# Geochemical Correlation of Mishrif Formation in AL-Nasiriyah Oil Field/ South of Iraq

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**Abstract**

Gas Chromatography GC, Gas Chromatography–Mass spectrometry GC/MS techniques used for analysis of the crude oils that taken from (10) producing wells in Nasiriyah oil field including (NS-1, NS-3, NS-4, NS-5, NS-6, NS-7, NS-8, NS-9, NS-10, and NS-12) from Mishrif reservoir . This reservoir is one of the important reservoirs in Al-Nasiriyah oil field, and it will be the main subject in the current study in order to provide information of crude oil analysis in this area, also to provide information on its characterizations. Mishrif Formation is one of the principle carbonate reservoir in central and southern Iraq. It is part of the wasia group and widespread throughout the Arabian gulf, It is deposited during Cenomanian-Early Turonian cycle with equivalence to Upper Sarvak reservoirs in Iran and the Natih Formation in Oman,This formation in central and southern Iraq is represented in many oil fields such as, Buzergan, Amara, Halfaya, Majnoon, Rumaila, West Qurna, and Nasiriyah. The analysis of various bulk parameters such as (API gravity ,Sulfur content ,Crude oil compositions and Stable carbon isotope compositions (δ 13C ‰))and biomarker parameters such as (Alkanes and Acyclic Isoprenoid Ratios, Terpanes ,and Steranes) shows that the all oil samples are represented one group, non-biodegraded, marine, and non-waxy deposits derived from carbonate source rocks deposited in anoxic marine environment, these oils are from Jurassic, with similar level of thermal maturity ,Hence the most appropriate sources for this crude oil may be Sargelu Formation.

**Keywords:** Nasiriyah oil field , Mishrif Formation ,Biomarkers .

# المضاهاة الجيوكيميائية لتكوين المشرف في حقل الناصرية النفطي في جنوب العراق

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**الخلاصة**

استخدمت تقنية الغاز كروماتوغراف والغاز كروماتوغراف الطيف الكتلي لتحليل نماذج النفط المأخوذة من 10 آبار منتجة للنفط في حقل الناصرية وهذه الآبار هي (الناصرية 1، 3، 4، 5، 6، 7، 8، 9، 10، 12) لتكوين المشرف. أن هذا التكوين أحد أهم التكاوين المهمة في حقل الناصرية النفطي وهو الموضوع الأساس في الدراسة الحالية وهو يمثل أحد التكاوين الكاربونية الأساسية في وسط وجنوب العراق وهو جزء من مجموعة وسيع ويمتد خلال الخليج العربي، ترسب هذا التكوين خلال العصر السينوماني– التوريناني المبكر وهو مكافئ لتكاوين السارفاك العلمية في إيران وتكوين النطيح في عمان. يتمثل هذا التكوين في وسط وجنوب العراق بمجموعة من الحقول وهي بازركان، العمارة، حلفاية، مجنون، الرميلة، غرب القرنة وحقل الناصرية.

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أن تحاليل (Api, Sulfur content, crude oil compositions, stable carbon isotope) وتحاليل العلامات الإحيائية Biomarkers بين أن جميع النماذج المأخوذة من حقل الناصرية تعود إلى عائلة واحدة غير محطمة، غير شمعية، تولدت من صخور مصدرية لها نفس المستوى من النضوج الحراري ولهذا فإن المصدر المناسب لهذه النفوط ممكن أن يكون تكوين ساركلو.

## Introduction

Nasiriyah oil field is located in Dhiqar Governorate, in southern Iraq. The field lies east of the River Euphrates, about 38 kilometers northwest of the city of Nasiriyah, It was discovered by the Iraq National Oil Company (INOC) in 1978**.**Fourteenth exploration wells have been drilled within the oil-bearing area figure-1. This field locates in unstable shelf close to Arab platform[1]exactly in the Euphrates sub zone (Mesopotamian zone)[2] which characterized with sub-surface anticline and domes with variable extension from North-south to North-west- South-eastern with anticlines that have limited extensions, and according to earthquake survey in 1987-1988 which proved that the structure is just like unstable anticline with dimension (30$\times$10 Km), expanded towards North –west South-east with structural closure about (65 m) upward the Mishrif formation[3,4].

The Mishrif Formation (Cenomanian-Early Turonian) represents a heterogeneous formation originally described as organic detrital limestones, capped by limonitic fresh water limestones[5].It is thickest in the Rumaila and Zubair fields (270 m), in the NahrUmr and Majnoon fields along the Iraq-Iran border it becomes (435 m) thick, and in Abo Amud field between kut and Amara it is (380 m) thick. Other isolated occurrence lie near Kifl (255 m) and Samarra (250 m)[6].It thins towards the W and NW, passing laterally into the Rumaila formation , its thickness at the southern part of Iraq between (150-200m) , which increased towards the Iraqi-Iranian borders until the thickness reached to(350m) , its thickness in the study area between (150-180 m)[7]. The curret study aimed to determination of the biomarkers distribution in oil samples like terpane and sterane as well nas stable carbon isotope values, oil families and their source affinities.

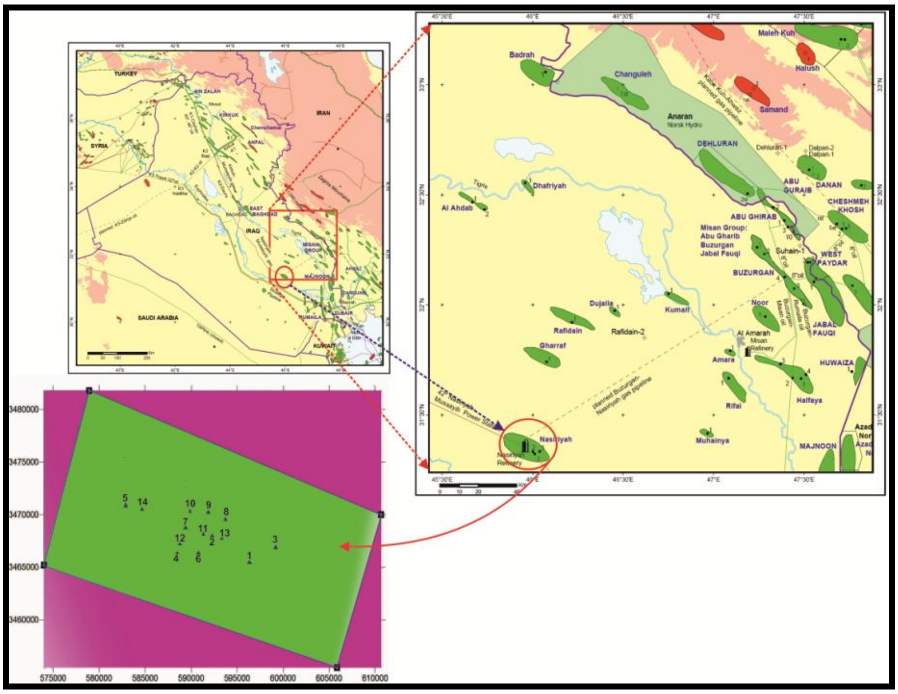


**Figure1-** Location of the studied area after (OEC).

## Materials and Methods:

Ten oil samples were recovered from ten oil producing wells table-1 . Adequate samples of crude oil are essential for their characterization [6], the common methods for geochemical characterization of crude oils are the measurement:

- **Bulk properties:** API gravity, Sulfur content, Crude oil compositions, and Stable carbon isotope compositions (δ 13C ‰).
- **Biomarkers Parameters:**
  - **Alkanes and Acyclic Isoprenoid Ratios**

    a) n-alkenes ratio:Terrigenous/ Aquatic Ratio (TAR),Carbon Preference Index (CPI) ,and Odd-to Even Preference (OEP)

    b) Acyclic Isoprenoids
- **Terpanes:** includes Tricyclic terpanes,$C_{26}/C_{25}$ tricyclic terpane ratio ,Extended tricyclic terpane ratio (ETR),$C_{24}$ tetracyclic terpane ratio,Hopanes,$C_{31}/C_{30}$hopane,30-Norhopane/hopane,17α-Diahopane/ 17α-Hopane,Oleanane/H, Gammacerane Index ,Ts/Tm,$C_{29}$ Ts /($C_{29}$ 17α- hopane + $C_{29}$ Ts) ratios, Mortane/ hopanes, and $C_{35}$ Homohopanes Index.
- **Steranes:** includes regular Steranes ($C_{27}$, $C_{28}$, $C_{29}$), $C_{28}$ / $C_{29}$ steranes, Diasterane / Steranes,and 20 S/ (20 S+ 20 R) isomerization.

The crude oil samples are analyzed by using gas chromatography/Mass spectrometry (GC/MS), in Geomark lab in Texas Houston to determine crude oil characterization and biomarker to predict age, environment, and lithology of source rock figure-2.

**Table 1-** Oil samples from Nasiriyah oil field

| Well Name | **Longitude(E)** | **Latitude(N)** | **Depth (M)** |
|---|---|---|---|
| NS-1 | 46°0 ′43.383″ | 31° 19′32.159″ | 2016 |
| NS-3 | 46°2 ′21.734″ | 31° 20′12.05″ | 2008 |
| NS-4 | 45°55 ′33.887″ | 31° 19′56.919″ | 2002 |
| NS-5 | 45°52 ′4.805″ | 31°22 ′19.975″ | 2001 |
| NS-6 | 45°57 ′14.989″ | 31° 19′45.227″ | 2007 |
| NS-7 | 45°56 ′8.275″ | 31° 21′18.076″ | 2010 |
| NS-8 | 45°59 ′7.783″ | 31° 21′33.207″ | 1991 |
| NS-9 | 45°57 ′56.943″ | 31° 21′49.713″ | 1988 |
| NS-10 | 45°58 ′1.07″ | 31° 22′6.22″ | 1987 |
| NS-12 | 45°55 ′46.955″ | 31° 20′17.552″ | 2005 |

**Results and Discussion:**

The bulk properties results of Mishrif reservoir crude oils are summarized in table-2. The high sulfur content (3.67% to 4.72%) in all samples associated with marine environment[8].API Gravity range from (23-26.2˚API), which represent medium oils[9]. Also crude oil becomes heavier and API gravity decreases as the percentage of aromatic and naphthenic hydrocarbons increases relative to the paraffin's and as the percentage of NSO compounds increases[10].

The API gravity shows negative correlation with sulfur contents and the plot of percent sulfur against API gravity recognizes the type of crude oils . While it shows positive correlation with the percentage of hydrocarbons < $C_{15}$ and the saturated-to-aromatic ratio figure 3. Light hydrocarbons percentage (<$C_{15}$) for all samples of the studied field, range from (33.2 - 35.5), and when correlated with thermal maturity, they represent a typical mid-oil window marine oils. The Nickel / Vanadium ratios for all studied samples ranged between (0.21-0.25) which indicate marine environment. A plot of the carbon-isotope values of aromatic versus saturated fractions of the Mishrif crude oils figure-3. These plots can be used to distinguish oil families and to infer a marine (non-waxy) versus a terrestrial (waxy) sourced [11]. And by depending on the relationship between the average of the stable isotope ratios for Mishrif oil versus age, suggest that the age of the source rock lies between Middle Jurassic to lower Cretaceous .

The Pr/Ph ratios for the same samples range from (0.76-0.83) and the low CV values that ranged from (-3.55 to -3.97), correlation of these two parameters indicates marine environment .

The source affinity of Mishrif crude oil is determined by using and comparing different biological parameters, the value of$C_{31}/C_{30}$hopane ranges between (0.33 to 0.35) that indicates a marine marl, shale, or carbonate environment[9] table-3. 30Norhopane/hopane values are greater than 1.0 which indicates to anoxic carbonate or marl source, so the shale source probability will be ruled out. At this point the use of $C_{22}/C_{21}$ and $C_{24}/C_{23}$ tricyclic trepane ratio is important to distinguish whether the source is marine marl or carbonate, the cross plot between these ratios indicate a marine carbonate source.

The $C_{27}$-$C_{28}$-$C_{29}$ steranes ternary diagram support the others parameters and referred to marine carbonate source figure 4. The Pr/Ph values is ranged from (0.76 to 0.83) which indicate anoxic carbonate, Crude oil samples of in this study show the values of $T_S/T_m$ ratio less than 1.0 which indicates anoxic marine depositional environment . Pr/n$C_{17}$values is ranged between (0.18 to 0.22), Ph/n$C_{18}$values range between 0.28 to 0.35, when these two ratios are cross plotted, it will give an indicator of kerogene type which is marine algal kerogen type II .

The absence of oleanane means rare of higher plant (flowering plant) contributions[12], while the low concentration of gammacerane indicate to low hyper salinity environments which are also reflected by the relative concentration of $C_{24}$ tetra cyclic terpane .

All these parameters give a direct or indirect indicator for Mishrif crude oil source environment to be considered as anoxic marine carbonate. Many age-related biomarkers can be related to specific taxa through natural-product chemistry, and the occurrence or relative abundance of these biomarkers parallels the taxonomic record[8] .The ratio of $C_{28}/C_{29}$ steranes for oil samples range from (0.55 to 0.60) table 4 figure 5, which roughly represent as Upper Jurassic to Early Cretaceous oils. Other parameter is the extended tricyclic terpane ratio (ETR) which has a value less than 1.2 in all oil samples table 3 and represent oils generated from Middle or Late Jurassic source rocks. Various compounds in source rocks show distributions through geologic time suggesting their use as age-related biomarkers in crude oils .

Biomarkers can be used as indicators of the total thermal history of the organic matter, and hence as indicators of maturity. The ratio of mortanes/ hopanes decreases with thermal maturity. All crude oils show values less than 0.15 table 3, which refer that these oils are mature. The low ratio of $T_s/T_m$ (less than one) for all oil sample refer that these samples are from carbonate sources, and within the stage of maturity according to the relative, amounts of $T_S$ and $T_m$ table 3. Also the $T_S$/ hopane ratio show closed values, which indicate that these oils at the same level of maturation table-3. [12]. The steranes isomerization ratios [20 S/ (20 S + 20 R)] in all Mishrif crude oil samples table 4. indicate that these oils have passed the onset of petroleum generation (within oil window and % 20S more than 40%).The low values of diasteranes/ steranes ratio in all Mishrif oil samples indicate as mature oils and does not reach the postmature range table-4.

Pristane/*n*C17 and phytane/*n* C18 decrease with thermal maturity as more*n*-alkanes are generated from kerogen by cracking[13].These isoprenoids/*n*-alkanes ratios can be used to assist in ranking the thermal maturity of related, non-biodegraded oils and bitumens table 5, the same table suggests a considerable odd versus even-predominance for the crude oil samples are mature in the in the study area, where CPI or OEP ratios more or less approach 1.0.The Mishrif crude oil samples show non-biodegradation effect according to the following reasons:

1. The crude oils of Mishrif formation in Nasiriyah oil field are normal class, having medium (API), and the main constituents of these oils are saturated and aromatic, and less amount of NSO compounds as in table 2.
2. The depth of reservoirs greater than (2000 m), and their temperatures equal or more than 80ºC[14].
3. The light hydrocarbons are greater than heavy hydrocarbons and low ratio of Pristine/C17 and Phytane/nC18 with presence of n-alkanes and n-isoprenoid alkanes indicate that the Mishrif crude oils samples are non-biodegraded [10].

**Table 2-** Bulk properties, gross compositional parameters, and stable carbon isotope composition of Mishrif crude oil fraction for the studied samples.

| N0. | Well Name | Depth (M) | API | S% | $<C_{15}$% | Ni ppm | Vppm | Liquid Chromatography wt% | | | | Stable Carbon Isotopes | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Sat. | Arom | NSO | Asphalt | Sat.% | Arom% | CV* |
| 1 | NS-1 | 2016 | 24 | 4.72 | 33.2 | 24.937 | 99.0 | 28.7 | 46.4 | 17.2 | 7.8 | -27.56 | -27.81 | -3.66 |
| 2 | NS-3 | 2008 | 23.6 | 4.11 | 33.5 | 16.709 | 76.0 | 28.3 | 45.9 | 19.1 | 6.6 | -27.55 | -27.90 | -3.89 |
| 3 | NS-4 | 2002 | 26.1 | 4.27 | 35.5 | 17.316 | 78.0 | 27.5 | 47.5 | 19.2 | 5.8 | -27.64 | -27.86 | -3.57 |
| 4 | NS-5 | 2001 | 25.6 | 3.84 | 34.8 | - | 60.0 | 28.5 | 46.7 | 18.5 | 6.3 | -27.55 | -27.84 | -3.75 |
| 5 | NS-6 | 2007 | 24.1 | 3.89 | 33.1 | 18.501 | 74.0 | 27.4 | 46.7 | 16.8 | 9.0 | -27.51 | -27.85 | -3.88 |
| 6 | NS-7 | 1993 | 25.3 | 3.99 | 34.2 | 17.42 | 80.0 | 28.4 | 47.3 | 18.1 | 6.3 | -27.55 | -27.81 | -3.69 |
| 7 | NS-8 | 1991 | 24.8 | 3.67 | 34.4 | - | 67.0 | 28.5 | 46.7 | 18.4 | 6.4 | -27.59 | -27.90 | -3.79 |
| 8 | NS-9 | 1988 | 25.0 | 3.79 | 33.7 | - | 57.0 | 28.5 | 46.2 | 18.7 | 6.6 | -27.59 | -27.88 | -3.74 |
| 9 | NS-10 | 1987 | 26.2 | 3.90 | 34.8 | 16.667 | 63.0 | 29.7 | 47.5 | 17.8 | 4.9 | -27.63 | -27.84 | -3.55 |
| 10 | NS-12 | 2005 | 23.7 | 3.98 | 33.9 | 15.954 | 75.0 | 27.5 | 48.1 | 16.1 | 8.2 | -27.48 | -27.86 | -3.97 |

**CV: Canonical Variable**

**Table3 -** The results of mass chromatograms of hopanes (m/ z 191) parameters for the studied crude oil samples

| Sample No. | Well No. | Depth (M) | $C_{22}/C_{21}$ | $C_{24}/C_{23}$ | ETR | Tet/$C_{23}$ | $C_{26}/C_{25}$ | $C_{28}$/H | $C_{29}$/H | $C_{30}$X/H | $C_{31}$R/H | OL/H | GA/31 | $C_{35}S/C_{34}S$ | $C_{27}$Ts/Tm | $C_{29}$Ts/Tm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | NS-1 | 2016 | 1.05 | 0.26 | 0.85 | 1.15 | 0.72 | 0.00 | 1.48 | 0.00 | 0.34 | 0.00 | 0.22 | 1.06 | 0.17 | 0.07 |
| 2 | NS-3 | 2008 | 1.07 | 0.26 | 0.86 | 1.22 | 0.73 | 0.01 | 1.63 | 0.00 | 0.34 | 0.00 | 0.22 | 1.04 | 0.17 | 0.07 |
| 3 | NS-4 | 2002 | 1.05 | 0.26 | 0.86 | 1.22 | 0.74 | 0.01 | 1.67 | 0.00 | 0.35 | 0.00 | 0.22 | 1.06 | 0.17 | 0.07 |
| 4 | NS-5 | 2001 | 1.03 | 0.26 | 0.85 | 1.19 | 0.74 | 0.01 | 1.58 | 0.00 | 0.34 | 0.00 | 0.22 | 1.11 | 0.17 | 0.07 |
| 5 | NS-6 | 2007 | 1.09 | 0.26 | 0.86 | 1.15 | 0.75 | 0.01 | 1.66 | 0.00 | 0.34 | 0.00 | 0.23 | 1.15 | 0.17 | 0.07 |
| 6 | NS-7 | 1993 | 1.06 | 0.27 | 0.87 | 1.21 | 0.75 | 0.01 | 1.57 | 0.00 | 0.34 | 0.00 | 0.22 | 1.12 | 0.18 | 0.07 |
| 7 | NS-8 | 1991 | 1.04 | 0.27 | 0.88 | 1.27 | 0.74 | 0.01 | 1.62 | 0.00 | 0.33 | 0.00 | 0.22 | 1.15 | 0.16 | 0.07 |
| 8 | NS-9 | 1988 | 1.03 | 0.26 | 0.85 | 1.15 | 0.73 | 0.01 | 1.57 | 0.00 | 0.33 | 0.00 | 0.23 | 1.11 | 0.18 | 0.07 |
| 9 | NS-10 | 1987 | 1.07 | 0.27 | 0.86 | 1.20 | 0.72 | 0.01 | 1.50 | 0.00 | 0.33 | 0.00 | 0.23 | 1.14 | 0.17 | 0.07 |
| 10 | NS-12 | 2005 | 1.10 | 0.27 | 0.85 | 1.19 | 0.73 | 0.01 | 1.63 | 0.00 | 0.34 | 0.00 | 0.23 | 1.18 | 0.17 | 0.07 |

**Table 4 -**The results of mass chromatograms of steranes (m/ z 217) , for the studied crude oil samples

| | **Well No.** | **Depth (M)** | ***%$C_{27}$*** | ***%$C_{28}$*** | ***%$C_{29}$*** | **$C_{28}$/ $C_{29}$** | $C_{29}$20S/ R |
|---|---|---|---|---|---|---|---|
| 1 | NS-1 | 2016 | 33.13 | 24.80 | 42.08 | 0.58 | 0.60 |
| 2 | NS-3 | 2008 | 33.73 | 24.65 | 41.62 | 0.59 | 0.62 |
| 3 | NS-4 | 2002 | 34.24 | 24.22 | 41.54 | 0.58 | 0.57 |
| 4 | NS-5 | 2001 | 33.72 | 24.17 | 42.11 | 0.57 | 0.60 |
| 5 | NS-6 | 2007 | 33.71 | 23.64 | 42.65 | 0.55 | 0.64 |
| 6 | NS-7 | 1993 | 34.20 | 24.42 | 41.38 | 0.59 | 0.60 |
| 7 | NS-8 | 1991 | 33.53 | 24.94 | 41.53 | 0.60 | 0.61 |
| 8 | NS-9 | 1988 | 33.09 | 24.53 | 42.38 | 0.57 | 0.67 |
| 9 | NS-10 | 1987 | 33.39 | 24.40 | 42.20 | 0.57 | 0.60 |
| 10 | NS-12 | 2005 | 33.54 | 24.53 | 41.93 | 0.58 | 0.64 |

**Table5-** The Total Ion chromatogram (TIC) peak areas of Pr, Ph, $nC_{17}$and $nC_{18}$, and calculating parameters for the Mishrif crude samples.

| **Sample No.** | **Well No.** | **Depth (M)** | **Pr** | **Ph** | **$nC_{17}$** | **$nC_{18}$** | **Pr/Ph** | **Pr/$nC_{17}$** | **Ph/$nC_{18}$** | **CPI** | **OEP** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | NS-1 | 2016 | 2.13 | 2.79 | 11.08 | 9.51 | 0.76 | 0.19 | 0.29 | 0.932 | 0.91 |
| 2 | NS-3 | 2008 | 2.04 | 2.60 | 10.97 | 8.80 | 0.79 | 0.19 | 0.30 | 0.935 | 0.99 |
| 3 | NS-4 | 2002 | 2.21 | 2.78 | 10.83 | 9.27 | 0.80 | 0.20 | 0.30 | 0.996 | 0.95 |
| 4 | NS-5 | 2001 | 2.14 | 2.72 | 10.91 | 9.08 | 0.78 | 0.20 | 0.30 | 0.979 | 0.93 |
| 5 | NS-6 | 2007 | 2.14 | 2.65 | 10.88 | 8.99 | 0.81 | 0.20 | 0.29 | 0.943 | 1.02 |
| 6 | NS-7 | 1993 | 2.09 | 2.64 | 11.02 | 9.19 | 0.79 | 0.19 | 0.29 | 0.953 | 0.95 |
| 7 | NS-8 | 1991 | 2.14 | 2.70 | 11.23 | 9.49 | 0.79 | 0.19 | 0.28 | 0.980 | 0.97 |
| 8 | NS-9 | 1988 | 2.06 | 2.61 | 10.90 | 9.23 | 0.79 | 0.19 | 0.28 | 0.975 | 0.99 |
| 9 | NS-10 | 1987 | 2.00 | 2.59 | 11.09 | 9.17 | 0.77 | 0.18 | 0.28 | 0.957 | 0.97 |
| 10 | NS-12 | 2005 | 2.10 | 2.54 | 10.82 | 9.12 | 0.83 | 0.19 | 0.28 | 0.968 | 0.96 |

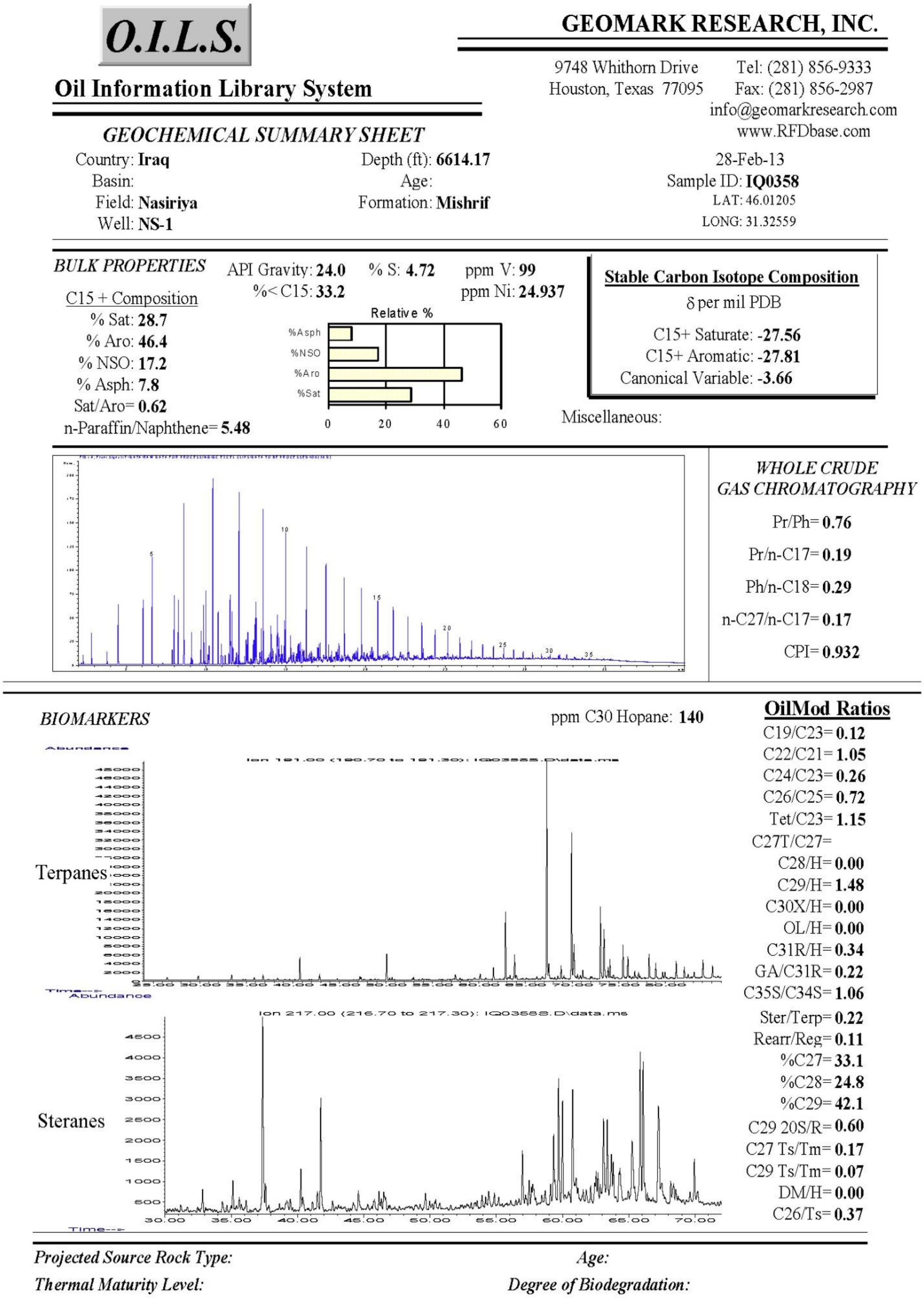


**Figure 2**- Geochemical summary sheet for Mishrif crude oil from NS-1.

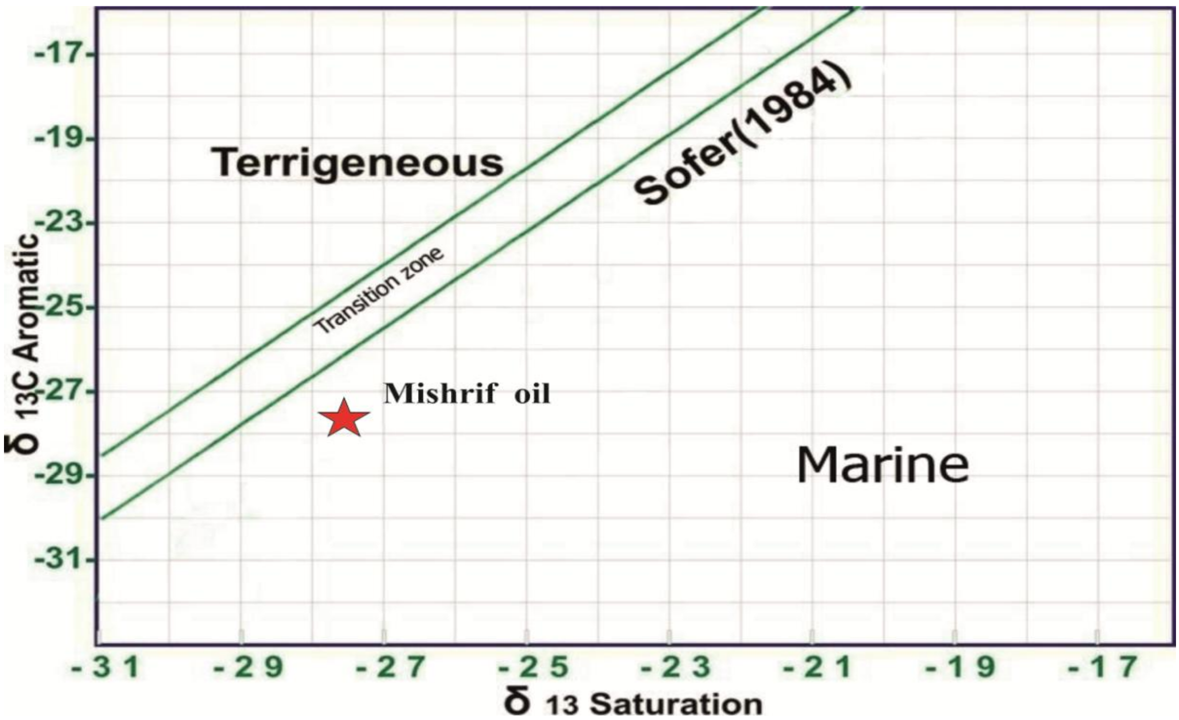


**Figure 3 -** Cross plot of Carbone-13 isotope ratios of saturate versus aromatic hydrocarbon of Mishrif oils (Sofer,1984).

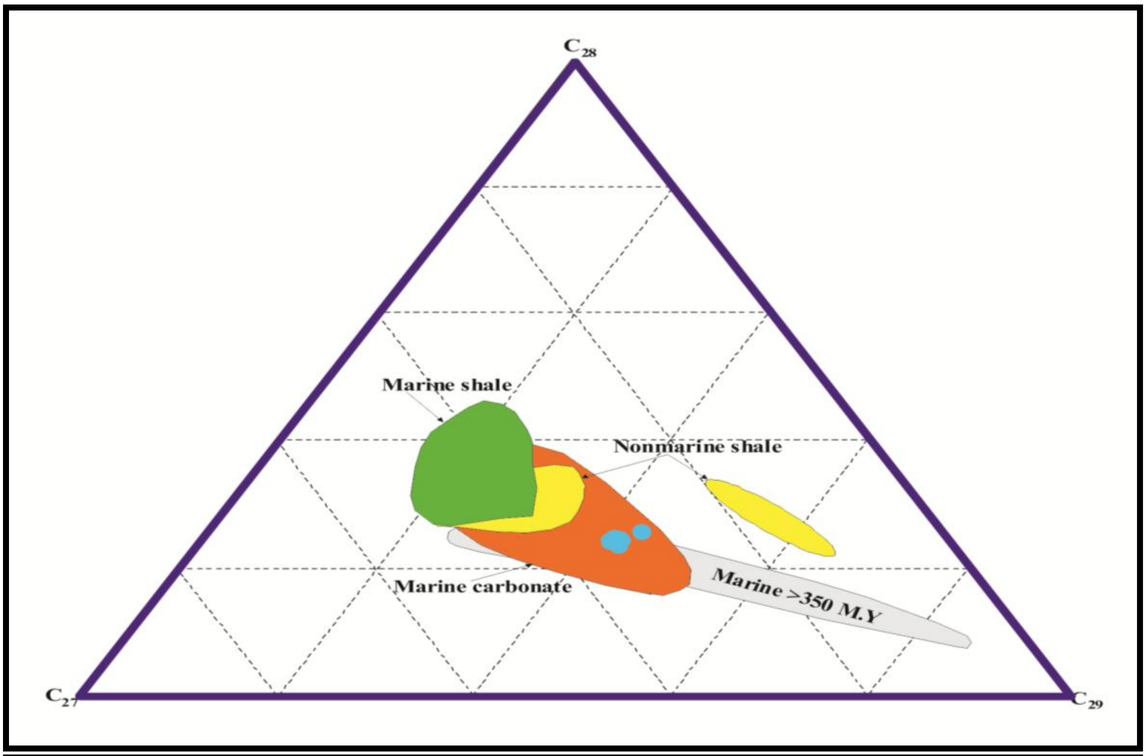


**Figure 4 -** Ternary diagram show relation between $C_{27}$-$C_{28}$-$C_{29}$steranes of Mishrif crude oil.

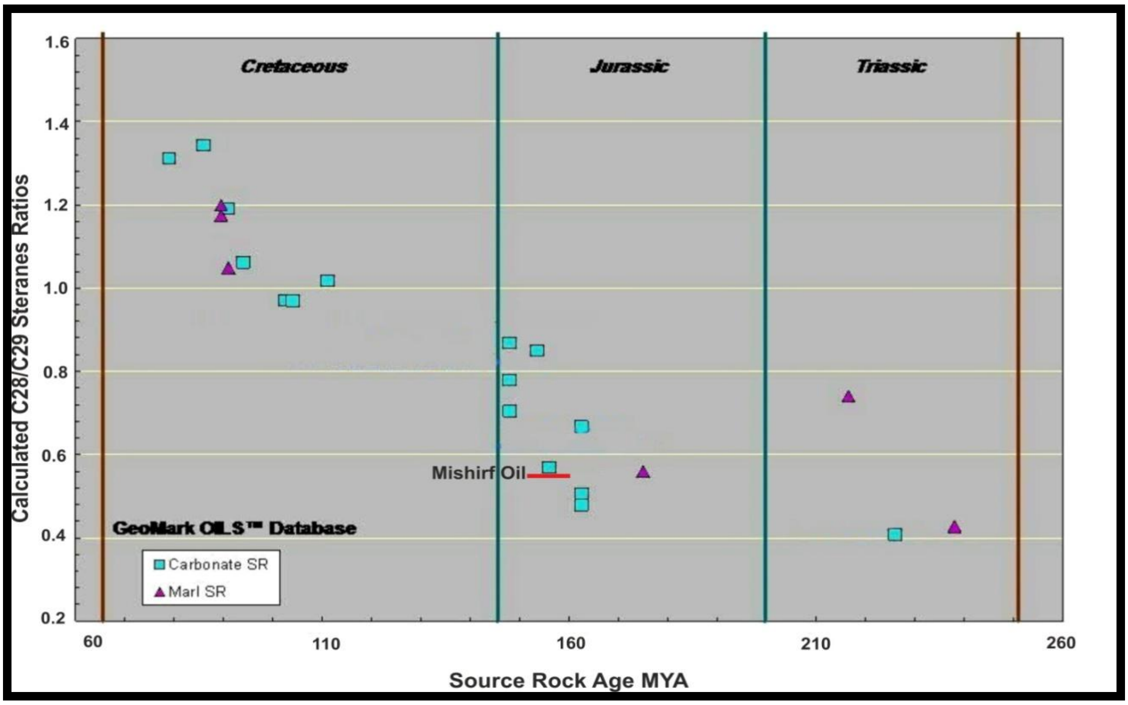


**Figure 5-** The $C_{28}/C_{29}$steranes ratios for 150 global petroleum system source rocks for different environments.

## Conclusion

The bulk properties of Mishrif crude oils in Nasiriyah oil field can be classified as a one group of oils , non-biodegraded, marine, non-waxy originated from organic matter deposited in marine anoxic environments. Biomarker compounds provide in formations, which explain that the Mishrif oils in the interesting area also represented as a one group generated from anoxic, non terrigenous, marine carbonate source rocks, from Jurassic rock, with similar level of thermal maturity ,Hence the most appropriate sources for this crude oil may be Sargelu Formation.

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