



Organic Geochemical Investigation of Crude oils from the Al Bayda Platform Area (Samah formation), Central Part of the Sirte Basin, Northern Libya

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ABSTRACT

In this paper, the geochemical studies of API gravity, content of asphaltenes and gross compositions were performed on samples from two crude oils collected in the Al Bayda Platform Area (Samah formation), central part of the Sirte Basin. The results showed that the fraction of saturates is the dominant fraction in oils in comparison to aromatics and NSO components, with high API gravity and low content of asphaltenes which indicates that the oils are mature, generated from marine organic sources and that they can be classified as light crude oils. The aim of this study is to provide evidence about precursor of organic material, depositional environment, and maturity of the studied oils. Saturated hydrocarbons were analyzed by gas chromatography–mass spectrometry and gas chromatography–mass spectrometry–mass spectrometry technique. Results indicates that the oil samples are originating from high marine organic matter phytoplankton and algae, with few terrestrial inputs, reflecting that oils can be sourced from siliciclastic, possibly marine shales deposited in a clay-rich marine, deposited under intermediate conditions with high maturity. All results showed that the oil samples are similar in their characteristics, likely due to the migration pathways in the same region.

Keywords: Libya, Crude oils, Sirte basin, Samah formation, Geochemical characteristics.

INTRODUCTION

Petroleum is composed of paraffin

and naphthene mixed compounds, aromatic components, and trace elements^{11,40}. All crude oils are grouped into 4 fractions: aliphatics, aromatic



hydrocarbons, NSOs (resin) compounds and asphaltenes³⁷.

A biomarker is a geochemical fossil fuel, originated from the lipid or organic matter found in petroleum and source rocks^{13,19}. The most important biological markers which are applied in organic geochemical methods are:

- N-alkanes
- Isoprenoids
- Steranes and triterpanes, as well as
- Aromatic non-biomarkers (bicyclic and tricyclic compounds)^{18,28}.

This study is related to the area of Al Bayda platform (Central Area of the Sirte Basin) Fig. 1. The Sirte Basin is located in northern Libya. It is the youngest sedimentary basin in the Africa, and has onshore area of about 375,000 Km² and contains more than 23 significant oil fields and 16 large fields^{1,2,10,17}.

The Sirte Basin contains a series of troughs and platforms, trend in a northwest to southeast and an east west direction in the eastern part of this Basin Fig. 2^{22,36}. A general stratigraphic chart of Sirte Basin is shown in Fig. 2³⁶. The Al Bayda Platform (Kalash Formation) is characterized by dolomitic where Barr and Weegar (1972) named this Formation the Samah formation and estimated the age in their source rocks (Upper Cretaceous Period)^{3,23}.

The Kalash or Samah formation are characterized by slightly high marine organic matter deposited in a clay-rich environment under sub-oxic conditions and are dominated by type-II kerogen. These source rocks have TOC content in range 0.34 -1.25 wt%^{6,11}. The Al-Bayda platform is bordered from east to west by the Abu Tamim and the Marada basin and from south by southern shelf of the Sirte Basin Figure 1^{23,24,36}.

Previous study on the Samah oils were performed on the well L3-59. Results indicated that oil sample was characterized by quartzites, deposited in a marine-source, and generated from the Cretaceous or younger source rocks^{23,24}.

In the present study, bulk geochemical characteristics and saturate hydrocarbons

distributions and parameters of crude oils samples were investigated to evaluate the precursor of organic material, depositional environment of source rocks and maturity.

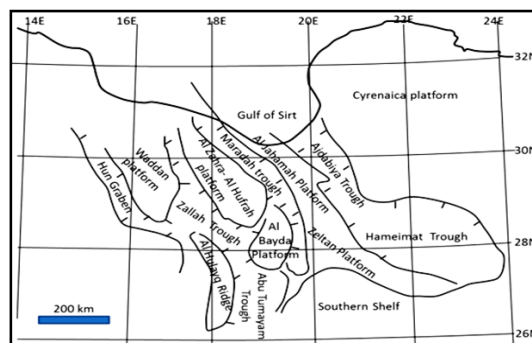


Fig. 1. Sirte Basin Tectonic³⁶

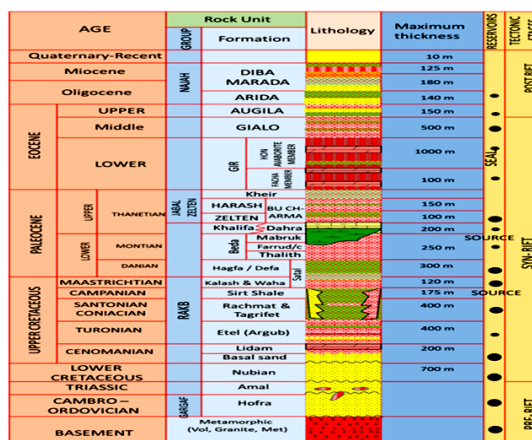


Fig. 2. Stratigraphic chart of the Sirte Basin³⁶

MATERIALS AND METHODS

Organic geochemical methods were applied in 2 oil samples that originated from the Samah field Figure 3.

API gravity is a measure of oil density at 21C° using 50 mL glass bottles (pycnometers) and is related to this equation:

$$API = 141.5 / \text{specific gravity (d)} - 131.5^{11,18,34}$$

The asphaltene was separated from the crude oils by adding n-pentane to beaker until mass ratio of n-heptane to crude oil 40:1. Solution was placed in a dark place at 21°C. After that, this solution is placed in a boiling water bath for 20-25 minutes. Then, the hot mixture is filtered. The filter material which was used in this filtration was dried

to a constant weight and the asphalt content was measured^{16,19,34}.

Maltene oil samples were separated by liquid chromatography. Silica gel was mixed with alumina 1:2 weight(%). Saturates were removed firstly with *n*-hexane, and then aromatics were eluted by *n*-hexane and benzene (2:1, Vol: Vol) respectively and the NSO fractions (polar fraction) with methanol^{11,17}.

Gas chromatography–mass spectrometry analysis for alkanes was performed by using gas chromatograph of an Agilent Technologies GC 7890N System gas chromatograph (30mx0.25mm capillary column, with 0.25µm coating of H5-MS stationary phase. The carrier gas He, 1.5 cm³/min, FID) was coupled to an Agilent 5975C mass selective detector (70eV). The column was heated from 80 to 300°C, at a rate of 2°C/min and the final temperature of 310°C was maintained stable for an additional 20 minute.

Normal alkanes, pristane and phytane alkanes were analyzed by gas chromatography–mass spectrometry technique. The saturates (*n*-alkanes and isoprenoids) were applied in the single ion monitoring (SIM) system, and by using ions *m/z* 71.

The distribution of *n*-alkanes and isoprenoids of oil samples studied, is shown in Figure 5. Gas chromatography–mass spectrometry–mass spectrometry analysis of terpene and sterane fractions was performed through an Agilent 6890N gas chromatograph coupled to a Waters (Micromass) Quattro Micro GC tandem quadropole MS selective. A Phenomenex ZB-5 column (30mx0.25mm i.d., film thickness 0.10µm) was used. The temperature program was: 30°C min⁻¹ from 70 to 100°C and 4°C min⁻¹ from 100 to 308°C (hold 8 minute).

Sterane and terpene compounds were analyzed by gas chromatography–mass

spectrometry–mass spectrometry, and by using ions *m/z* 217 (for steranes) and *m/z* 191 (for terpenes).

The distribution of steranes and terpenes of studied oil samples, are shown in Fig. 7 and 8. Specific parameters of saturated hydrocarbons calculated from GC-MS and GC-MS-MS technique are given in Tables 2-4.

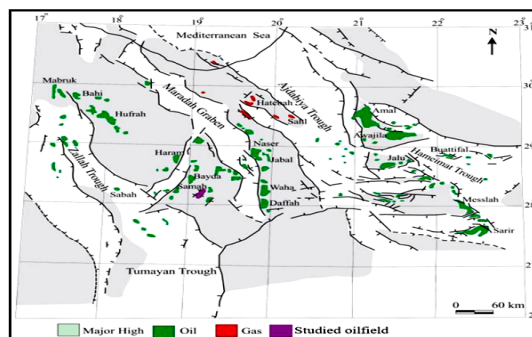


Fig. 3. Map of the northern part of Libya with the location of estimated oil field^{25,33}

RESULTS AND DISCUSSION

Bulk compositions

Bulk composition of the studied crude oils, content of asphaltenes, and API gravity are shown in the Table 1. Investigated samples are distinguished by high content of saturated hydrocarbons%, ranging from 63.78%-66.12% relative to the content of the aromatics% from 21.76%-23.69% and resins components 11.72%-12.09% with low percentage of asphaltenes (<0.50) and high API values (>30) Table 1. From these results conclusion is that soluble organic matter in 2 samples of crude oil are mainly represented by high amount of saturates of the total content of oils, and high API values, and also with low percentage of asphaltenes indicating that the investigated oils are derived from marine materials and are classified into light oils^{11,17,34,41}. The low amount of NSO compounds and asphaltenes compared to hydrocarbon components (saturated and aromatic fractions) indicate that the oil samples are non-biodegraded³².

Table 1: The American Petroleum Institute gravity (API gravity), percent of asphaltenes and gross composition of the investigated oil samples

S. No	API value(°)	Content of asphaltenes(%)	Saturated hydrocarbons(%)	Gross composition	
				Aromatic components(%)	Resins components(%)
S1	36,87	0.44	63,78	23,69	12,09
S2	37,08	0.40	66,12	21,76	11,72

Normal alkanes

Normal alkane distributions in oils and source rocks are widely applied as indicator of organic matter type^{20,32}. Gas chromatography–mass spectrometry of normal-alkanes and isoprenoid alkanes, m/z 71 from oils are present in Fig. 4. GC-MS analysis shows that the oils are identified in range C14-C42 maximizing at n-C17 in the sample (S1) Fig.4, while n-alkane fractions in the sample (S2) are identified in range C13 to C42 maximizing at n-C16 Fig. 4, indicating that the studied oils are marine algal. Based on the abundance of normal alkanes ranging from C15-C22, with low abundance of heavy alkanes, these oil samples appear to be

more mature with non-biodegraded. High abundance in range C15-C22, is showing that the studied oils are marine matters (plankton and algae)^{14,30}. The ratio of Carbon Preference Index (CPI) is calculated from distributions of n-alkane with odd carbon number alkanes to even carbon number alkanes^{11,40}. This parameter (CPI) is one of the most widely applied with purpose to obtain information about depositional environment and thermal maturation. CPI values = 1 or ≈ 1 suggest high maturity of oils and marine input while higher CPI values indicate low maturity^{11,32}. CPI (carbon preference index) values for these samples) in range 1.01-1.04 Table 1, are showing more reduction with high maturity levels.

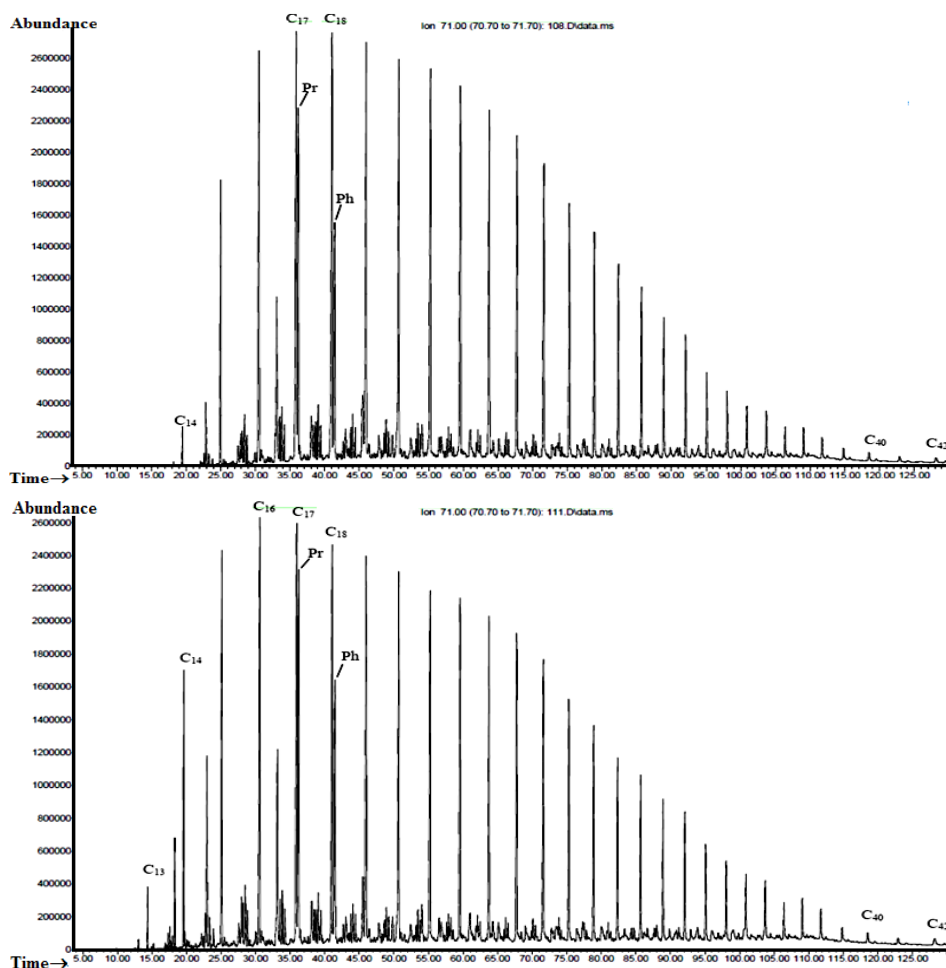


Fig. 4. Typical ion fragmentograms of normal alkanes and isoprenoids- m/z 71,(S1 and S2 samples, respectively)

Isoprenoid alkanes

The value of pristane/phytane is widely applied to identify depositional environment of source rocks^{14,17}. Oils with a value <1 indicate an anoxic origin while Pr/Ph values >3 suggest oxic conditions²⁷.

Pr/Ph values for oil samples in range 1.41-1.48 Table 2 indicate a mixed origin of the organic matter.

The ratio of pristane/n-C17 and phytane/n-C18 can be used to bring information about the

maturation and origin^{14,27}. Values of these ratios smaller than one indicate a non-biodegraded and high maturity of oils¹¹. Pristane/n-C17 and Phytane/n-C18 for oil samples (S1 and S2) are from 0.72-0.86 and 0.50-0.67, respectively indicating a mixed sources (marine and terrestrial organic matter) and non-biodegraded oil¹¹ Figure 5. The cross-plot of pristane/n-C17 versus phytane/n-C18 ratios can also be used to make genetic differences among oils²⁷. The cross-plot of pristane /n-C17 versus phytane/n-C18 ratios shows that the oil sample (S1) is slightly more thermally mature than the oil sample (S2) Figure 5.

Table 2: Specific parameters of normal alkanes and isoprenoides

S. No	CPI	Alkanes range	Alkanes maximum	Pristane/Phytane	Pristane/n-C17	Phytane/n-C18
S1	1.04	n-C14-n-C42	n-C17	1.48	0.72	0.50
S2	1.01	n-C13- n-C42	n-C16	1.41	0.86	0.67

CPI-Carbon Preference Index⁸

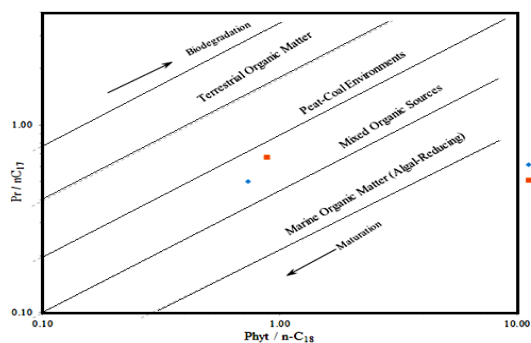


Fig. 5. Diagram of Pristane/n-C17 values (y) versus Phytane/n-C18 values (x) of the investigated oils^{27,35}

Steranes

The concentration of C27, C28 and C29 steranes might be significant for evaluation of organic material sources¹⁵. The major abundance of C27 steranes shows a marine plankton, while C28 steranes presence indicate algae and fungi, and presence of C29 steranes are plants^{12,17,32}.

Results of presence in studied oils show the highest abundance of C27 steranes in the sample (S1); in the sample (S2) C28 steranes; also, it is showed that concentrations of C27-C29 steranes in these samples are higher, which possibly suggest that they are produced from marine sources (plankton and algae) with few terrestrial inputs. Additionally, the appearance of C30 steranes, confirms a marine source¹². C27 dia/ dia+ster and C29 20S/20S+20R values can be used for thermal

The dibenzothiophene/phenanthrene (DBT/P) ratio values and pristane/phytane (Pr/Phy) ratio values can provide information on reservoir lithology and depositional environment. Higher values of the DBT/P ratio and Pr/Phy ratio, suggest that certain oils are originating from carbonates and marine shales, whereas low values of these ratios indicate that oils are originating from marine shales deposited under suboxic conditions²⁶. DBT/P values for both samples are <1 while Pr/Phy values are between 1-2, showing that they are product of marine shales deposited under intermediate conditions Figure 6²⁶.

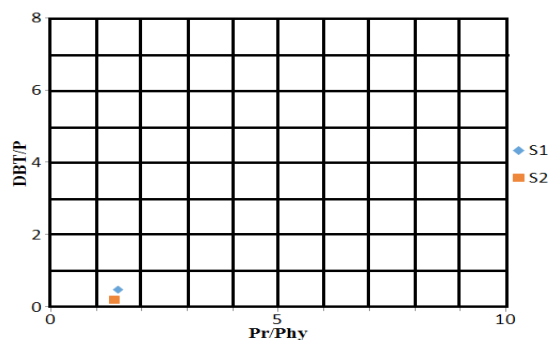


Fig. 6. Diagram of dibenzothiophene/phenanthrene values (y) versus Pristane/phytane values(x) of the investigated oils²⁶

maturity assessment¹⁴. The investigated oils have C27 dia/dia+ster values from 0.55-0.64 and C29 20S/20S+20R from 0.48-0.49 Table 3, which is indicator that oil samples are more mature.

C29 dia/C29 ratio can be used to distinguish crude oils produced from carbonates and from clastic rocks^{15,32}. The investigated oils show high values of this ratio, from 0.82-1.10 Table 3, indicating that oil samples were produced from siliciclastic source rocks.

C28/C29 steranes values could be used as an indicator of geologic age^{4,21,31}.

Values <0.5 suggest that petroleum was generated from Lower Paleozoic period, while values from 0.4-0.7, indicate that oils were generated from Upper Paleozoic and Lower Jurassic period. Oils

with a value >0.7 suggest Upper Jurassic to Tertiary oils^{4,21,31}. The studied oil samples show the ratio of C28/ C29 steranes is 1.04 in the sample (S1) while 1.12 in the sample (S2), suggesting that oil samples

are generated from Upper cretaceous source rocks age. The ratio of C27 dia/ C27 ster R has big values Table 3 indicating more mature samples with rich clay in source rocks.

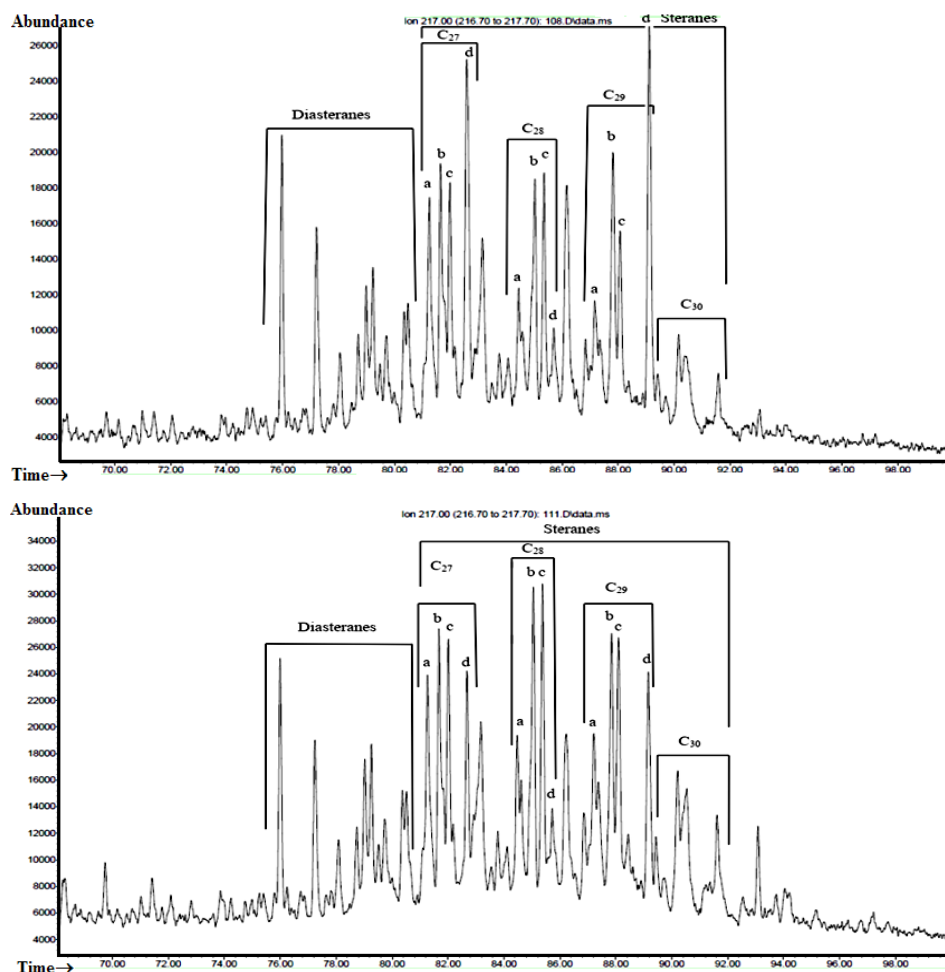


Fig. 7. GC-MS-MS chromatogram of sterane components, m/z 217 of the Samah oil field (S1 and S2 samples, respectively) a=14 α (H), 17 α (H), 20(S)-steranes; b= β 14(H), 17 β (H), 20(R)-steranes; c=14 β (H), 17 β (H), 20(S)-steranes; d= α 14(H), 17 α (H), 20(R)-steranes.

Table 3: Sterane and diasterane fractions parameters

S. No	C27dia/dia+ster	20S/(20S+20R)	C29 dia/C29	C28R/C29R	C27 dia/C27 sterR
S1	0.64	0.49	1.10	1.04	1.77
S2	0.55	0.48	0.82	1.12	1.25

C27 dia/dia+ster = C27diasteranes S+R/(C27 diasteranes+R)+C29 steranes S+R); 20S/(20S+20R)=C29 $\alpha\alpha\alpha$ -sterane 20S/C29 $\alpha\alpha\alpha$ -sterane 20S+20R; C29 dia/C29 ster=(C29 $\beta\alpha$ 20(S+R)+C29 $\alpha\beta$ 20(S+R)) Diasteranes/(C29 $\alpha\alpha$ 20(S+R)+C29 $\alpha\alpha$ 20(S+R)) Steranes; C28R/C29R= C28 $\alpha\alpha$ -sterane 20R/C29 $\beta\alpha$ -sterane 20R;C27 dia/C27 sterR=C27 $\beta\alpha$ -diasterane 20S/C27 $\alpha\alpha$ -sterane 20R

Terpanes

Terpenes distribution is shown by GC-MS-MS technique, m/z 191 Fig. 8. Terpene abundances in these samples are similar and the concentration of

hopanes is higher than the concentration of tricyclic terpenes, which can indicate that the type of organic sources in these oils are similar. The concentration of the tricyclic terpenes is relatively high Fig. 8,

suggesting more mature and marine material in their source rocks^{14,38,39}. The marine sources are supported by low concentrations of C31-C35 homohopanes (20S and 20R) and the presence of gammacerane 30 Fig. 8. The oil samples show the highest abundance of C3017 α (H)-hopanes and C29 with values of C29/C30 hopane ranging from 0.53-0.74 Table 4. This refers to a marine environment with clay-bearing

character of the source rocks⁴. The ratio of C29/C30 hopanes < 1 Table 4, indicating that oils are clastic in the source rocks^{17,29}. Sterane/hopane values are higher in petroleum derived from marine material, while low of sterane/hopane ratios indicate terrestrial inputs^{14,32}. Sterane/hopane values of the studied samples ranged from 1.42-1.99 Table 4, suggesting that they are derived from high marine material^{12,14,32}.

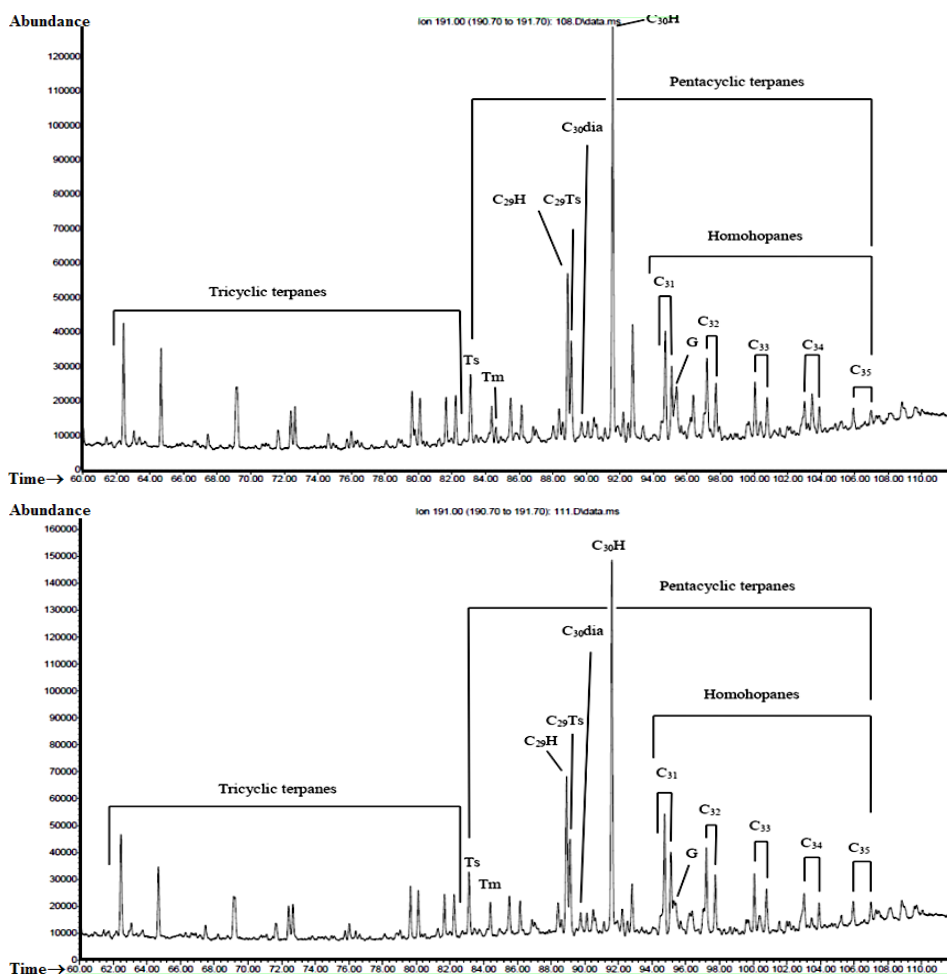


Fig. 8. GC-MS-MS chromatogram of terpane components, m/z 191 of the Samah oil field (S1 and S2 samples, respectively)
 Ts = 18 α (H),22,29,30-trisnorneohopane; Tm=17 α (H),22,29,30-trisnorhopane; C29Ts= C2918 α (H), 30-norneohopane; C30dia= C3017 α (H)-diahopane; C29H=C2917 α (H),21 β (H)-hopane; C30H=C3017 α (H),21 β (H)-hopane; G=Gammacerane

Table 4: Hopanes parameters

S. No	C29H/C30H	Ster/hop
S1	0.53	1.42
S2	0.74	1.99

C29H/C30H = C29/C30 hopane; Ster/hop = Steranes/17 α (H)-hopanes

CONCLUSION

Based on the API values, content of

asphaltenes and gross compositions of the studied oils recovered from the Al Bayda Platform Area (Samah formation). The high amount of saturated hydrocarbons compared to aromatics and NSO compounds amount, with high API values and low percentage of asphaltenes in oil samples, indicate that samples are more mature, and that they are originating from marine organic sources which classify them in group of light oils. Saturated hydrocarbons were analyzed by gas

chromatography–mass spectrometry and gas chromatography–mass spectrometry–mass spectrometry technique for the assessment of organic material type, depositional environment of source rocks, and maturity of the oils. Mass chromatogram of alkanes showed that the oils are marine algal, more mature, and non-biodegraded. CPI values of samples are indicating more reduction and mature oils. The ratios of pristane/phytane, dibenzothiophene/phenanthrene, pristane/n-C17 and phytane/n-C18 of oil samples are indicating origin from marine organic matter, possibly marine shales with terrestrial materials, deposited under intermediate conditions with more thermal maturity and non-biodegraded. C27-C29 steranes have high concentrations, suggesting that they are products of marine sources (plankton and algae) with few terrestrial materials. Sterane/hopane values of oils ranged from 1.42-1.99, indicating that they derived from high marine

material. The marine sources are also supported by low concentrations of C31-C35 homohopanes, the presence of gammacerane and C30 steranes. The ratios of C27 dia/dia+ster, C29 20S/20S+20R and C27 dia/ C27 ster R confirm high maturity of oils. The oil samples have C29/C30 hopane ratios less than one, indicating that oil samples are clastic nature of the source rocks. C28/ C29 steranes values of oils are in the range 1.04-1.12, showing that oil samples are generated from Upper cretaceous source rocks age.

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Conflict of interest

The author declare that we have no conflict of interest.

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