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معامل التأثير العربي 1.5
العدد 19

مجلة التربوي

مجلة علمية محكمة تصدر عن كلية التربية

جامعة المرقب

العدد التاسع عشر

يوليو 2021م

هيئـــة تحريـر
مجلة التربوي

- المجلة ترحب بما يرد عليها من أبحاث وعلى استعداد لنشرها بعد التحكيم .
- المجلة تحترم كل الاحترام آراء المحكمين وتعمل بمقتضاها .
- كافة الآراء والأفكار المنشورة تعبر عن آراء أصحابها ولا تتحمل المجلة تبعاتها .
- يتحمل الباحث مسؤولية الأمانة العلمية وهو المسؤول عما ينشر له .
- البحوث المقدمة للنشر لا ترد لأصحابها نشرت أو لم تنشر .

ضوابط النشر:

يشترط في البحوث العلمية المقدمة للنشر أن يراعى فيها ما يأتي :

- أصول البحث العلمي وقواعده .
- ألا تكون المادة العلمية قد سبق نشرها أو كانت جزءا من رسالة علمية .
- يرفق بالبحث تزكية لغوية وفق أنموذج معد .
- تعدل البحوث المقبولة وتصحح وفق ما يراه المحكمون .
- التزام الباحث بالضوابط التي وضعتها المجلة من عدد الصفحات ، ونوع الخط ورقمه ، والفترات الزمنية الممنوحة للتعديل ، وما يستجد من ضوابط تضعها المجلة مستقبلا .

تنبيهات :

- للمجلة الحق في تعديل البحث أو طلب تعديله أو رفضه .
- يخضع البحث في النشر لأولويات المجلة وسياستها .
- البحوث المنشورة تعبر عن وجهة نظر أصحابها ، ولا تعبر عن وجهة نظر المجلة .

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Molecular fossil characteristics of crude oils from Libyan oilfields in the Zalla Trough

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Abstract: The main aim of this study is to determine the organic geochemistry of the two crude oils samples recovered from Zalla Trough oilfields to assess oil characterization, Maturation and source depositional environments. The organic geochemical analyses were determined by gas chromatography and gas chromatography/mass spectrometry . n-alkanes distribution, Pristane/phytane, isoprenoids/n-alkanes, CPI, homohopanes abudance, diasteranes, Ster/hop, C_{29} 20S/20S+20R and C_{29}/C_{30} hopane were evaluated and determined. The results suggest that all of the oils are belonged to source rocks rich in marine organic matter deposited under suboxic saline and siliciclastic conditions and are characterized by high level of maturation and sourced mainly from organic matters of marine origin.

1- Introduction

Crude oil is a complex mixture of a large number of chemical compounds, commonly dominated by hydrocarbons that can be connected to their original organisms during deposition of the rocks (Tissot and Welte, 1984; Faraj et al., 2017; Albaghdady et al., 2018).

The molecular fossil or biological marker patterns of crude oils are commonly used for oil/oil and oil/source rock correlations and to assess such source rock attributes as lithology, depositional environment, kerogen type, maturity and to distinction of ancient marine and non marine petroleum source rocks (El Nady et al., 2017).

The Zallah Trough is one of the most complex areas of the Sirt Basin, containing a number of elements which differ markedly in structural style. The main petroleum system in the Zallah Trough is the Sirt Shale source rock and reservoirs in the Palaeocene and Eocene (Hallett, 2002). The Zallah Trough has an area of about 10,000 km^2, and is about 200 km from north to south (Hallett, 2016). Total oil in the whole Zallah Trough are characterized by generally low content of sulphur (≤ 0.6 % and often < 0.3 %, wt %), and API gravity in the 22 – 51.4 º range (Hallett, 2002., Burwood, et al. 2000).

In this study, some of crude oils samples from Zallah Trough oil fields are investigated to identify the thermal maturity, organic type and depositional environment of source rocks.

2- Regional settings

The Zallah Trough is an irregular faulted graben which connects northwards to the Dur al Abd Trough and southwards to the Kotlah Graben and Abu Tumayam Trough (Hallett, 2016). The Zallah Trough is located between the Waddan Uplift in the west and the Az Zahrah-Al Hufrah platform on the east (Fig 1). The Zallah Trough is one of the most complex areas of the Sirt Basin, containing a number of elements which differ markedly in structural style. The main petroleum system in the Zallah Trough is the Sirt Shale source rock and reservoirs in the Palaeocene and Eocene (Hallett, 2002). It is separated from the Abu Tumayam Trough by the Hulayq Spur which projects into the Trough from the south, and the Barrut Spur which projects from the north (Hallett, 2016).The Trough is floored with metamorphic basement and Cambro-Ordovician quartzites The Triassic and Jurassic sediments are deposited more in the northeastern part of the basin, while the Lower Cretaceous sediments are located more in the southeastern part of the basin. The Upper Cretaceous marine sequence is the largest sequence in the basin, ranging in age from Cenomanian to Maastrichtian with the thickest sediments found in the Troughs (Albaghdady et al., 2018).

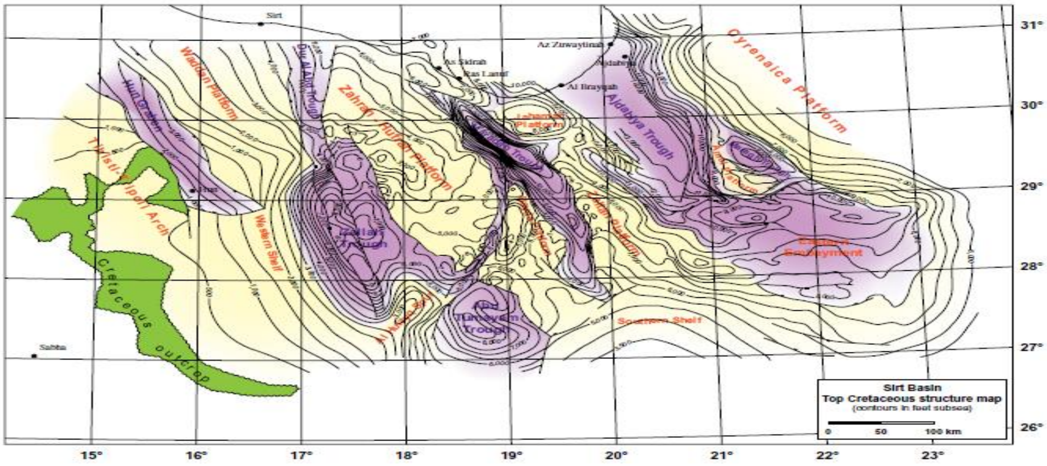

Fig 1. Map shows location and the structural elements of the Sirt Basin (Hallet et al, 2016)

3- Samples and analytical methods

Methods two of crude oil samples used in this study were collected from Zalla Trough Basin. Fig 3 shows the location of the oil fields in the Zalla Trough for these samples.

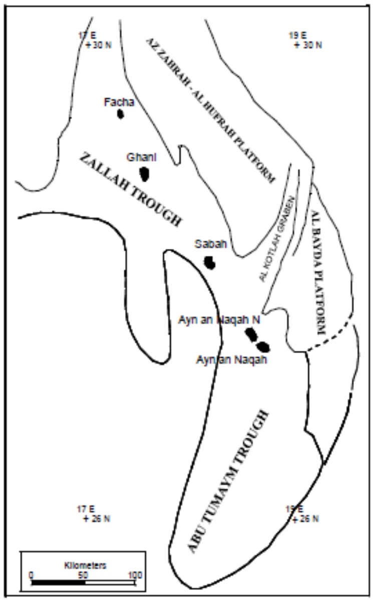

Fig 3. Map shows the location the oil fields in the Zalla Trough B asin included in this study (Albaghdady et al., 2018).

Two oil samples were isolated from malthene fraction of crude oils using column chromatography. A chromatographic colum packed with alumina and silica adsorbents was used. Saturated hydrocarbons were eluted with petroleum ether, aromatic hydrocarbons with mixture of petroleum ether and benzene (2:1, v:v) and the NSO fractions (polar fraction) was determined from the difference to 100% (Stojanovic et al., 2007; Faraj et al., 2016).

GC analysis for alkane and isoprenoid alkane fractions was used gas chromatograph Agilent 6890N with flame ionization detector (FID) and Phenomenex ZB-5 capillary column (30 m x 0.25 mm, film thickness 0.10 microns). The column was heated at a rate of 30 ° C / min in the temperature range of from 70 to 100 ° C, and then at a rate of 4 ° C / min in the temperature range of 100 to 308 ° C. Final temperature of 308 ° C was maintained for 8 min.

GC-MS analysis for terpane and sterane fractions was used gas chromatograph an agilent 7890N gas chromatograph fitted with a HP5-MS capillary column (30 m x 0.25 mm, 0.25 µm film; temperature range: 80 ºC for 0 min; then 2 ºC min^{-1} to 300 ºC and held for 20 min) with helium as the carrier gas (flow rate 1 cm^3 min-1) was used. The GC was coupled to a Hewlett-Packard 5972 MSD operated at 70 eV in the 45–550 scan range

4- Results and discussion

4.1. Normal- alkanes

The distribution of n-alkanes in crude oils can be used to indicate the organic matter source (El Nady et al., 2017; Peters et al., 2005). Fig 3 shows the fingerprints of gas chromatography on saturate fraction of Zalla Trough oil shows a normal alkane distribution range from C_{12} to C_{42} maximizing at C_{17} and C_{18}, which is indicating that the oil samples have marine algal origin. These figures show that the oils appear to be mature, based on the abundance of n-alkanes

In the range n-C_{15} to n-C_{25}, with low concentration of heavy normal alkanes. The increase in the n-C_{15} to n-C_{20}, suggests marine organic matters with a biomass contribution to the from algae and plankton (El Nady et al., 2017; Peters et al., 1993).

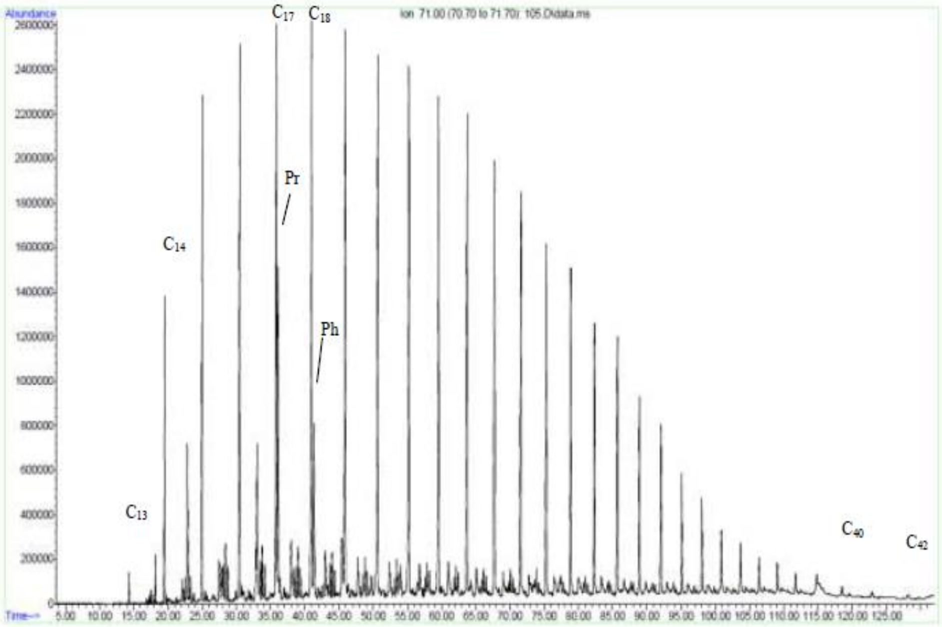

Fig 3. Gas chromatograms of saturated hydrocarbons fraction, *m/z* 71 of the Zalla Trough oilfields.

4.2. Pristane/phytane

The Pristane/phytane is widely used as a redox indicator of the depositional environment. Pristane/phytane ratios for two oil samples are similar ≈ 1.5 (Table 1) indicating intermediate (suboxic) conditions during deposition of precursor organic material. CPI (carbon preference index) values for these samples are close to 1 (Table 1), which indicates that the oils fall in the field of more reducing zone of thermal maturation level and also these results indicate significant proportion of algal biomass in precursor material of the source rocks.

Table 1: n-alkanes and isoprenoids parameters

	CPI	***n*-Alkane range**	***n*-Alkane max**	**Pr/Phyt**	**Pr/ *n*-C_{17}**	**Pr/ *n*-C_{17}**
N-1	1.07	C_{13}- C_{42}	*n*-C_{17}	1.92	0.49	0.25
N-2	1.05	C_{12}- C_{42}	*n*-C_{18}	1.79	0.60	0.41

4.3. Isoprenoids/n-alkanes

Isoprenoids to n-alkanes are widely used since they provide information on maturation and biodegradation as well as source (Hunt et al., 1996). For oil samples the Pr/*n*-C_{17} and Phyt/*n*-C_{18} values is < 1, which can be suggested marine organic matters source (mainly algae) deposited under reducing environment.

4.4. Steranes

The relative abundance of C_{27}, C_{28} and C_{29} steranes have been found to be a good indicator for organic matter type. The distribution of steranes is best studied on GC/MS by monitoring
the ion m/z = 217. The resulting mass chromatograms for samples are shown in Fig 4. All of the studied samples show a high abundance of C_{27} steranes, C_{28} steranes and C_{29} steranes that are believed to be derived from marine organic matter phytoplankton and algae with terrestrial inputs. C_{30} steranes are present in low concentration in these samples (Figure 8), which can be confirmed marine depositional environment of the Zalla oils (Holba et al., 2003). The amount of C_{27} diasteranes, C_{27} dia/ dia + ster and concentration of 20S and 20R isomers are important to detect the maturity level of crude oils (El Nady et al., 2017). The maturity level of oils increase with the increase of these parameters (high

concentration of C_{27} diasteranes, C_{27} dia/ dia + ster, and C29 20S/20S+20R> 0.1) (El Nady et al., 2017; Andrew et al., 2001). It is obvious that the studied oils have slightly high concentration of C_{27} diasteranes (Fig 4) with C_{27} dia/ dia + ster range from 0.58 and 0.60, C29 20S/20S+20R from 0.44 and 0.49 (Table 2). These data reveal that the studied oils are characterized by high maturity level.

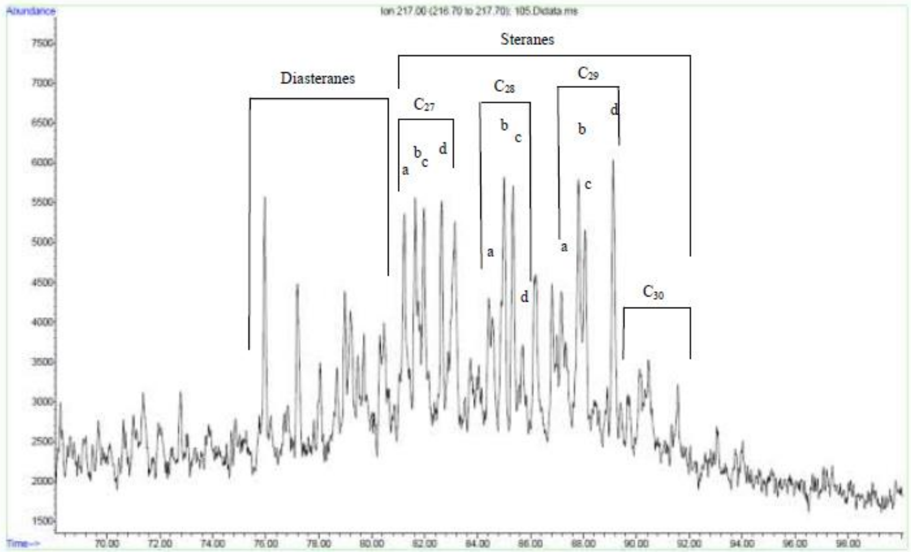

Fig 4. Gas chromatograms–mass spectrometry of steranes , *m/z* 217 of the Zalla Trough oilfields (a - 14α(H),17α(H),20(S) - steranes; b - 14β(H),17β(H),20(R)-steranes; c - 14β(H),17β(H),20(S)-steranes; d - 14α(H),17α(H),20(R)-steranes).

Table 2: steranes, diasteranes and terpanes parameters

	20S/ 20S+20R)	**ββ/ (βββ+ αα)**	**Dia/27R**	**%27 R**	**%28 R**	**%29 R**	**C_{27} dia/ dia + ster**	**Ster/hop**	**C_{29}H/C_{30} H**
N-1	0.44	0.59	1.74	30.38	37.95	31.68	0.60	0.72	0.61
N-2	0.49	0.53	1.61	32.3	35.1	31.0	0.58	0.91	0.65

20S/(20S+20R) = C29 ααα-sterane 20S/C29 ααα-sterane 20S + 20R; ββ/(ββ+αα) = C29 αββ-sterane 20S+20R/C29 ααα + αββ-sterane 20S + 20R; 27Dia/27R = C27 βα-diasterane 20S/C27 αα-sterane 20R; %27R = percentage of C27 αα 20R to sum C27, C28, C29 αα 20R steranes; %28R = percentage of C28 αα 20R to sum C27, C28, C29 αα 20R steranes; %29R = percentage of C29 αα20Rto sum C27, C28, C29 αα 20R steranes; C_{27} dia/ dia +

ster = C27 diasteranes S +R/ (C27 diasteranes+ R) + C29 steranes S +R) ; Ster/hop = Steranes/17a (H)-hopanes; $C_{29}H/C_{30}H$ = C29/C30 hopane.

4.5. Terpanes

Mass fragmentogram at m/z= 191 was used to detect the presence of tricyclic, tetracyclics, hopanes in the saturate hydrocarbon fraction of the studied oils (Fig 5). All crude oil samples have similar terpane distributions and show a high number of hopanes than tricyclic terpanes which may indicate that they have similar organic matter type. In high mature oils, the tricyclic terpanes is dominated more than in low mature oils. Our study reveals that the concentration the most of tricyclic terpanes in the studied oil samples (Fig 5) is relatively high which may support the idea that the oils are more mature (Walples et al 1991; Van Graas et al., 1990; El Nady et al., 2017). Table 3 shows the terpane parameters which used in this study. Low C_{35} homohopanes is an indicator of highly reducing marine conditions during deposition, whereas high C_{35} homohopane concentrations are generally observed in oxidizing conditions during deposition (El Nady et al., 2017; Peters et al., 1993). The studied crude oils have low concentrations of C_{31}-C_{35} homohopanes (20S and 20R) (Fig 5) which is more significant to hypersaline marine oils. High contribution from marine material to the source rocks was additionally supported by the relatively high abundance of the tricyclic terpanes (Figure 4) (Faraj et al., 2016). In the studied samples, C_{29} and C_{30} 17α (H)-hopanes is the two most abundance terpanes and the C_{29}/C_{30} hopane ratios between 0.59 and 0.61 may indicate the clay-bearing character of the source rocks (Albaghdady et al., 2018). Steranes/hopane ratio is relatively high in marine organic matter. In contrast, low steranes and sterane/hopane ratios are more indicative of terrigenous and (Peters et al., 2005). Steranes/ hopanes ratio of the studied crude oils is relatively high range between 0.72 and 0.91 (Table 1). This indicates that the studied crude oils are generated from marine organic matter source with few terrestrial inputs. These results show an agreement with the results of pr/n-C_{17} and ph/n-C_{18} ratios (El Nady et al., 2017; Peters et al., 2005). C_{29}/C_{30} hopane ratios are generally high (>1) in oils generated from organic rich carbonates and evaporates (Walples et al 1991). The studied oil samples have high C_{29}/C_{30} hopane ratios that source rocks range from 0.61 to 0.65 (Table 1).These ratios illustrate that the oil samples are clastic nature of the respective (Moldowan et al., 1985; Faraj et al., 2016).

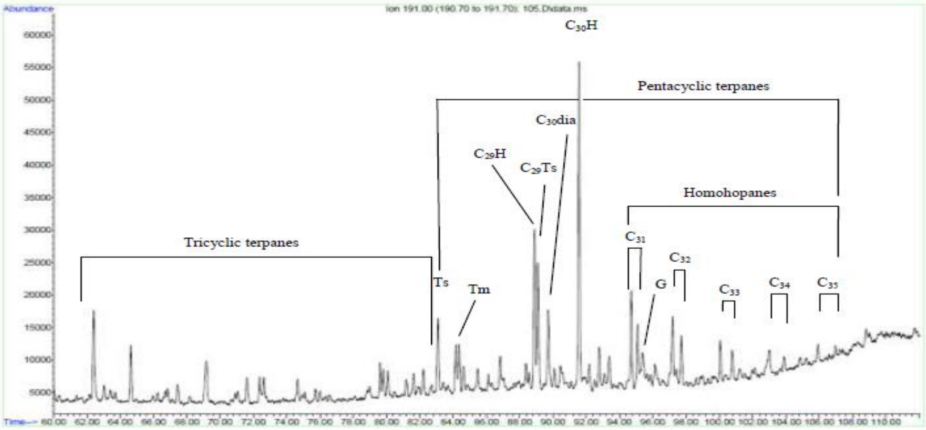

Fig 5. Gas chromatograms–mass spectrometry of terpanes, *m/z* 191 of the Zalla Trough oilfields (Ts - 18α(H),22,29,30-trisnorneohopane; Tm - 17α(H),22,29,30-trisnorhopane; C_{29}Ts - C_{29}18α(H),30-norneohopane; C_{30}dia - C_{30}17α(H)-diahopane; C_{29}H - C_{29}17α(H),21β(H)-hopane; C_{30}H - C_{30}17α(H),21β(H)-hopane; G- Gammacerane).

5- Conclusions

The organic geochemical characteristics and parameters of the crude oils recovered from Zalla Trough oil fields to assess and estimate maturation and source depositional environments. The depositional environment and type of organic matter of crude oil samples show generally marine characteristics. Pristane/phytane ratios for two crude oil samples suggest an intermediate (suboxic) conditions during deposition of precursor organic material. The high abundance of low molecular weight n-alkanes of crude oils supports a high contribution of marine organic matter. CPI values suggest that the studied crude oils fall in the field of more reducing zone of thermal maturation level and also these results indicate significant proportion of algal biomass in precursor material of the source rocks. pristane/phytane ratios are also influenced by the precursor organic matter type, maturity and salinity. Pr/*n*-C_{17} and Phyt/*n*-C_{18} values can be suggested marine organic matters source (mainly algae) deposited under reducing environment. High contribution from marine material to the source rocks was additionally supported by the relatively high abundance of the tricyclic terpanes. These oils have relatively high concentration of C_{27} diasteranes with high raios of C_{27} dia/ dia + ster and C_{29} 20S/20S+20R . These data reveal that the studied oils are characterized by high maturity level. The studied oil samples have high C_{29}/C_{30} hopane ratios that source rocks range from 0.61 to 0.65. These ratios illustrate that the oil samples are clastic nature of the respective. Steranes/ hopanes ratio of these samples is relatively high range between 0.72 and 0.91. This indicates that the crude oils samples are generated from marine organic matter source with few terrestrial inputs. The studied crude oils have low concentrations of C_{31}-C_{35} homohopanes (20S and 20R) which is more significant to hypersaline marine oils.

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