacholestane – 20*R*
C_{27}	5 α (H), 14 α (H),17 α (H)-cholestane - 20*S*
	5 α (H), 14 β (H),17 β (H)- cholestane - 20*R*
C_{28}	5 α (H), 14 α (H),17 α (H) -24 - methylcholestane -20*S*
	5 α (H), 14 β (H),17 β (H)- 24 -methylcholestane -20*R*
C_{29}	5 α (H), 14 α (H),17 α (H)- 24 - ethylcholestane -20*S*
	5 α (H), 14 β (H),17 β (H)- 24 - ethylcholestane -20*R*

Table 5. Biomarkers parameter for rock extracts occurring in the area of study.

Parameters	Al-Azizyah Formation - Sample No - Az8
C_{29}sterane 20*S*/(20*S*+20*R*)	0.48
Sterane % C_{27}	11
C_{28}	52
C_{29}	37

C_{29}sterane 20*S*/(20*S* + 20*R*) : 5 α (H), 14 α (H),17 α (H)-20*S*/ (5 α (H), 14 α (H),17 α (H)-20*S* +5 α (H), 14 α (H),17 α (H)-20*R*)of C29 sterane; C_{29}sterane 20*S*/20*R* : 5 α (H), 14 α (H),17 α (H)-20*S*/ (5 α (H), 14 α (H),17 α (H)-20*R*sterane C_{29}; n.d: not determined.

CPI and OEP (odd/even preference)

The Carbon Preference Index (CPI) was calculated especially for this $C_{25 - 33}$ range, and its value was influenced by the type of organic matter and by thermal maturity (Tissot and Welte, 1984). A high CPI value represents an odd carbon number preference over an even carbon number n-alkane. Plants synthesize paraffin almost exclusively with an odd number of carbon atom chains from C_{25} to C_{37}. Ancient shales had an odd/even ratio of n-paraffin between 1.0 and 3.0, whereas in oils it was 1.0, sediments composed only of marine source material have CPI of I.0 at the surface and at all defines.

In contrast, CPI of continental plants range up to 20, and samples with appreciable contribution from land plants have CPI> 1 (Hunt, 1995). If the total even and odd numbers of paraffins are equally abundant, the value of CPI will be equal to 1.0. The environment of deposition also influences the odd carbon preference, in oxic or suboxic environments. In this study sample, there is a slightly odd over-even predominance of higher molecular weight n - alkanes nC_{24-34} has been produced CPI value of 1.4.

Tricyclic and Tetracyclic Terpanes (m/z191)

The tricyclic C_{23} and tetracyclic C_{24} were determined by examining the m/z191 ion by GC-MS (Peters et al. 2005; Seifert and Moldowan, 1980). Many of the terpenes originate from bacterial membrane lipids (Ourrisson et al. 1982). The bacterial terpenes include several homologue series such as bicyclic, tricyclic, tetracyclic, and pentacyclic terpenes. These compounds can be used for the characterization of organic input, maturity, and depositional environments.

The distributions of the tricyclic and tetracyclic terpenes in the selection studied sample (Figure 5) are characterized by a pattern with a dominance of C_{24} tetracyclic trepans peak over C_{23} tricyclic trepans. These features may indicate the presence of an algal kerogen component, in addition to higher plant input in these sediments.

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Pentacyclic Terpanes m/z 191

Pentacyclic terpenes commonly contain 27 – 35 carbon atoms in a naphthenic structure. Hopanes originate from bacterial membranes, the specific precursor being thought to be bacteria hopane tetrol, synthesized by the cyclisation of squalane (Rohmer 1987). The three main series of hopanes common in sediments and petroleum are 17α (H), 21β (H) hopane, 17 β (H), 21 α (H) hopane (mortanes) and 17 β (H), 21 β (H) hopanes. Other hopanes widely used are the 17α (H), 22, 29, 30 trisnorhopane referred to as Tm and 18 α (H) 22, 29, 30 trisnorneohopane referred to as Ts.

The m/z191 mass chromatograms of the studied sample (Fig.5), show that the pattern of the sample belong mostly to the 17α (H), 21β (H) hopanes series. The component (C_{27}17α (H)-22, 29, 30-trisnorhopane (Tm) dominates over its counterpart (C_{27}18α (H)-22, 29, 30-trisnorneohopane (Ts) with Tm/Ts ratios of 6.0 (Table 4). The (Tm/Ts) has been recognized to be affected by both maturity and diagenetic conditions (Moldowan et al. 1986).

The C_{30} regular hopane is the most predominant member series followed by C_{29}norhopane and the ratio of $C_{29}/C_{30}$is 0.63. The oleanane is present in the analyzed sample and is identified as one peak representing 18α (H) - oleanane and 18β (H) - oleanane, thus giving (oleanane/ C_{30}hopane) ratio of 0.15 (Table 5). The C_{31} – C_{35} extended hopanes are thought to be derived from C_{35} bacterio hopane tetrol (Ourrisson et al. 1979; 1984; Rohmer 1987) or other polyfunctional C_{35}hopanoids as a general indicator of highly reducing marine conditions (Peters and Moldowan, 1991).

The extended hopanes which occur as stereoisomeric pairs, from $C_{31}$to C_{35}, are dominated by the C_{31}homohopane and decrease towards the C_{34} homohopane (Fig. 5). (i.e. display a staircase distribution as a result of uniformly lower amounts with increasing molecular weight). The S-isomers are more dominant than the R-isomers among the homohopane (C_{31}–C_{34}).

The homohopane index (C_{35}/C_{31}-C_{35}) is applied as an indicator of the redox potential of marine sediments during diagenesis, although there is also a thermal maturity control (Peters and Moldwan, 1991). Demaison et al. (1983) related high C_{32} homohopane to the availability of free oxygen, which is used to oxidize bacteriohopane tetrol to a C_{32} acid followed by loss of a carboxyl group to C_{31} and/or preservation of the C_{32}. High C_{32} homohopane therefore indicates an oxic to sub-oxic environment of deposition.

The m/z 191 mass chromatogram displayed the presence of Gammaceran with a reasonable abundance in the analyzed sample. Gammacerane is a C_{30}- triterpane that appears to represent a marker for highly saline marine and non-marine environments (Moldowan et al. 1985; Mann et al. 1987; Hills et al. 1986; Fu Jiamo et al. 1986; Brassel et al. 1988).

Gammacerane may be derived from the reduction of tetrahymanol (Vankatesan, 1989; Ten Haven et al., 1989), which is a lipid thought to replace steroids in the membrane of certain protozoa (Capsi et al., 1968; Nes and Mckean, 1977), phototrophic bacteria (Kleemann et al., 1990), and possibly other organisms.

Steranes and diasteranes m/z 217

Steranes, which are commonly found in mature sediments and crude oils, are normally derived via digenesis from sterols that are widely dispersed in plants and microorganisms, with the C_{27} and C_{28} sterols most abundant in marine organisms and the C_{29} sterols in higher plants (Gonzalez-vila, 1995). The C_{27}, C_{28} and C_{29}steranes occur as 20S and 20R epimers. Steranescan also be used as indicators of depositional environments. An abundance of C_{29} over C_{27}steranes would suggest a terrestrial source, whereas when C_{27}steranes are predominating over C_{29}steranes, it could indicate mainly a marine or aquatic source (Palaces et al., 1984).

In this study, the m/z 217 mass fragmentograms of the analyzed sample dominated by steranes over diasteranes with C_{28} sterane being the predominant component (Fig. 6) followed by the C_{29} and the C_{27}steranes which are the lowest. Relative abundances of C_{27},C_{28} and C_{29} regular steranes are calculated and the results are given in (Table5). The distribution of C_{27}: C_{28}: C_{29} steranes in the examined shale of this study gave varied percentage, suggesting that the organic matter of these sediments was derived from mixed terrestrial and marine source material.

The rearranged steranes (diasteranes),either are absent or present in minor or trace amounts in the analyzed sample. It has been proposed that the relative concentration of the diasteranes reflect the presence of clay minerals and their ability to catalyze sterane rearrangement reactions. However, it has become clear that the oxicity/anoxicity of the depositional environment provides another explanation to the fate of the sterols. Highly anoxic environments will rapidly reduce the steranes, hence reducing the amount of steranes available for the rearrangement reactions; therefore, more oxic environments will leave more of the steranes unaffected and hence available for rearrangement (Philp 1994).

It can be said that the presence or absence of rearranged steranes in minor or trace amounts in shales of the Al Azizyah Formation possibly related to the limited occurrence of acid- catalyzed rearrangement of regular steranes and /or more closely reflect the oxicity/anoxicity environment rather than presence or absence of the clay minerals (Moldowan et al., 1986).

Rock-Eval Pyrolysis Data and Kerogen Type

A Rock-Eval diagram presents three characteristic peaks; S_1 and S_2 correspond respectively to the free hydrocarbon and the pyrolyzed hydrocarbons of the source rock. S_3 is the amount of organic CO_2 generated during heating until 330^0 C. The temperature at which the maximum of the pyrolyzed hydrocarbon or $S_2$is generated referred to as Tmax. It used as a hydrocarbon parameter to assess the thermal maturity of a source rock and should be confirmed with other maturity parameters, because Tmax is known to be dependent on other factors such as type of organic matter (Peters and Moldowan, 1993).

Plot of oxygen index (OI) vs. hydrogen index (HI) (Figure 7) shows the kerogen types I, II, and III of ten-selected outcrop black shale samples, from the Al Aziziyah formations. The plots on a modified Van Kerevlen diagram for the samples of the studied Shales, suggest that the organic matter is made up of a mixture of type III vegetation derived kerogen, and some contribution from type II (mixed terrestrial and marine source material).

The positive correlation between S1 & S2 for the studied samples, suggests that the organic matter of these sediments was derived from different origin, thus supporting data presented in (Figures 8). Fair and good total organic carbon content (as much as average value of 0.47 wt. %) and vary over the wide range of HI values between 14 to 268 mg HC/g TOC, indicating different kerogen types associated with these sediments.

HI values are positively correlated with TOC contents in the study sample (Figure 9), which is possibly due to the presence of organic background population (vitrinite – and inertinite, with relatively high amounts of HI values), and suggests a relatively high TOC values of these sediments are due to the additional of hydrogen- rich organic matter such as algae or bacteria (Sachsenhofer et al. 1995).

Table 6. Rock –Eval Pyolysis data of the carboniferous sediments of the Al Aziziyah Formation

Sample No	S1 mg/g	S2 mg/g	Tmax^{0}C	TOC wt%	HI	OI	S1+S2 mg/g	PI mg/g
AZ_1	0.01	0.05	428	0.23	22	139	0.06	0.17
AZ_2	0.02	0.08	427	0.23	34	161	0.10	0.20
Az_3	0.01	0.02	416	0.06	40	349	0.03	0.30
AZ_4	0.02	0.16	426	0.45	35	151	0.18	0.10
AZ_5	0.00	0.26	423	0.58	44	138	0.26	0.00
AZ_6	0.02	0.06	435	0.45	14	151	0.08	0.25
AZ_7	0.06	0.16	439	0.47	35	208	0.22	0.27
AZ_8	0.24	4.15	436	1.55	268	19	4.39	0.05
AZ_9	0.01	0.07	433	0.28	25	86	0.08	0.13
AZ_{10}	0.05	0.42	431	0.35	119	72	0.46	0.11
Average	**0.44**	**0.45**	**430**	**0.47**	**64**	**145**	**0.59**	**0.16**

TOC, total organic carbon; Tmax, maximum temperature; S_1, thermally extracted source rock sample; S_2pyrolyzed source rock; HI, hydrogen index; OI, oxygen index, S_1+S_2, pyrolysis yield; PI, production index.

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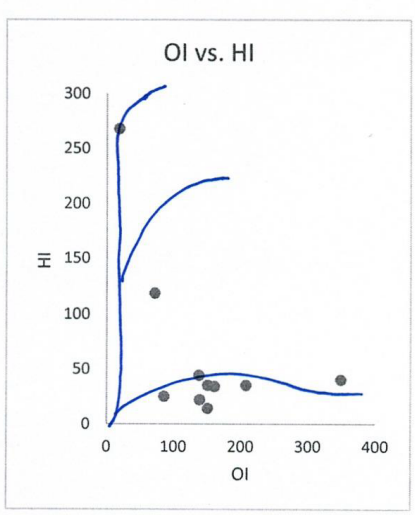

Figure 7. Cross-plot of OI vs. HI**,** from Rock-Eval pyrolysis of the study. Shales, showing the predominance of type III organic matter.

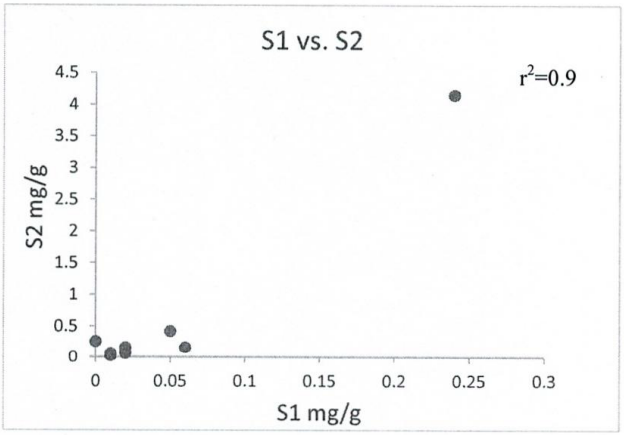

Figure 8. Cross - plot of S1 vs. S2, showing + ve correlation, implies that the organic matter of different derivations.

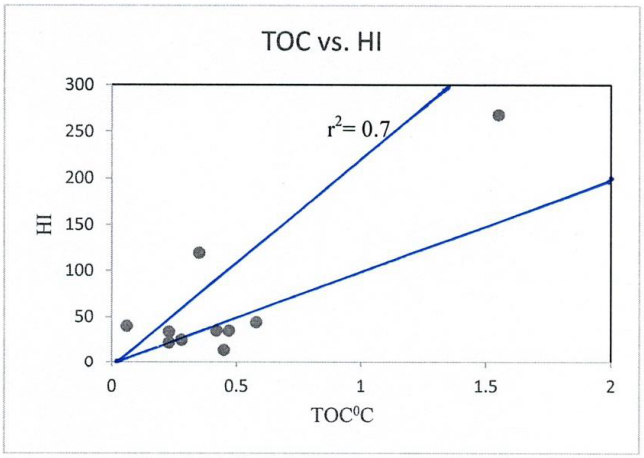

Figure 9. Plot of TOC vs. HI defines I, II and III kerogen type, Indicating predominance of type III organic matter.

Maturity and Hydrocarbon Generating

Maturation of organic matter in sediments is a chemical change in which temperature acts during the burial of sediments, causing many changes in the original organic matter. Many varied parameters have been suggested and used as possible indicators of organic maturity, such as the amount of extractable soluble organic matter, n-alkane preference index (CPI) and pentacyclic triterpene isomer ratios (Douglas and Williams, 1981).

In immature source rock, isoprenoid hydrocarbon pristine and phytane stand out above the n-paraffins peaks; Pr/nC_{17} and $Ph/n\text{-}C_{18}$ ratios are high. This indicates that the source rock has not been heated high enough to generate oil. Maturation yields paraffin, hence Pr/nC_{17} and Ph/nC_{18} ratios decrease with increasing maturity as more paraffin ($n\ C_{17}$ & $n\ C_{18}$) are generated from the kerogen by cracking and diluting the isoprenoids (Tissot et al., 1971). These ratios can be used therefore in ranking the thermal maturity of related non-biodegraded oils and bitumens.

The Production Index (PI) together with Tmax values were used to evaluate maturity levels. The PI produce an average value of 0.16 mg/g, (Table 1) of the analyzed samples. The cross plots of the Tmax vs. HI diagram (Figure 10) show that the vast majority of the analyzed samples of the Al Aziziyah Formation lie in the Kerogen type III immature level and Kerogen type II maturation pathway. However, the maturity determined by Tmax suggests that most of the studied samples of the Al Aziziyah Formation lie below the maturation zone (430-465^0 C) (Espitalie et al., 1986),

The Rock-Eval data (Table 1) display variations in the HI and OI among the studied samples. However, most of the analyzed samples from the Al Aziziyah formations show low HI values with some exceptions (HI, typically 14-268 mg/g,) and high oxygen indices OI, typically 19 - 208mg/g). Relatively high oxygen indices for the shales from Al Aziziyah Fm. (OI, 349 mg/g, e.g. sample Az 3 & OI, 08 mg/g, e.g. sample Az 7, and HI, 268 mg/g, e.g. sample Az8). The elevated oxygen indices in these samples indicate that maturation effects on Rock-Eval parameters are minimal because increased thermal maturity lowers OI values and decreasing HI values (Harris et al., 2004). On the other hand, the low Hydrogen and high oxygen indices in these samples are indicative of the decreasing contribution of kerogen type I and increasing kerogen type II and III in the sediments.

The cross plot of OI vs. HI (Figure 7) shows that the analyzed samples in this study lie either within type I and/or close to type II and within type II – III maturation paths. The amount of organic matter within a potential source rock can be assessed using its generative potential (S1 + S2) (Tissot and Welte, 1984). The data presented in (Table 6) shows that the S1+S2 values for the study shales varied between 0.06 to 4.46 mg/g, with an average value of 0.46mg/g. By contrast, the S2 values for the Shales are between 0.02-4.15 mg/g. These values indicate that the vast majority of organic matter in the Al Aziziyah Formation has not reached the stage of hydrocarbon generation.

The analyzed samples of this study have TOC valued < 0.5 wt %, (Table 6) which in general can be considered as being below the begging limit for hydrocarbon generation, (TOC > 0.5 wt %). However, the total organic carbon contents (TOC), exhibit a distinct variation of the abundance of organic matter present in these sediments. The results have read TOC values extending from 0.06 to 1.55 wt. % with an average value of 0.47 wt. %, which can be identified as poor and fair in terms of organic richness (Peters, 1986). Therefore, from the standpoint of TOC content alone, the Al Aziziyah Formation seems to contain insufficient amounts of organic matter that can considered as a possible source rock to generate some quantities of hydrocarbons.

The cross plots of TOC vs. S2 (Figure 11) define type I, II and III Kerogen, the plots indicate a predominance of type III and some contributions of type II organic matter. The lower S2 value at relatively higher TOC in the study samples implies the presence of a hydrogen index in low concentrations and immature organic matter (Sikander et al., 2000).

In general, the ratio of Tm/Ts (17α (H), 22, 29, 30-trisnorhopane/18α (H), 22, 29, 30-trisnorneohopane) in samples derived from similar sources decreases with increasing maturity so that the ratio can be used as a maturity indicator for samples from similar sources (Seifert and Moldowan, 1978). No distinct variation has been observed for the Tm/Ts ratios. However, for this particular sample, Tm is predominant with very low concentrations of Ts isomer in the formation rock extracts. The examined rock extracts have Tm/Ts ratio of 6.0. Among the samples studied here, the Tm/Ts ratio may not be indicative of thermal maturity, but more likely, is strongly influenced by source differences (Palacas et al., 1984).

It is well established that the carbon preference index (CPI) values are influenced by the type of organic matter and by the degree of maturity. Higher CPI values >1.5 always refer to relatively immature samples; low CPI values do not necessarily mean higher maturity; they can also mean a lack of higher normal alkanes originating from terrestrial input (Tissot and Welte, 1984). Bray and Evans (1961) quantified the odd/even preference in n-alkane distributions by defining a carbon preference index (CPI) and they found this value to be higher in immature sediments but near unity, or just below, in crude oils. The slight odd-even predominance of n-alkane in a sample studied here (CPI 24-35:- 1.43, Table 1) is consistent with its thermal maturity range. The decrease in CPI values began as an indication of the increase in thermal maturity.

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In addition, the m/z191 mass chromatograms, also display relative abundance of C_{30} m and the C_{31}-C_{35} extended hopanes. The higher moretane concentration and very low concentrations of Ts isomer in the formation rock extracts reflect the low maturity of these sediments. The stereoisomeric ratios, 22S/22R of the extended hopanes (C_{31-35}), have also been used as maturity indicators (Mackenzie et al., 1980; Seifert and Moldowan, 1978). The amount of 22S/22R ratios is 1.5 for the C_{31}, C_{32} and C_{33}hopanes (Table 4), indicating that these shales have a low level of thermal maturity.

The 20S/20S+20R for the C_{29} sterane ratios and the 22S/22S+22R for the C_{31} and C_{32} extended hopane ratios have been widely used as maturity indicators. The C_{32}homohopane maturity indicators 22S/22S+22R is not close to the equilibrium value (0.57-0.62; Peters and Moldowan, 1993). However, the 22S/2S+22R ratio for C_{32} hopane in the preventative study sample is about 1.5, (Table 4). The 22S/22S+22R ratio has an equilibrium value of 0.6, which corresponds to the onset of hydrocarbon generation (Mackenzie, 1984).

The oil-generating potential of source rock is directly related to its hydrogen-rich organic matter, which is usually quantified by hydrogen indices (Wan Hasiah, 1992). In the sample analyzed, hydrogen indices varied between 14 and 268 mg HC/g TOC with average values of 64 mg/g, this in general can considered as being very low to medium hydrogen indices. This could be caused by the major contribution of continental organic matter (Raja and Zahra, 2005).

The isomerisation ratio of the C_{29} steranes, as shown by the epimer ratio of 20S/20S+20R, is of 0.67 for the extracts of the Az8 sample, thus did not support the 22S/22S+22R for the C_{32} extended hopane ratios and the steroisomeric ratios, 22S/22R of the extended hopanes (C_{31-33}). This result suggests that the sediments have been buried to a considerable depth, prior to being uplifted to their present position, and the black shales under investigation have not been too severely affected by thermal metamorphism or active tectonic activity of Jabal Nefusah, NW Libya.

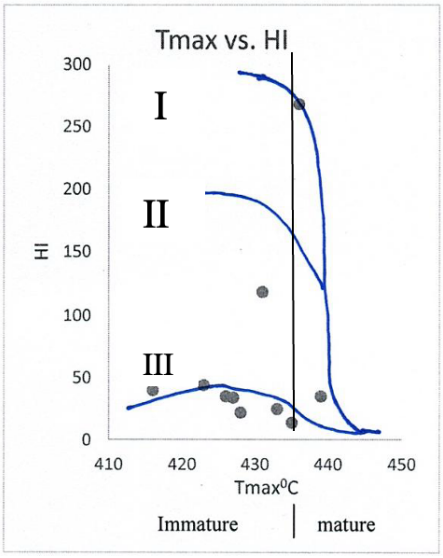

Figure 10. Plot of Tmax vs. HI from Rock-Eval pyrolysis of Shales

from Al Aziziyah Fm. showing that

the vast majority of the samples lie in the immature pathway of kerogen type III with few samples falling within the maturation pathway of kerogen type I and II.

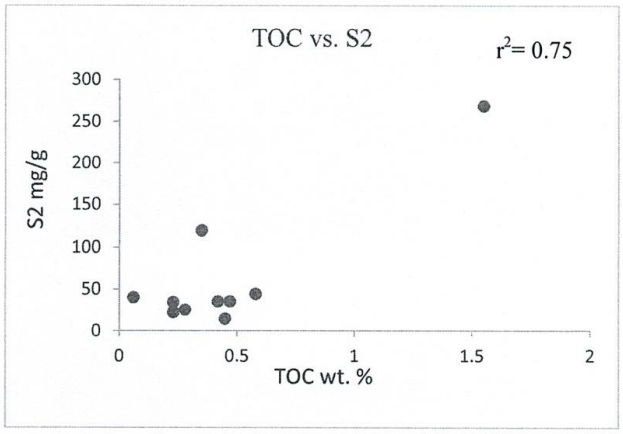

Figure 11. Cross - Plot of TOC vs. S2, showing (+ ve) correlation, possibly due to the presence of organic background population (vitrinite and inertinite with contribution from HI values).

Source/type of Organic Matter

The distribution of n-alkanes can used to indicate the organic matter source (Han and Calvin, 1969, Volkman et al., 1981; Duan, 2000 and Duan and Ma, 2001). The gas chromatograms of the saturated hydrocarbons in this study display a waxy appearance, (slight biodegradation) loss of the lower molecular weight n-alkanes, high relative concentration of long-chain n-alkanes, and slightly odd-even predominance, suggesting that the study sediments have organic matter sourced from aquatic organisms and land plants organisms, with the latter being dominant.

The main feature that distinguishes the rock extracts in this study is the relative abundance of oleanane, a biological marker diagnostic of higher plants. It has been suggested as a marker for angiosperms (flowering plants) (Ekweozor et al., 1979; Moldowan et al., 1994). The ratios of oleanane /C_{30}hopane provide information on the age of the source rock for oil (Moldowan et al., 1994). Oleanane/hopane ratios over 20% are characteristic of Tertiary source rocks and oils. On the other hand, oleanane can be absent from source rocks deposited far from angiosperm input.

Applying these parameters to assess the oleanane contribution to the source rocks of the extracts, it can be said that the presence or absence of bicadinanes in minor or trace amounts and the high abundance of oleanane in these rock extracts also suggests considerable terrigenous input. The distribution of regular steranes has been used to determine the organic matter source of crude oils (Moldowan et al., 1985 and Philp et al., 1991).

The m/z 217 mass fragmentograms of the analyzed sample illustrate the relative abundance of C_{27}, C_{28} and C_{29} regular steranes in the range of 11 %, 52 % and 37 % respectively (Table 5). The distribution of regular steranes shown in Figure 7.13 reveals a preference for C_{28} steranes over C_{27} and C_{29}, the C_{29} steroid is synthesized by higher plant and marine organisms have been reported to contain both C_{27} and C_{29} steroids (Brassel and Eglinton, 1986). These characteristics of the regular steranes further reflect the fact that the organic materials of these samples originated from higher plant organic sources with marine organic matter.

Aquino Neto et al. (1983) suggested a microbial origin for both the tricyclic and tetracyclic terpenes series. Philp and Gilbert (1986), on the other hand, associated a high abundance of C_{24} tetracyclic with a high input of terrestrially derived organic matter. The relatively high abundance of C_{24} tetracyclic terpenes in the study samples could therefore be associated with higher land plant, algae, or microbial sources. The presence of tricyclic terpenes in sediment extracts and oils has been associated with the presence of marine influence by workers such as Aquino Neto et al. (1983) and Mello et al. (1988), therefore supports the marine depositional setting of these formations as proposed by workers such as Asserto and Benelli, (1971) and Hammuda et al. (2000).

The Pr/Ph ratios in most of the studied samples are within the range of <1.0, which seems to be diagnostic of highly reducing to anoxic marine depositional environments (Alexander et al., 1997). The moderate molecular weight n-alkanes (n-C_{10}–*n*-C_{20}) and acyclic isoprenoids, such as pristane and phytane, occur in a low concentration in the analyzed sample, with Pr/Ph ratio < 1.0, suggesting reducing environment (anoxic

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condition). Pr/n-C_{17} and Ph/n-C_{18} ratios have been widely used as indicators of source rock types, depositional environments and organic matter maturation (Connan and Cassou, 1980; Peters et al., 1999; Duan et al., 2006).

Pristane concentrations and eluting *n*-alkane (*n*-C_{17}) are generally low compared with phytane and eluting *n*-alkane (*n*-C_{18}) ratio in the analyzed sample, thus giving distinctively lower/C_{17} and Ph /C_{18} ratios of 1.0 & 0.81, respectively (Table 4). The lower Pr/n-C_{17} and Ph/n-C_{18} ratios in most of the studied samples are probably being caused by the source of organic matter.

Depositional Environment

The high Pr/Ph ratios have generally been inferred to indicate that the organic matter has undergone some degree of oxidation and decarboxylation of the phytol sidechain of chlorophyll which leads to the formation of pristane. Under reducing conditions, phytane is more likely to be produced through hydrogenation and dehydration of phytol (Brooks et al., 1969). Organic matter derived predominantly from terrestrial plants would therefore be expected to show a high Pr/Ph ratio and organic matter derived predominantly from aquatic photosynthetic organisms, such as algae, could also have a high Pr/Ph ratio if the water column was well oxygenated (Clayton, 1993).

In peat swamp environments, with low aerobic bacterial activity, most of the phytol is converted to pristane with only small amounts of phytane. Thus, oils from source rocks deposited under peat swamp conditions will have high Pr/Ph (>3.0) and pr/nC_{17} (>1.0) ratios (Didyk et al., 1978; Lijmbach, 1975), whereas in marine or open water, sediments with high bacterial activity yield only relatively small amounts of pristane and phytane as a result giving low Pr/Ph (<1.0 ratio).

The low ratio is observed in this investigation (Table 1). Although the Pr/Ph ratio in the samples studied is most likely source-influenced, the low Pr/Ph (<1) suggests an aquatic depositional environment under reducing bottom conditions. This is in agreement with the depositional environments postulated by workers such as Assereto and Benelli (1971); the Al Aziziyah Formation was deposited in low energy from sub-tidal to inter-tidal marine environment; and Hammuda, et al. (2000), black shales and dolomite interbedes, occur in this unite of the Al Aziziyah Formation, thought to represent more open marine subtidal conditions.

The m/z 191-hopane distribution patterns of the study sample are characterized by a regular stair-step progression of C_{31} to C_{35} homophones. The very small homophone indices (C_{35}/C_{31}- $_{35}$) suggest anoxic conditions.

According to Peters and Moldowan (1993), the oxygen concentrations in the depositional environments can be evaluated using the 17α (H)-diahopane/18α (H)-30- norneohopane (C_{30}*/C_{29}Ts) ratio. This ratio increases with increasing oxygen concentrations. That is, a low ratio indicates anoxic, and a high ratio indicates oxic conditions. Because 17α (H)-diahopanes are more stable than 18α (H)-30- norneohopanes, increasing maturity should also result in increased ratios (Peters and Moldowan, 1993).

The relatively enhanced concentrations of the C_{31}-C_{35} compared to the C_{30}hopane and C_{29}norhopane have been proposed to be typically associated with carbonate sedimentary environments (Palaces et al., 1984). However, a relatively high concentration of extended hopanes and C_{29}-norhopanes was found in the rock extracts of the study sample (Figure 5), although the extracted samples were actually black shales and mudstones, not carbonates. Enhanced concentrations of extended hopanes in the analyzed sample suggest reflecting the more anoxic nature of a depositional environment (Moldowan, 1988).

The high relative abundance of gammacerane in the studied sample suggests a hypersaline source rock deposited in stratified anoxic marine conditions (Peters and Moldowan, 1991; Sinninghe et al., 1995). This suggestion is supported by high gammacerane indices (gammacerane/hopane) and Pr/Ph ratios (< 1) for both ratios (Table1).

Based on the above-discussed parameters, although differences between the lithologies within a particular formation could not be made, a distinction can be made between the dominant types of organic matter that are present in the shales. It can be said that the Al –Al-Aziziyah Formations seem to have received substantial amounts of land-derived organic matter that has been transported into an open marine subtidal depositional setting and was deposited in a photosynthetic-organisms dominated environment (thereby suggesting a mixed source input).

CONCLUSIONS

The results from this study of the organic–rich sediments within the Al-Aziziyah Formation, using geochemical Rock-Eval pyrolysis data, show that the Tmaxvalues ranging from 416-439^0 C implying immature level kerogen type, (As confirmed by reliable PI, HI and OI values).On the other hand, the analyzed samples have TOC valued < 0.5 wt %, which in general can be considered as a poor source of rock generation potential.

The plot of Tmax vs. HI & OI vs. HI on the modified Van Krevelan, shows that the vast majority of the analyzed samples of the Al Aziziyah Formation lie in the Kerogen type III immature level and Kerogen type I & II maturation pathway, indicative of the decreasing contribution of kerogen type I and increasing kerogen type II and III in the sediments.

Immature level, suggesting these samples have not been too severely affected by thermal metamorphism, or active tectonic activities of the Jabal Nefusah, NW Libya. The high abundance of oleanane biomarkers in these rock extracts and relative index (oleanane/C_{30}hopane) with the value of 0.15. Extended hopanes are dominated by the C_{31}homophoneand decreasing towards the C_{34}homophone, suggesting considerable terrigeneous input.

The relative high abundance of gammacerane, suggests a hypersaline source rock deposited in stratified anoxic marine conditions, this suggestion is supported by high gammacerane indices (gammacerane/hopane) and Pr/Ph ratios (< 1) for both parameters ratios.

The m/z 217 mass fragmentograms of the analyzed samples show that the distribution of regular steranes reveals a preference for C_{28} steranes over C_{27} and C_{29}, the C_{29} steroid is synthesized by higher plant and marine organisms. The Al Aziziyah Formations seem to have received substantial amounts of land-derived organic matter that has been transported into a subtidal marine depositional setting and was deposited in a photosynthetic-

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