Ministry of Higher Education and Scientific Research Baghdad University College of Science Geology Department



## Affinity and Distribution of Crude Oil, Nasiriyah Oil Field

A Thesis Submitted to the council of the College of Science, University of Baghdad, in Partial Fulfillment of the Requirement for the Degree of Master in Geology

By Murtadha Doghiam Abdullah Al-Zaidi B.Sc. University of Baghdad, 1997

Supervised by Prof. Dr. Thamer Khazaal AL- Ameri

2013 A.D.

1434 A.H.



#### **Declaration**

This is certify that the dissertation / thesis titled:

Affinity and Distribution of Crude Oil, Nasiriyah oil field

Submitted: Murtadha Doghiam Abdullah Al-zaidi

Department: Geology

College: College of Science

Has been written my linguistic supervision its language, in its present form, is quite acceptable.

Name: Prof. Zuhair D. Al-Shaikh

Address: University of Baghdad Signature: Z. P. alfheit

#### The Supervisor Certification

I certify that this thesis entitled "Affinity and Distribution of Crude Oil, Nasiriyah Oil Field" has been prepared under my supervision at the Department of Geology, College of Science, University of Baghdad, in partial fulfillment of requirements for the degree of Master in Geology.

Thamer K. Al-Ameri Signature: Thamer Khazaal Al- Ameri Assist. Professor

College of Science

Department of Geology

University of Baghdad / / 2013

Name: Title: Address:

Date:

Recommendation of the head of the Department of Geology:

In view of the available recommendations, I forward this thesis for debate by the examining committee.

sh. Al-Banne

Signature: Name: Title: Address:

Ahmad Shehab Al- Banna Professor Department of Geology College of Science University of Baghdad / 2013 1

Date:

#### **Committee Certification**

We certify that we have read this thesis entitled "Affinity and **Distribution of Crude Oil, Nasiriyah Oil Field**" and as the examination committee examined the student in its content, and in our opinion it adequate for award of the degree of Master in Geology.

Signature: D. AL-raus Name: Dia'a Y. Al Rawi Title: Professor Address: Department of Earth Science College of Science University of Baghdad Date: / / 2014 (Chairman)

Signature: Nass

Name: Madhet A. Nasser Title: Assist. Professor Address: Department of Earth Science College of Science University of Baghdad Date: / / 2014 (Member)

Signature: Amer Althopy

Name: Amer J. Al- Khfaji Title: Assist. Professor Address: Department of Chemistry College of Science for women University of Babylon Date: / / 2014 (Member)

Signature: 7

Name: Thamer Khazaal Al- Ameri Title: Assist. Professor Address: Department of Earth Science College of Science University of Baghdad Date: / / 2014 (Member and supervisor)

#### Approved by the deanery of the College of Science:

Signature: Name: Dr. Saleh Mahdi Ali Title: Professor Address: The Dean of the College of Science, University of Baghdad Date: / / 2014

## Dedication

To the blessed spirits ... My Father, cousin (Raheem), and Daughter (Fatima) To tree of Merciful... My Mother To the spring of cordiality... My brothers and sisters To my love and supported... My darling wife To my flowers...

My children (Ali, Noor alhuda, Zaharaa, Tiba, Hussein)

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#### Abstract:

The Nasiriyah Oil Field is located in DhiQar Governorate, in southern Iraq, it lies east of the River Euphrates, and about 38 kilometers northwest of the Nasiriyah city. The field includes fourteenth (14) wells, all of these wells have attained the Mishrif Formation, while only five of these wells have attained the deep Yamama Formation(NS-1,2,3,4&5) and one well (NS-1) attained to the Sulaiy Formation.

Gas Chromatography GC, Gas Chromatography–Mass spectrometry GC/MS techniques used for analysis of the crude oil that taken from (10) producing wells (NS-1, NS-3, NS-4, NS-5, NS-6, NS-7, NS-8, NS-9, NS-10, and NS-12) from Mishrif reservoir. The analysis shows that all oil samples are from one family, non-biodegraded, marine, and non-waxy deposits, derived from carbonate source rocks deposited in anoxic marine environment.

Rock–Eval pyrolysis for twenty –nine samples were taken from NS-1 well of Yamama and Sulaiy Formations. These analyses include the determination of quantity and quality organic matter; indicated that the rocks of Sulaiy Formation had poor to good content of TOC(0.45-1.11)wt% with poor to fair potentiality and attained the immature to early stage of oil generation and expulsion with kerogen type II/III, while the TOC content for Yamama Formation (0.15-0.86)wt %, generally was fair for oil expulsion with poor generation potential and the maturity of this formation was between the immature to early stage. Facies analysis of Yamama Formation shows the presence of Distal suboxic – Anoxic basin Faceis. The results gathered from the pyrolysis and palynofaceis analysis show that the kerogen type of yamama Formation was type II/III.

Seismic section of the studied area shows presence of faults in the Jurassic formations reached to Gotnia Formation and fractures in the cretaceous formations, this may forms conditions for the generated oil to migrate upwards indicating that the most appropriate source rock is Sargelu Formation.

The log interpretations have been carried out using Interactive Petrophysics Program (IP) and show that the Mishrif Formation consists of mainly limestone with inclusion of dolomite and indicated that this formation is divided in to three units (MA, MB1and MB2),the MB1unit represents the principle oil-bearing unit in Nasiriyah oil Field in Mishrif Formation.

The log interpretations of Yamama Formation show that this formation consists of mainly limestone with lenses of differential compaction of sandstone, indicated that this formation is divided in to four units (YA, YB1, YB2 and YB3), theYB2 and YB3 units represent the principle oil-bearing units in Nasiriyah oil Field in Yamama Formation.

# CHAPTER ONE INTRODUCTION

#### CHAPTER ONE INTRODUCTION

#### 1.1. Preface

Iraq is a large, insufficiently explored petroliferous country with generally large structures and multiple hydrocarbon-bearing intervals in most structures. It is considered to be the only country in the Middle East where structurally controlled giant oil fields can still be found (Al- Khafaji, 2010). There are a number of new oil discoveries have been made utilizing basic requirement for exploration and development. The Nasiriyah field was explored by the Iraq National Oil Company (INOC) in 1975. Fourteenth exploration wells have been drilled within the oil-bearing area. Mishrif Formation is one of the important reservoirs in Al-Nasiriyah oil field, and it will be the main subject in the recent study, in order to provide information of crude oil analysis in this area, also its characterizations. The 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 (Jassim and Buday ,2005). The Mishrif Formation in central and southern Iraq is represented in many oil fields such as, Buzergan, Amara, Halfaya, Majnoon, Rumaila, Weast Qurna, and Nasiriyah.

#### 1.2 Aims of study

- 1. Geochemical correlation of oil-oil samples like terpane and sterane as well as stable carbon isotope values, to determine the geochemical relationship.
- 2. Source rocks evaluation and its relation to the oil and gas that charged the reservoir rocks of the Nasiriyah field in south Iraq to determine depositional environment of the Formations, and initial hydrocarbon potential.
- 3. Determination of palynofacies types via transmitted light microscopy.
- 4. Determination of reservoir characterization for Mishrif and Yamama Formations in order to locate the best accumulation places.

#### 1.3. Geographical location of the studied area :

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 which includes fourteenth (14) wells. The field is grouped within the Gharraf axis, which includes the undeveloped Gharraf and Rafidain fields. The studied area is about (578) kilometers square at the beginning of the exploration, whereas it is about (1273) Km<sup>2</sup> according to the last reports in oil exploration company(OEC)(Figure1-1).



Figure 1-1: Location map of study area after (OEC).

#### **1.4 Geological and Structural regional setting :**

Iraq lies in the border area between the Arabian part of the African (Nubio-Arabian) Platform and the Asian branches of the Alpine fore arc basin. The platform of Iraqi territory is divided into two basic units, the Stable and Unstable Shelves. The Stable Shelf is characterized by reduced thickness of sedimentary cover and by the lack of folding; the unstable Shelf has thick and folded sedimentary cover (Buday, 1980). Al-Nasiriyah oil field locates in unstable shelf close to Arab platform (Buday ,1980), exactly in the Euphrates sub zone (Mesopotamian zone) (Al-Naqib,1967) which characterized with monoclonal structures with variable extension from North-south to Northwest- 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 (Handel, 2006).

The studied area is not complicated structurally because the lithological column is not affected by strong structural movements as in the eastern areas of the country are affected by these movements during both periods (early Jurassic –Cenomanian) (Buday and Jassim, 1984).

#### 1.5 Stratigraphy and Equivalents of Mishrif Formation

The successful characterizing of carbonate reservoirs depends upon the sequence stratigraphic framework because it provides the constraining boundaries within which data is distributed away from wells into the inter well area (Kerans and Tinker, 1997). In addition, sequence stratigraphy provides a predictive approach to potential porosity occurrence, and considers some of diagenetic processes that affect porosity evolution in subsurface carbonate rocks, which some of them may related to the history of depositional sequences (Mazzullo, 1994).The Mishrif Formation (Cenomanian-Early Turonian) Formation represents heterogeneous а

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originally described as organic detrital limestones, capped by limonitic fresh water limestones (Bellen *etal.*,1959 in Aqrawi *etal.* 2010 ). The Mishrif Formation 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(Jassim and Goff,2006). The formation thins towards the W and NW, passing laterally into the Rumaila Formation , its thickness at the southern part of Iraq between (150-200)m , its thickness in the studied area between (150-180)m (Owen and Naser ,1958 in Aqrawi *etal.* 2010). The Mishrif succession indicates general shallow from open –shelf to fore-reef slope ,then reef flat and finally inner-shelf conditions (figure 1-2).

The formation is a carbonate sequence represented by rudist shallow open marine carbonates (Sadooni and Aqrawi, 2000). It was deposited as rudist shoals and patch reefs over growing subtle structural highs developing in an otherwise relatively deeper shelf on which open marine sediments of the Rumaila Formation were deposited. This formation is considered to be an overall progradational marine shelf sequence. Following the deposition of the transgressive shales and marly limestones of the Ahmadi and Rumaila Formations, rudist reefs and other related builds-up represented the deposition of the Mishrif Formation (figure1-3)( Sherwani, 1983). Jassim and Buday in (Jassim and Goff, 2006) divided Late Jurassic and Cretaceous units in Iraq into Late Tithonian-Early Turonian Megasequence (AP8)Late Turonian-Danian Megasequence (AP9) at ~92 Million years which correspond to that of Sharland *et al*., 2001.

#### 1) Late Tithonian-Early Turonian Megasequence (AP8)

This Megasequence is deposited in a large intra shelf basin contemporaneous with a new phase of opening of southern Neo–Tethys which has led to forming a new passive margin along the north east margin of the Arabian plate. Late Tithonian-Early Turonian Megasequence is divided as follows:

- A. Late Tithonian-Hauterivian sequence: This sequence includes Sulaiy, Yamama, and Ratawi Formations.
- B. Barremian-Aptian sequence: The Barremian-Aptian sequence comprises from Zubair and Shuaiba Formations.
- C. The Albian sequence: includes Nahr Umr and Mauddud Formations.
- D. The Cenomanian-Early Turonian sequence: This sequence comprises from Ahmadi, Rumaila and Mishrif Formations.

#### 2) Late Turonian-Danian sequence Megasequence (AP9):

The Late Turonian–Danian Megasequence is most widespread megasequence in Iraq. It is locally more than 2000 m thick in a North west – South east foredeep basin formed due to Late Cretaceous-Early Maastrichtian thrusting and ophiolite obduction along the southern Neotethys suture zone. Longitude and transversal structural features affected this megasequence. The megasequence (AP9) is divided into:

- A. Late Turonian-Early Campanian sequence: Which include Khasib, Tanuma and Sadi Formations.
- B. Late Campanian Maastrichtian Sequence: This sequence includes Hartha ,Tayarat and Shiranish Formations .

The equivalent formations of the Mishrif Formation are Gir-bir Formation in the North and the Balambo Formation of the deeper eastern and intra basin part of the same basin of the Dokan Formation (Jassim and Buday ,2005 in Aqrawi *etal.*, 2010). The Wasia Group in Saudi Arabia is the time equivalent to the Mishrif (Cenomanian part) because of the same assemblages of foraminifera. In the southeastern Iran, the same fossil assemblage has been recorded in the upper part of the Sarvak Formation (Al-Sharhan&Nairn, 1988) and the Natih Formation in Oman (VanBuchem *etal.*, 2002).

BASIN	LOWER SLOPE	UPPER SLOPE	SHELF Margin	LAGOON	SHORE- ZONE COMPLEX	s
Very Wide Bell		ETTER A STATE		Very Wide Facies Belts		PROFILE
Very line-grained carbonate, siliciclastic turbidites associated with basin floor tans Shaley, chert bearing thin bedded limestones Cemented mounds with exotic methanogenetic faunas associated with gas seeps Chalks and bedded cherts	Coarse-line grained carbonate and siliciclastic turbidites Uniform tine bedded mudstone units Large-scale low relief channel cut-outs	Mega-breccia debris flows Algal mounds Thin bedded wackestones to mudstones Coarse-grained carbonate and siliciclastic turbidites Coarse-grained packstone submarine channel fills	Framework reefs including patch, tringing and barrier Submarine mobile sand flats Grainstone islands Biohermal mounds on the interior margin	Tidal flats associated with islands and on lagoon margins Patch reets Grainstone wash-over tans along outer lagoon margin Thick lagoon-wide subaqueous evaporites Widespread restricted, burrowed tossiliterous pellet packstone to wackestones units Collumnar stromatolites on the lagoon margins	Low energy tidal flats, sabkhas wi siliciclastics, evaporites, dolomites Tee Pee structures Low relief stromatolites and tidal channels Beaches spit- channel com- plexes along the margin	FACIES COMPONENTS

Figure 1-2: Mishrif Reservoir – Depositional environment in Al-Nasiriyah

field (Repsol,2004).



Figure 1-3: Stratigraphy Section of Nasiriyah Oil Field in NS-1(OEC).

#### 1.6. Field work and data collection

Ten oil samples were taken from ten oil producing wells, (Table 1-1).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 in order to correlate it with previous studies related with crude oil analysis of surrounding area, also predict age, environment, and lithology of source rock.

Well Name	Longitude	Latitude	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 <sup>°</sup> 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 <sup>°</sup> 55 '46.955"	31° 20′17.552″	2005

Table 1-1: Oil samples from Nasiriyah oil field

Thirty-one (31) rock core samples are analyzed in Oil Exploration Company (OEC.), to quantify the total organic carbon (TOC%) of potential source rocks and determine the different organic geochemical parameters of these rocks by "Rock-Eval Pyrolysis Technique". Samples were collected from possible source rocks at different depths in NS-1 well (Table 1-2).

#### Table 1-2: Geochemical data for rock samples

Sample NO.	Formation	Depth (M)
1	Yammama	3229
2	Yammama	3236
3	Yammama	3266
4	Yammama	3274
5	Yammama	3279
6	Yammama	3320
7	Yammama	3351
8	Sulaiy	3443
9	Sulaiy	3450
10	Sulaiy	3455
11	Sulaiy	3461
12	Sulaiy	3469
13	Sulaiy	3478
14	Sulaiy	3484
15	Sulaiy	3491
16	Sulaiy	3498
17	Sulaiy	3504
18	Sulaiy	3509
19	Sulaiy	3524
20	Sulaiy	3544
21	Sulaiy	3556
22	Sulaiy	3564
23	Sulaiy	3569
24	Sulaiy	3575
25	Sulaiy	3578
26	Sulaiy	3583
27	Sulaiy	3588
28	Sulaiy	3592
29	Sulaiy	3595
30	Sulaiy	3606
31	Sulaiy	3612

The palynological analysis applied to different core samples of the formation and source rocks were performed by published standard methods (Table 1-3).

Table1-3:The Palynological analyses performed in the laboratories of t	he
Geology Department .	

Sample . No.	Formation	Sample Type	WellNo.	Depth(m.)
1	Yammama	core	NS-1	3385
2	Yammama	core	NS-1	3285.2
3	Yammama	core	NS-1	3378.2
4	Yammama	core	NS-1	3228.4
5	Yammama	core	NS-2	3371.1
6	Yammama	core	NS-2	3346.5
7	Yammama	core	NS-2	3186.2
8	Yammama	core	NS-2	3277.55
9	Yammama	core	NS-3	3366.8
10	Yammama	core	NS-3	3291
11	Yammama	core	NS-3	3404.6
12	Yammama	core	NS-3	3210.7
13	Yammama	core	NS-5	3196.6
14	Yammama	core	NS-5	3291.3
15	Yammama	core	NS-5	3378.4
16	Yammama	core	NS-5	3303.55

Four core samples from one well from Mishrif Formation and sixteen core samples from Yammama Formation were available (Table 1-4), A thin section for these samples are made in order to determine porosity type.

Sample NO.	Well name	Formation	Depth(M).
1	NS-1	Mishrif	2024.3
2	NS-1	Mishrif	2033.5
3	NS-1	Mishrif	2047.8
4	NS-1	Mishrif	2084.5
5	NS-1	Yammama	3238
6	NS-1	Yammama	3263.7
7	NS-1	Yammama	3285.2
8	NS-1	Yammama	3358.3
9	NS-2	Yammama	3249.9
10	NS-2	Yammama	3342.7
11	NS-2	Yammama	3331.5
12	NS-2	Yammama	3361.5
13	NS-3	Yammama	3219.7
14	NS-3	Yammama	3262
15	NS-3	Yammama	3317.5
16	NS-3	Yammama	3382.5
17	NS-5	Yammama	3175.6
18	NS-5	Yammama	3255.4
19	NS-5	Yammama	3276.7
20	NS-5	Yammama	3371.5

#### Table1-4: Core samples taken from Nasiriyah oil field.

A wireline log data for fourteenth wells from Mishrif Formation and five wells from Yamama Formation is also available (Table 1-5), well log data will be interpretive using computer software to determine porosity, lithology, saturation of fluids, and type of fluid in the reservoir.

Log No. Well Name		Formation	Locality	
Log Ito.	Wen Plane		Latitude	Longitude
1	NS-1	Yamama, Mishrif	31° 19′32.159″	46°0 ′43.383″
2	NS-2	Yamama, Mishrif	31° 34′38.19″	45°0 '96.9966"
3	NS-3	Yamama, Mishrif	31° 20′12.05″	46°2 '21.734"
4	NS-4	Yamama, Mishrif	31° 19′56.919″	45 <sup>°</sup> 55 '33.887"
5	NS-5	Yamama, Mishrif	31°22 '19.975"	45 <sup>°</sup> 52 '4.805"
6	NS-6	Mishrif	31° 19'45.227"	45 <sup>°</sup> 57 '14.989"
7	NS-7	Mishrif	31° 21′18.076″	45 <sup>°</sup> 56 '8.275"
8	NS-8	Mishrif	31° 21′33.207″	45 <sup>°</sup> 59 '7.783"
9	NS-9	Mishrif	31° 21′49.713″	45°57 '56.943"
10	NS-10	Mishrif	31° 22′6.22″	45°58 '1.07"
11	NS-11	Mishrif	31° 34′67.86″	45°95 '93.58"
12	NS-12	Mishrif	31° 20′17.552″	45°55 '46.955"
13	NS-13	Mishrif	31° 34′138.0″	45°97 ′99.06″
14	NS-14	Mishrif	31° 36'73.31"	45 <sup>°</sup> 88 '89.91"

Table 1-5: The studied wells with log data available.

#### **1.7. Previous Studies:**

The description of Mishrif Formation for the first time was given by Rabanit(1952)in well Zubair-3 from the upper part of what was previously called Khatiyah Formation, which was divided later on into three separated Formations, i.e. Ahmadi ,Rumaila and Mishrif Formation .The Formation was studied by Smout 1956 and Fox 1957. Owen and Naser (1958) described the lithological cross-section of this formation in well Zubair-3; they considered it as a typical section. During recent years, many petroleum geochemistry studies were published and the following studies are selected according to their concept in this study:

 Al-Khersan(1973) believed that Mishrif Formation was deposited within five marine environments ; they are intertidal , littorial , banks margins , banks and open sea environments .

- 2. AL-Sharhan,(1997) studied the sedimentary basin and *petroleum geology* of Iraq.
- 3. Jafar (2001) used the models of burial history for the sediments and rates of sedimentary and tectonic subsidence influencing the area of West Qurna, Zubair, North and South Rumaila, and Luhais oil fields in addition to geochemical evaluation of Mishrif and Zubair Formations. He was referred that the tectonic subsidence is more than the sedimentary subsidence towards the east and decreases towards the west.
- 4. Pitman *etal.*,(2004) developed 3-D total *petroleum* system model and evaluated *petroleum* generation and migration histories in the Mesopotamian basin and Zagros fold belt in Iraq, their model indicate that at present the majority of Jurassic source rocks in Iraq have reached or exceeded peak oil generation and most rocks have completed oil generation and expulsion.
- 5. Handel,(2006) studied the reservoir properties of Mishrif Formation in Nasiriyah field and its Relationship with oil production ,she found that the Formation is subdivided into two main lithological units separated by impermeable unit depending on self-potential and Gamma ray logs. Lower lithological unit is also subdivided into two reservoir units separating by barrier rocks, and the Mishrif Formation contains different quantities of water, residual oil, and mobile oil hydrocarbon.
- 6. Al-Yaseri ,(2007) indicates that the organic facies in the Uppermost Jurassic (Gotnia Formation) and late Cretaceous (Sulaiy, Yamama, Ratawi, Zubair, and Shuaiba Formations) of Southern Iraq are investigated as potential for oils. According to bulk parameters and isotopic results as well as molecular parameters, he also suggested that Mishrif crude oil is least mature, while Nahr Umr and Zubair crude oils are most mature; these oils of Cretaceous reservoirs are derived from a very similar source with
the exception of Nahr Umr oils which have a different source in south Iraq basin.

- 7. Al-Ameri *etal.*,(2009) used biomarkers and carbon isotopes in correlation between Mishrif crude oil and possible source rocks in southern Iraq. He concludes that most of the crude oil accumulated in the Mishrif Formation in Ratawi, north and south Rumaila oil fields are from Jurassic source rocks suchas Naokelekan and Sargelu Formations, and the rest of the oil is from Sulaiy Formation.
- 8. Al-Dulaimy,(2010) studied the biostratigraphy of Mishrif Formation in Amara field and considered its age to be of Cenomanian-Early Turonian.
- 9. Al- Khafaji,(2010) studied large total Jurassic Sargelu/Najmah–Cretaceous Zubair/NahrUmr /Zubair/Hartha Petroleum system are associated with Widyan Basin-Interior Platform and Mesopotamian For deep Basin in the Middle and Western Iraq. He refers that the TPS have traps that formed on reactivated basement fault blocks with a component drape resulting in elongated and broad anticline structures .Trap growth took place through most of the Mesozoic, although Late Cretaceous and Miocene to recent are the principal periods of growth.
- 10.Al-Ismaily, (2011) Study of reservoir properties of Yamama Formation in Nasiriyah field and its relationship with oil production.
- 11.Jafar,M.S.A.(2010) studied the hydrocarbon sources and oil accumulations in Cenomanian-early Turonian Mishrif formation reservoirs in selected fields southern.

# CHAPTER TWO CRUDE OIL CHARACTERIZATION

# CHAPTER TWO CRUDE OIL CHARACTERIZATION

# **2.1 Preface:**

*Petroleum* is a form of bitumen composed principally of hydrocarbons and existing in the gaseous or liquid state in its natural reservoir. The word *petroleum* originates from Latin *petra*(rock) and *oleum*(oil), oil, or crude oil, sometimes colloquially called black gold, is a thick, dark brown or greenish flammable liquid, which exists in the upper strata of some areas of the Earth's crust .The main forms of petroleum are natural gas which does not condense at standard temperature and pressure (STP = 760 mm Hg or 101k Pa , 60° F or 15.6  $^{\circ}$ C, condensate, which is gaseous in the ground but condenses at the surface, and crude oil, the liquid part of the petroleum (Hunt, 1996). Crude oils are complex mixtures of organic compounds covering a wide range of polarity, molecular weight, size, shape, solubility, and elemental composition (Hunt, 1996; Tissot and Welte, 1984). Oil is a complex mixture containing a large number of closely related compounds (Tissot and Welte, 1984). The compounds present and their relative amounts are controlled initially by the nature of the organic matter in the source rock. The fact that, variations in crude oil composition are to a certain extent inherited from different source rocks. For instance, coaly material in general yields more gaseous compounds, while high-wax crude oils are commonly associated with source material containing high proportions of lipids of terrestrial higher plants and of microbial organisms (Hunt, 1996). Crude oils as well as bitumen extracts from source rocks are divided into fractions corresponding to the main structural types. Specific compounds within each structural group can be obtained by gas chromatography and mass spectrometry. Hydrocarbons contain only organic carbon and hydrogen. Alkanes are non-cyclic compounds that contain carbons and hydrogen. Cycloalkanes are cyclic

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compounds that contain carbons and hydrogen .High- sulfur crude oils frequently related to carbonate-type source rock. A side from the influence of source rock facies, the state of maturity of the source material is also of importance. The processes of crude oil alteration (thermal alteration, deasphalting, biodegradation and water washing) tend to obscure the original character of the oil, and therefore affects crude oil correlation, furthermore influence the quality and economic value of petroleum (Tissot and Welte, 1984). Therefore, the carefully studying of the chemical compositions of the rock extracts, seeps and produced oil can minimize the risk associated with finding petroleum accumulations. Consequently, the present study throw more light on the composition, classification and the geochemical characterization of crude oil samples, through several routine and advanced geochemical analyses from productive fields within the study area. Crude oil samples were taken from (10) producing wells from Mishrif Formation in Nasiriyah oil field , these samples were analyzed by using Gas chromatography /Mass spectrum (GC/MS) in Geomark laboratories / USA.

# 2.2. Classification of crude oils

The geologists and geochemists are more interested in identifying and characterizing the crude oils, to relate them to source rocks and to measure their grade of evolution. Therefore, they rely on the chemical and structural information of crude oil constituents, especially on molecules which are supposed to convey genetic information. A well-known used classification of crude oils based on distillation and specific gravities of two key fractions of distillation. Other classifications have been proposed based on refractive index, density and molecular weight. The newly proposed classification is based on the content of the various structural types in crude oils (alkanes ,cycloalkanes, aromatics) plus NSO compounds (resins and asphaltenes) and the distribution of the molecules within each type. It also takes into account the sulfur content (Tissot and Welte, 1984). According to Tissot and Welte (1984), the main classes of crude oils are:

- a. Paraffinic class: crude oils will be considered as paraffinic, if the total content of saturated hydrocarbons is over 50% of a particular crude oil, paraffins content is more than 40%, naphthenes is less than 50%. The amount of asphaltenes plus resins is below 10%, and sulfur content is less than 1%.
- b. Paraffinic naphthenic class: the class paraffinic naphthenic oils has a moderate resins plus asphaltenes content (usually 5 to 15%) and a low sulfur content (0 to 1%). Aromatics amount to 25 to 40% of the hydrocarbons.
- c. Naphthenic class: the naphthenic oil includes mainly degraded oils, they originate from biochemical alteration of paraffinic naphthenic oils and usually have more than 40% naphthenes and they usually have a low sulfur content (below 1% although they are degraded).
- d. Aromatic intermediate class: is comprised of crude oils which are often heavy. Resins and asphaltenes amount 10 - 30 % and sometimes more, and the sulfur content is above 1%. This oil class the aromatics amount to 40 - 70 %.
- e. Aromatic naphthenic and aromatic asphaltic class: are mostly represented by altered crude oils. Therefore, most aromatic naphthenic and aromatic asphaltic oils are heavy, viscous oil resulting originally from degradation of paraffinic naphthenic, or aromatic intermediate oils.

The resin plus asphaltene content is usually above 25% and may reach60%. However, the relative content of resins and asphaltenes, and the amount of sulfur, may vary according to the type of the original crude oils. This type can be subdivided into:

- Aromatic naphthenic class: is mainly derived from paraffinic or paraffinic naphthenic oils. The resins to asphaltenes ratio of 2% or more, with a sulfur content below 1%.
- Aromatic asphaltic class: includes a few true aromatic oils, apparently non-degraded. However, it is mainly comprise of heavy, viscous, or even solid oils, resulting from alteration of aromatic – intermediate (particularly high sulfur) crude oils.

# 2.3. Crude oil geochemistry

Adequate sampling of crude oils is essential for their characterization. According to Tissot and Welte (1984), the common methods for geochemical characterization of crude oils are the measurement:

# 2.3.1.Bulk properties:

- 1. API gravity.
- 2. Sulfur content.
- 3. Crude oil compositions.
- 4. Stable carbon isotope compositions ( $\delta$  13C ‰).

The results of the routine bulk properties for oil samples are summarized in (Table2-1).

#### 2.3.2.Biomarkers.

#### **2.3.1.1.** API gravity

API gravity is a bulk physical property of oils that can be used as a crude indicator of thermal maturity. It is a scale of the American Petroleum Institute that related inversely to the density of liquid petroleum (Murchison, 1987), and is a measure of how heavy or light petroleum liquid is compared to water (a measure of the density or specific gravity of crude oils). Its report in degrees (°API). According to Waples (1985), the API gravity could be calculated as the following equation: API = (141/Specific gravity) – 131.5

During thermal maturation, the heavy components in oil, NSO compounds, asphaltenes, and heavy saturated and aromatic compounds undergo increased cracking, resulting in increased API gravity, however API gravity is also affected by other factors, including original organic input, biodegradation, water washing and inspissation (Peter *etal.*, 2005 a). Most normal oils have API gravities from 20° to 45°, and are designated as medium (25° -35° API) to light oils (32° -45 °API). Heavy oils that have API gravities less than 20 are usually biodegraded, while condensate has gravities above 45° API (Repsol, 2007). API gravity of Mishrif crude oil in the studied area is ranging from (23° -26.2°API) (Figure2-1), it is considered as medium oil.



Figure 2-1: API gravity of Mishrif crude oil in Nasiriyah oil field.

#### 2.3.1.2. Sulfur content

Sulfur content is a bulk parameter commonly used to evaluate the economics of refinery operations to support inferred genetic relationship among crude oils (Peter *etal.*, 2005 a).Except for very waxy crudes and condensates, most crude oils contain some sulfur compounds. A few organic sulfur compounds in crude oils may be formed in the organisms for example

sulfur bacteria contain 5 to 8% sulfur and brown, red algae contain 0.7, (0.1% to more than 0.3%) respectively. However, the greater quantities of sulfur compounds and their structural diversity in crude oils compared with the biomass rule out organisms as an important direct source (Hunt, 1996). There is inverse relationship between sulfur content and maturity, where the sulfur content decreases with increasing maturity (Tissot and Welte, 1984). This conclusion was confirmed by Waples (1985) who considered the sulfur content as a maturity influenced parameter. In particular, the sulfur content is not specifically related to the heaviest fractions of crude oils, as is the case for nitrogen. Tissot and Welte(1984) suggested that, oils with low sulfur content less than unity classified as paraffinic, paraffinic – naphthenic or naphthenic classes, while oils of high sulfur (more than unity) belong to the aromatic intermediate class.

The sulfur content can be used as a source indicator, as oils of marine origin has more than 0.5% sulfur content, the high sulfur content is derived from carbonate source rocks, on the other hand oils derived from clastic source rock are typically low in sulfur(Moldwan *etal.*, 1984 in Peter *etal.*, 1984). Mishrif Formation in Nasiriyah oil field characterized by high sulfur content ranging from 3.67% to 4.72% (Figure2-2), hence indicated marine depositional environment of the source.



Figure 2-2: Sulfur content of Mishrif crude oil in Nasiriyah oil field

### 2.3.1.3. Composition of crude oils

From a chemical point of view the organic compound of *petroleum* is subdivided into:

Hydrocarbons: hydrocarbons are compounds containing only carbon and hydrogen. They are subdivided into:

**Light Hydrocarbons** ( $\% < C^{15}$ ): Light hydrocarbons are gases that are volatile liquids at standard temperature and pressure and range from methane to octane, including normal, iso-, cyclic alkanes, and aromatic compounds. Light hydrocarbons (C<sub>4</sub>–C<sub>9</sub>) are not biomarkers because their carbon skeletons are too small to preserve evidence of a unique biological origin. It may refer to hydrocarbons ranging from C<sub>1</sub> to approximately C<sub>15</sub>, depending on context. The abundance of light hydrocarbons in crude oils is considered as a significant portion of most crude oils. In unaltered oils, the amounts of light hydrocarbons correlate with thermal maturity. Low-maturity, early-expelled oils may have less than 15%, typical mid-oil window marine oils

have approximately 25% to 40% as in these studied samples, and highmaturity condensates may be nearly 100% light hydrocarbons.

#### Saturated Hydrocarbons:

Compounds saturated with respect to hydrogen could contain only single carbon-carbon bounds these are:

- Normal- paraffins (normal alkanes) are straight chains of various lengths.
- Branched paraffins (branched alkanes) are saturated hydrocarbons whose carbon atoms form branched chains.
- Cyclic paraffin's (Cyclicalkanes; Napthenes) are cyclic saturated compounds like the steranes and triterpanes.

#### Aromatic Hydrocarbons:

Aromatic hydrocarbons are unsaturated compounds that have at least one benzene ring, a flat six-carbon ring in which the fourth bond of each carbon atom is shared throughout the ring. They can have saturated side chains of various sizes.



#### **Resins and Asphaltenes:**

Resins and Asphaltenes Compounds: are not discrete compounds but high -molecular -weight heteroaromatic molecules that are poorly defined. The difference between Resins and Asphaltenes is defined by their relative solubility in hydrocarbons, which roughly corresponds to size. Asphaltenes precipitate from crude oil when a large quantity of low molecular weight alkanes is added (e.g. n- pentane ), while resins (polars) remain in solution (Peter *etal.*, 2005). NSO Compounds (resins) molecules are usually with less than 40 carbon atoms. Asphaltenes are not soluble complex molecules with more than 40 carbon atoms. The amounts of asphaltenes plus resins generally less than 10% in paraffinic oils and less than 20% in paraffinic -naphthenic oils; they may reach 10 to 40% in aromatic-intermediate oils. Among them, asphaltenes amount only 0 to 20% of those normal, non-degraded oils (Tissot and Welte, 1984). The Mishrif crude oil is mainly aromatic (Figure2-3), where saturated hydrocarbon percentage is ranging from 27.4% to 29.7%, while aromatic is ranging from 45.9%- 48.1%, and NSO and resin compound is between 22.7%-25.8% (Table 2-1), and by plotting these data on ternary hydrocarbon plot of Aromatic HC, Saturated HC, and NSO compounds could assess a normal crude oil for Mishrif with no degradation with abundant aromatic compounds (figure2-3).

#### • Organometallic Compounds (Nickel and Vanadium):

Concentrations and ratios of Nickel / Vanadium can be used to classify and correlate crude oils, these metals exist in *petroleum* largely as porphyrin complexes. Oils from marine carbonates or siliciclastics show low wax content, moderate to high sulfur, high concentrations of Nickel and Vanadium, and low Nickel / Vanadium ( $\leq 1$ ) ratios.

Dominance of Vanadium over Nickel in these oils is caused by the greater relative stability of vanadyl porphyrins under low redox potential (Eh) conditions associated with sulfate reduction during diagensis of marine source rocks.

Oils from lacustrine source rocks show high wax, low sulfur, moderate quantities of metals and high Nickel / Vanadium (>2).

Non –marine oils are derived from higher- plant organic matter show high wax ,low sulfur and very low metals .N/V ratios for Mishrif crude oil ranged from (0.21 -0.25) which referred to marine carbonate source rock( Peter *etal.*, 2005).

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Figure2-3: Ternary plot shows the composition of Mishrif crude oil in Nasiriyah oil field

# 2.3.1.4. Stable carbon isotope composition (δ13C ‰)

Nearly all the mass of atoms is in the dense nucleus as protons with a positive electrical charge of +1and as neutrons that are electrically neutral. The protons are balanced by an equal number of electrons with charges of -1, obtaining around the nucleus. The number of protons is unique to each element and is called the atomic number. The sum of the masses of protons and neutrons is the atomic weight. Protons and neutrons have the same mass (Hunt, 1996).

Atoms whose nuclei contain the same number of protons but different numbers of neutrons are called isotopes. All Carbon atoms have 6 protons but there are 3 carbon isotopes containing 6,7 and 8 neutrons, giving them atomic masses, respectively, is the dominant element in *petroleum* and because more is known about it due to the relative ease of its analysis by bulk and compound-specific methods. Carbon-12 ( $C^{13}$ -depleted) and carbon-13 ( $C^{13}$ -

enriched) are stable isotopes and account for approximately 98.99 and 1.11 wt.% of all carbon, respectively. Stable isotope data are presented as delta ( $\delta$ ) values representing the deviation in parts per thousand (‰, per ml, or ppt), the value of ( $\delta^{13}$ C‰)can be obtained from the following equation:

 $\delta^{13}C$  (%)=[( $^{13}C/^{12}C_{sample} - ^{13}C/^{12}C_{standard})/^{13}C/^{12}C_{standard}$ ] x 1000

A positive value means the sample is riched in  ${}^{13}$ C isotope relative to the standard and it's called  ${}^{13}$ C-enriched, while the negative value means the sample is depleted in  ${}^{13}$ C isotope relative to the standard and it's called  ${}^{13}$ C-depleted (Peter *etal.*, 2005).

The geochemical significance and range of carbon isotopic composition of crude oil and crude oil fractions has been the subject of many studies, as an indicator of the depositional environment, and as a tool in oil-oil and oil–source correlations (Alexander *etal.*, 1981 and Sofer, 1984).

Degens (1969), has reported the results of 600 isotope analyses of a crude oil and showed that the average of those measurements is identical to the average composition of lipid fraction obtained from present – day marine planktons. He also added that the average carbon isotope composition of crude oils from various geologic ages changes from -30 ‰ for pre-Devonian oils to -27 ‰ for Pennsylvanian oils, then back to -31 ‰ for Tertiary oils. Andrusevich *etal.*, (1998) compared stable carbon isotope compositions of the saturated and aromatic hydrocarbon fractions from 514 crude oils representing 13 age divisions from Paleozoic to Neogene (Figure2-4).The average of stable carbon isotope ratio for Mishrif oil is -27.7%, that suggested the age of source rock lies between Jurassic to Paleocene, however the reservoir is Upper Cretaceous so the source age according to this relation is Jurassic to Lower Cretaceous.

Sofer (1984) suggested that the isotope composition of oils could change owing to maturation and possibly migration effects and due to minor inhomogeneities in the source material. He also recognized that, the isotope

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composition of oil fractions (saturates and aromatics), excluding the biodegraded oils, by a mathematical relation known as canonical variable (CV). The relation between the canonical variable (CV) and the isotope composition of the saturate and aromatic hydrocarbons is given by the following equation (Sofer, 1984):

 $CV = -2.53 \delta$  13Csaturate + 2.22  $\delta$  13Caromatic - 11.65

The oil sample with a canonical variable (CV) value larger than 0.47 is classified as waxy (terrigenous) oil and the sample with a canonical variable(CV) less than 0.47 is classified as non – waxy (marine) oil. However, this value (0.47) is arbitrary in a way, because it is obtained mostly from statistical considerations and very little from geochemical consideration (Sofer, 1984).

Hence, the classification based on the canonical variable (CV)have to be correlated and supported by other geochemical parameters such as *n*-alkane distribution ,Pristane / Phytane ratios show some kind of correlation with the canonical variable (CV). Sofer (1984) suggested that, terrigenous oils with high Pristane / Phytane ratio (> 1.0) are usually associated with high values of CV, and marine oils with low Pristane / Phytane ratio (< 1.0) are associated with low Pristane / Phytane ratio (< 1.0) are associated with low Pristane / Phytane ratio (< 1.0) are usually associated with low Pristane / Phytane ratio (< 1.0) are associated with low the comparison of CV. However, many terrigenous oils show low Pristane / Phytane ratios and marine oils show high Pristane / Phytane ratios, this is due to the effect of maturity (Sofer, 1984).

Table 2-1 shows that there is no variation among the carbon isotopes of the oil fractions of the ten crude oil samples, indicating that, these samples are isotopically similar and genetically related.

The carbon isotope value of saturate fraction ranges from -27.48 to -27.64 ‰ and for aromatic fraction ranges from -27.81 to -27.90 ‰, suggesting a marine oil samples (Denison *etal.*, 1990; Hunt, 1970; Tissot and Welte, 1978 and Rogers, 1980). The calculated canonical variable (CV) values of the oil samples ranged from (-3.55 to -3.97) indicated non waxy oils

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derived from carbonate marine sources, as described by (Sofer, 1984) (Figure 2-5).

Zumberge (1993) used the relation between the carbon isotopes of the saturated fractions and those of aromatic to differentiate between marine and non-marine oils. It is obvious from figure 2-6 that, the oil samples within the study area are derived mainly from marine source rocks(Sofer,1984). Biomarkers (or geochemical fossils) are molecules inherited from the organisms living at the time of sediment deposition, which have preserved without subsequent alteration, or with only minor changes, so that they keep the main features of their chemical structures (Tissot and Welte, 1984).Stable isotope, composition and ratios of carbon are used in characterizing *petroleum*, including gases, crude oils, sediments and source-rock extracts, and kerogen. They are also used with biomarkers to determine genetic relationships among oils and bitumen.



Figure 2-4: Average of stable carbon isotope ratios of crude oil versus age.



Figure2-5: The relationship between the canonical variable (CV) and Pr/Ph ratios.



Figure2-6: Cross plot of Carbon-13 isotope ratios of saturate versus aromatic hydrocarbon of Mishrif oils (Sofer,1984).

**Chapter Two** 

# Table 2-1: Bulk properties, gross compositional parameters, and stable carbon isotope composition of Mishrif crude oil fraction for the studied samples

NO	Well Name	Depth	API	S%	<c<sub>15%</c<sub>	Ni	Vnnm	Liqui	id Chrom	atograp	Stable Carbon Isotopes			
		(M)	1 1 1	570		ppm	• ppm	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** 

### 2.3.1.5. Bulk Parameters Relationship:

The bulk properties results of Mishrif reservoir crude oils are summarized in Table 2-1.

- High sulfur content (3.67% to 4.72%) in all samples of Mishrif crude oils, associated with marine environment (Peter and Moldowan, 1993).
- API Gravity for all samples, ranged from (23-26.2°API), represented medium oils (Peter *etal.*, 2005). Variations in API gravity may be caused by different thermal maturities, whereas low in API mean less in thermal maturity (Peter *etal.*, 2005). Also crude oil becomes heavier and API gravity decreases as the percentage of aromatic and naphthenic hydrocarbons increasing relative to the paraffin's and as the percentage of NSO compounds increases (Hunt, 1996). The API gravity shows negative correlation with sulfur contents and the plot of the sulfur percentage against API gravity recognized the type of crude oils (Figure 2-7). While it shows positive correlation with the percentage of hydrocarbons < C<sub>15</sub> and the saturated-to-aromatic ratio (Hunt, 1996).
- Light hydrocarbons percentage (<  $C_{15}$ ) for all samples of the studied field, ranged from (33.2 -35.5), and when correlated with thermal maturity, they represented a typical mid-oil window marine oils(Peter *etal.*, 2005).
- The Nickel / Vanadium ratios for all studied samples ranged between(0.21-0.25) which indicated marine environment(Peter *etal.*, 2005).
- A plot of the carbon-isotope values of aromatic versus saturated fractions of the Mishrif crude oils is shown in Figure (2-6). These plots can be used to distinguish oil families and to infer a marine (non-waxy) versus a terrestrial (waxy) sourced by Sofer (1984). And by depending on the relationship between the average of the stable isotope ratios for Mishrif oil versus age ,suggested that the age of the source rock lies between Jurassic to lower Cretaceous .The Pr/Ph ratios for the same samples ranged from

(0.76-0.83) and the low CV values that ranged from (-3.55 to -3.97), correlation of these two parameters is indicated carbonate marine environment (Figure 2-5).





#### Gas Chromatography – Mass Spectrometry

It is the principle method to evaluate the biomarkers, Atypical GC/MS system performs several functions including : compound separation by gas chromatography, transfer of separated compounds to the ionizing chamber of the mass spectrometer, Ionization, Mass analysis, detection of the ions by the electron multiplier and acquisition, processing and display by computer (Peter, 1996). The GC technique is used to analyze the whole crude oil to obtain the normal alkane and acyclic isoprenoids, whereas mass spectrometry is a method used to supply information on the molecular structure of compounds, particularly biomarker. MS technique is used to analyze the terpanes and sterans. GC/MS analysis for Mishrif crude oil were done in Geomark lab /USA.

#### 2.3.2. Biomarkers:

Biomarkers are molecular fossils , meaning that these compounds originated form formerly living organisms . Biomarkers are complex organic compounds composed of carbon , hydrogen and other elements ( Peter *etal.* , 2005). Biomarker compounds are identified from total ion chromatograms (TIC) and are typically measured by using selected ion monitoring (SIM/ GCMS), and their distribution calculated using areas under the peaks (Peter *etal.* , 2005).

In order to diagnose biomarkers in the formed oil, they should be present at high concentrations as the original organism and they must be constant to resist diagenetic process and regressions that are formed oil. Some of them have high concentrations, but they are destroyed during diagenetic operations such as proteins, and some of will not remain in their state after the stage of oil evolution (Hunt, 1996). Biomarkers in oils are valuable for estimating the level of maturity at which the oils were generated, provided that the oils have been reservoir at temperatures low enough to minimize maturation in the reservoir. "In case where the reservoir temperatures are high, biomarkers may indicate the thermal history of the reservoir instead of that of the source rock".

Also the biomarker ratios are used in the correlation between crude oil crude oil, crude oil - source rocks .The biomarkers and maturity coefficient are used to calibrate oil and gas production models with time for the trap and from them we can predict the oil size which may migrate to reservoir to for accumulation.

Biomarkers indicate the distribution of organic matters with amorphous structures in sea, lacustrine and terrestrial locations in addition to redox of sediments (Peter *etal.*,2005). The current study will be focus on the most used and available biomarkers are alkanes and acyclic isoprenoids, sterans, and terpanes.

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**2.3.2.1.** Alkanes and Acyclic Isoprenoid Ratios : Alkanes and acyclic isoprenoids are obtained from the gas chromatograms device (Figures 2-8, 2-9, 2-10, 2-11, 2-12, 2-13, 2-14, 2-15,2-16,2-17).

#### 2.3.2.1.1 n-alkenes ratio :

These variables are used to know the terrigenous hydrocarbons from the aquatic; they are used with care because they are affected by thermal maturity and biological corrosion. n-Alkanes identified in crude oils, range from n  $C_{15}$  to n  $C_{35}$ . The amount of n-alkanes is largely dependent on genetic conditions, and especially on the nature of the original organic matter. A high concentration of these types of compounds can be used to deduce the precursor organic matter when the sample is at an early stage of catagenesis. Table 2-2 shows the amount of n-alkanes and their ratios, which are described as follows:

#### a. Terrigenous/ Aquatic Ratio (TAR):

Ratios of certain n-alkanes can be used to identify changes in the relative amounts of terrigenous versus aquatic hydrocarbons in sediments or rock extracts (Peter *etal.*, 2005). Where:

 $TAR = (n C_{27} + C_{29} + n C_{31}) / (n C_{15} + C_{17} + n C_{19})$ 

Vertical distributions of TAR measurements are useful in order to determine relative changes in the contributions of land versus aquatic flora through time, particularly in young sediments (Meyers, 1997). TAR must be used with caution because it's sensitive to thermal maturation and biodegradation (Peter *etal.*, 2005).

### b. Carbon Preference Index (CPI):

It is the common n-alkanes ratio and called carbon preference index (Bray and Evans, 1961), and it is also affected by thermal maturity of organic matter depending on the transformation in the distribution of systematic paraffin hydrocarbon using the range of series from range C24-C34 which depends the gradual change to distribute long series of n-alkanes during

maturity process. CPI which decreases with the maturity increase, and this nalkanes distribution from kerogen which is derived from different biological processes and thermal distribution, can be measured from this equation :

CPI=[(C25+C27+C29+C31+C33)/(C26+...+C34+(C25+...+C33)/C26+...+ C34)]/2

The generation of n-alkanes produced from kerogen derived from different biological processes and from thermal destruction during the initial diagenetic processes of hydrocarbon. The high CPI values of indicates low maturity and continental environment, while oils and source rocks reach CPI~1 indicate marine environment with higher thermal maturity and the ratio CPI<1 indicates hyper saline environment, which describes redox paleoenvironment. CPI values significantly above or below 1 indicate low thermal maturity. The CPI value for the analyzed crude oil sample of the Mishrif Formation was (0.96), i.e., nearly (1) (Table 2-2), which refers that the environment of source rocks is a marine environment with thermal maturity and indicate the presence of mixed sedimentary organic matters.

#### c.Odd-to Even Preference (OEP):

Other common n-alkane ratio is the OEP, which is influenced by both source input and maturity as the TAR and CPI(Scalan and Smith, 1970). The OEP can be adjusted to include any specified range of carbon numbers, and its calculation has been done by:

 $OEP_{(1)} = (C_{21} + 6 C_{23} + C_{25}) / (4 C_{22} + 4 C_{24})$  $OEP_{(2)} = (C_{25} + 6 C_{27} + C_{29}) / (4 C_{26} + 4 C_{28})$ 

The OEP values of Mishrif crude oil samples are close to 1 (Table 2-2), which suggest that these oils are thermally mature(AL-Obaidi Q.A.,2012).

#### 2.3.2.1.2. Acyclic Isoprenoids:

The two most common branched alkens are pristane ( $C_{19}$ ) and phytane( $C_{20}$ ), which represent a branched acyclic (no rings), isoprenoid hydrocarbon containing 19 to 20 carbon atoms respectively. A prominent peak elutes immediately after the  $C_{17}$  n-alkane for pristane (Pr), and after the  $C_{18}$  n-alkane for phytane (Ph) in petroleum on most GC columns. These two compounds are abundant in most crude oils and rock extracts, and are very useful as marker points in chromatography profile. The most abundant source of Pristane (C19) and Phytane (C20) is the phytyl side chain of chlorophyll (a) in phototrophic organisms and bacteriochlorophyll (a) and (b) in purple sulfur bacteria ( Powell and McKirdy, 1973).Reducing or anoxic conditions in sediments cleavage of the phytyl side chain to yield phytol, which undergoes reduction to dihydrophytol and then phytane. Oxic conditions promote the competing conversion of phytol to pristane by oxidation of phytol to phytenic acid, decarboxylation to pristane, and then reduction to pristane.

High Pr/Ph (>3.0) indicates terrigenous organic matter input under oxic conditions, while low values (<0.8) typify anoxic, commonly hyper saline or carbonate environments (Peter *etal.*, 2005). The Pr/Ph in Mishrif Formation crude oils is ranging from( 0.76 to 0.83)(Table 2-2), accompanied with high sulfur content as discussed in previous section, this indicates anoxic conditions of the source environment. In this case Mishrif crude oils derived from carbonate anoxic environment source, especially samples with values less than 0.8 and the other samples that have values little higher than 0.8 may be due to other factors (Figure2-18). The isoprenoids/ n-alkanes ratios also could be used in petroleum correlation studies such as Pristane/nC<sub>17</sub> and Phytane/ nC<sub>18</sub> ratios. Both Pr/nC<sub>17</sub> and Ph/nC<sub>18</sub> are decreased with thermal maturity of petroleum, while Biodegradation increases this ratio because the aerobic bacteria attack the *n*-alkanes before the isoprenoids, (Peter *etal.*, 2005 a). These ratios in Mishrif crude oils is ranging from 0.18 to 0.22 for Pr/C<sub>17</sub>,

and ranging from 0.28 to 0.35 for  $Ph/nC_{18}$ (Table 2-2), this indicate mature non-biodegraded marine algal kerogen type II (Figure2-19).

Table2-2:	The Tota	ıl Ion	chromatogra	m (TIC)	peak a	reas of Pr	, Ph,
nC <sub>17</sub> and n	$C_{18}$ , and c	alculat	ing paramete	rs for the	e Mishrif	crude sam	ples.

Sample	Well	Depth	Dr	Dh	nC	nCa	Dr/Dh	Dr/nC-	Dh/nC.	CDI	OFP
No.	No.	( <b>M</b> )	11	III	IIC <sub>17</sub>	IIC18	11/11	11/110-17	1 11/11/18	CII	014
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 2-8: Whole crude chromatograms for NS-1.



Figure 2-9: Whole crude chromatograms for NS-3.



Figure 2-11: Whole crude chromatograms for NS-5.



Figure 2-12: Whole crude chromatograms for NS-6.



Figure 2-13: Whole crude chromatograms for NS-7.



Figure 2-14: Whole crude chromatograms for NS-8



Figure 2-15: Whole crude chromatograms for NS-9.



Figure 2-16: Whole crude chromatograms for NS-10.



Figure 2-17: Whole crude chromatograms for NS-12.



Figure 2-18: Pr/Ph ratios of Mishrif crude oils and correlation with other





Figure 2-19: Pristane/ nC17 Versus phytane/nC18 for Mishrif crude oils from Nasiriyah oil field (after Peters *etal.*, 1999 a).

# 2.3.2.2. Cyclic Terpanes

Many terpanes in petroleum originate from bacterial (prokaryotic) membrane lipids (Ourisson *etal.*, 1982). These bacterial terpanes include several homologous series, including acyclic, bicyclic (drimanes), tricyclic,tetracyclic and pentacyclic compounds, commonly monitored using m/ z 191 mass chromatograms (Figures 2-20, 2-21, 2-22, 2-23, 2-24, 2-25, 2-26, 2-27,2-28,2-29).Tricyclic terpanes are noticed for the first time in rocks of Green River Formation as indicated in a study by Anders and Robinson, (1971). Tricyclic terpanes are mostly cheilanthanes, which range from C<sub>19</sub> to C<sub>54</sub>, Abundant tricyclic terpanes commonly correlate with high paleolatitud Tasmanits-rich rocks, suggesting an origin from these algae, although other sources are possible (Peter *etal.*, 2005).

- Tricyclic terpanes are used to correlate crude oils and source-rock extracts, to predict source rock characteristics, and to evaluate the extent the thermal maturity and biodegradation (Seifert and Moldowan, 1981; Zumberge, 1987; Peters and Moldowan, 1993). Because of their extreme resistance to biodegradation, tricyclic terpanes permit correlation of intensely biodegraded oils (Seifert and Moldowan, 1986; Palacas *etal.*, 1984). They are also more resistant to thermal maturation than hopanes, although the lower-carbon-number homologs are favored at high thermal maturity . Tricyclic terpanes/ Hopane increases with thermal maturity of petroleum (Peter *etal.*, 2005).
- 2. The  $C_{26}/C_{25}$  tricyclic terpane ratio is useful as a supporting method to distinguish lacustrine from marine oils when cross plotted with  $C_{31}/C_{30}$ hopane (Figure2-30), this relationship indicate a marine source carbonate environment for Mishrif crude oil (Table 2-3).

# 3. Extended tricyclic terpane ratio (ETR):

ETR can be used to differentiate crude oils generated from Triassic, early Jurassic, and Middle-late Jurassic source rocks, where:

ETR=  $(C_{28} + C_{29}) / (C_{28} + C_{29} + T_s)$  (Holba *etal.*, 2001)

ETR decreases with age, and the Mishrif crude oil samples have a value of ETR ranged from (0.85-.088) which is less than 1.2 (Table 2-3), which may indicate that these oils are generated from middle to late Jurassic.

# 4. C<sub>24</sub> tetracyclic terpane ratio:

Tetracyclic terpane which occur in most crude oils and rock extracts range from  $C_{24}$  to  $C_{27}$  with tentative evidence for homologs up to  $C_{35}$ . Some of these compounds are identified on the m/z 191 chromatogram . Ratios of tetracyclic terpanes to hopanes increase in more mature source rocks and oils, indicating greater stability. Also tetracyclic terpanes are more resistant to biodegradation than hopane (Aquino Neto *etal.*, 1983). Abundant  $C_{24}$  tetracyclic terpane (commonly expressed as  $C_{24}$  Tet/ hopane,  $C_{24}$  Tet/  $C_{23}$  tricyclic , and  $C_{24}$  Tet/  $C_{26}$  tricyclic) in *petroleum* appears to indicate carbonate and evaporate source-rock settings (Clark and Philp, 1989). The values in this ratio in Mishrif crude oils show high with similarity (Table 2-3) , which refer that these samples are mature and from carbonate and evaporate sources.

- 5. Hopanes are a  $C_{27}$  to  $C_{35}$  pentacyclic triterpanes that originate from bacteriohopanoids in bacterial membranes and generally dominate the triterpanes in *petroleum*. These are typical biomarkers for prokaryotic cyanophytes (Schwark and Empt, 2006). Ratios of various tricyclic terpanes by carbon number can be useful in order to distinguish marine, carbonate, lacustrine, coal/resin, and evaporated oils.
- 6.  $C_{31}/C_{30}$ hopane is useful in order to distinguish between marine and lacustrine source-rock depositional environments, this ratio also expressed as  $C_{31}22R/C_{30}$  hopane( $C_{31}R/H$ ). Oils from marine shale, carbonate, and marl source rocks show high  $C_{31}/C_{30}$ hopane (>0.25) (Peter *etal.*, 2005 b). The  $C_{31}/C_{30}$ hopane value for Mishrif oil is ranging between 0.33 to 0.35 which indicate a carbonate marine source rock (Table2-3).

# 7. 30-Norhopane/hopane

High 30-norhopane/hopane is typical of anoxic carbonate or marl source rocks and oils. Measured using m/z 191 chromatograms, expressed asC29/C30 hopane(C<sub>29</sub>/H). The C29 17 $\alpha$ -norhopane rivals hopane as the major peak on m/z 191 mass chromatograms of saturate fractions of many oils and bitumens.C29/C3017 $\alpha$  hopane is greater than 1.0 for many anoxic carbonate or marl source rocks and related oils and less than (1) for other rocks.

All of the studied samples are greater than 1.0 which refers to anoxic carbonate source rocks (Table 2-3). The plotting of C29 / C30 hopane and C35 / C34 hopane suggests a positive relationship between them, where crude oils are generated from many marine carbonate and marl source rocks have high norhopane/hopane ratio and C35/C34 22S hopane, consistent with anoxia during deposition of the source rock (Zumberge, 2000), it compares with Mishrif oil tricyclic terpanes ratios and other known source environments ratios, Figure 2-31 shows that Mishrif crude oil was derived from carbonate marine environment.

# 8. 17α-Diahopane/ 17α-Hopane:

Also expressed as  $C_{30}$  X/ H,  $C_{30}$  X is found in oils,It may be related to bacterial hopanoid precursors originated from sediments containing clays deposited under Oxic or Suboxic conditions (terrigenous source rocks), the samples of Mishrif crude oils show zero values of the ratio (Table 2-3), which refer to the non-existence of  $C_{30}$  X, thus these oils could be generated under anoxic, non terrigenous source rocks(Peter *etal.*, 2005).

# 9. Oleanane/H:

Oleananes are well-known biomarkers arising from geological transformation of pentacyclic triterpenoids typical of higher plants. Oleanane in crude oils and rock extracts is a marker for both source input and geologic age. This compound originates from betulins (Grantham *etal.*, 1983), and other pentacyclic triterpenoids that are produced by

angiosperm (flowering land plants). It is also expressed as OL/H or OL/(OL + H), its normally elutes immediately before the C30 hopane.

Oleanane was found in crude oils (Peter etal., 2005). Small amounts of oleanane occur in Jurassic crude oil (Peter *etal.*, 1999) and rock extracts (Moldowan *etal.*, 1994) and extracts of megafossils from older rocks. It is difficult to distinguish oleanane if its ratio is small because of the interference of other components that have the same retention times when they get out from some columns of mass spectrum GC/MS but it is more precisely by GC/MS m/z -190Note(Figure 2-33). Environment deposition and diagenesis are additional factors that determine age-related biomarker distributions (Peter etal., 2005). Depositional environment and diagenetic processes affect in the distribution of biomarkers which are related to age determination, for example: Oleanane is absence in some carbonate source rocks and evaporates (marine) of Cretaceous and Tertiary age because (materials) terrigenous plants are absent in this sedimentary environment (Murray *etal.*, 1994). The oleanane is considered to be well observed by saline water, because of that oleanane is rare in fresh water environment. So, some non-clastic marine source rocks with some very little terrigenous inputs contain little oleanane because oleanane is preserved by effective diagenetic processes in this environment, while we note sediments in lacustrine environment, such as coal deposited in fresh water environment poor with oleanane in spite of the abundance of angiosperm prevalence of angiosperm inputs, which is considered as the origin from which oleanane is originated.

It can be noted from Table (2-3) that the ratio OL/H or (Oleanane /C30hopane) (Oleanane index) is absent (0.0) in crude oil samples, and from Figure(2-33) it is noticed that the age of productive source rocks for these oils is Lower Pre-Cretaceous, and it may be noted that the location of projected ratios refers to the age of source rocks generated oil is the age of Upper Jurassic - Lower Cretaceous.

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The calculated value of oleanane suggests that contribution from organic matter related to angiosperms was very low, also the absence of oleanane could be good indicator for carbonate marine environment.

# **10.Gammacerane Index :**

The origin of gammacerane is uncertain, but it may form by reduction of tetrahymonol (Haven etal., 1989). Diagenetic conversion of tetrahymonol to gammacerane most likely proceeds by dehydration to form gammacerane, followed by dehydration. tetrahymonol is a lipid that replace steroids in the membranes of certain protozoa (Caspi etal., 1968) .Gamacerane may also arise by sulfurization and subsequent cleavage of tetrahymonol. This ratio is useful to know the water-column stratification according to hyper salinity during the deposition of source rocks. It is measured by GC/MS-191 and it is called as (Ga/C31R) or 10 X gammacerane I(gammacerane + C30 hopane), which indicates to the water-column stratification in sediment environment of marine and nonmarine source rocks(Sinninghe Damsté *etal.*, 1995) and results from high salinity at depth and it results also of temperature gradients. Higher gammacerane indices refer to higher salinity, which is accompanied by density stratification and reduced oxygen content in bottom water (Peters etal., 2005). Gammacerane index ratio is ranged from (0.22-0.23) for analyzed oil samples of the Mishrif Formation (Table2-3).Generally, they are low and refer to sedimentlogical environment with normal salinity. This factor is widely present in marine oils of the carbonates source rocks (Moldowan *etal.*, 1991).

# 11.Ts/Tm:

Thermal parameter based on relative stability of C27 hopanes applicable over the range immature to mature to postmature . T<sub>s</sub> which is 18 $\alpha$  (H)-22, 29, 30-trisnorneohopane and T<sub>m</sub> which is 17 $\alpha$  (H)-22, 29, 30-trisnorhopane commonly Co-elute with tricyclic or tetracyclic terpanes on m/ z 191 mass chromatograms. Also expressed as T<sub>s</sub>/T<sub>m</sub> (C<sub>27</sub> Ts/Tm) (Peter *etal.*, 2005).  $T_s$  is more stable than  $T_m$ , and degrades less during diagenesis and catagenesis. Seifert and Moldowan (1986) proposed the ratio Ts / Tm ratio as a maturity indicator.

Mello *etal.* (1988) have shown that Ts/Tm values below 1 imply a lacustrine/saline, marine evaporated or marine carbonate depositional environment, whereas values above (1) indicate lacustrine fresh-water or marine deltaic environments. Thus the Tm/Ts ratio does not appear to be appropriates for quantitative estimation of maturity within a series of rock or oil samples representing the same facies ,a decrease in Tm/Ts may be a useful no quantitative indicator of relative maturity (Jones and Philip, 1990).

Oil from Mishrif Formation show low value of Ts/Tm ratio (0.16-0.18) this may be due to carbonate source that Oils from carbonate source rocks appear to have low Ts/Ts+Tm ratios compared with those from shale(Peter *etal.*, 2005)(Hunt , 1996) (Table2-3).

# **12.C29** Ts /(C29 17α- hopane + C29 Ts) ratios :

They are also factors of biomarkers indicator of thermal maturation. Thermal maturity affects them, but less than the effect of Ts/Tm, but both increase with thermal maturity (Fowler and Brooks, 1990). That means they are similar in thermal maturity and it is also called C29 Ts/Tm.

Ratios of C27 Ts/Tm and C29 Ts/Tm which are resulted from oil sample analyses of the Mishrif Formation in Nasiriyah field indicate thermally matured (Table2-3).

# **13.Mortane/ hopanes:**

The 17 $\beta$ , 21 $\alpha$  (H)-mortanes are thermally less stable than the 17 $\alpha$ , 21 $\beta$  (H)hopanes, and abundances of the C<sub>29</sub> and C<sub>30</sub> mortanes decrease relative to the corresponding hopanes with thermal maturity from approximately 0.8 in immature bitumens to less than 0.15 in mature source rocks and oils to a minimum of 0.05 (Moldowan, 1980 in Peter *etal.*, 2005). The C30 compounds used most commonly for moretane/hopane, although this ratio is also quantified using C29 compounds (e.g. Seifert and Moldowan, 1980). Others have used both C29 and C30 compounds for their moretane/hopane ratio (Mackenzie *etal.*, 1980). The C30 compounds are used for moretane/hopane in this study (Table 2-3). The crude oil samples show mortane/ hopane values less than 0.15, with that value, we have mature crude oil.

# 14.C<sub>35</sub> Homohopanes Index:

It is an indicator of redox potential in marine sediments during diagenesis. High values indicate anoxia, but are also affected by thermal maturity. It is also expressed as  $C_{35}/C_{34}$  and  $C_{35}$  S/  $C_{34}$  S hopanes. Most oils from marine carbonate source rocks show high C35/C34 hopane greater than (0.8) combined with C29/C30 hopane greater than (0.6). The high values of  $C_{35}$  S/  $C_{34}$  S ratio in the studied crude oils indicate that these oils are from marine carbonate source rock (Table2-3). This ratio is combined with high ratio of  $C_{29}/$  H (Table 2-3), which confirm the source of oils as explained by (figure 2-31).

Chapter Two

Sample	Well	Depth	C <sub>22</sub> /	C <sub>24</sub> /	БДО	Tet/	C <sub>26</sub> /	C <sub>28</sub> /	C <sub>29</sub> /	C <sub>30</sub> X	C <sub>31</sub>		GA/	C <sub>35</sub> S/	C <sub>27</sub> Ts/	C <sub>29</sub> Ts/
No.	No.	(M)	C <sub>21</sub>	C <sub>23</sub>	LIK	C <sub>23</sub>	C <sub>25</sub>	Н	Н	/H	R/H	UL/H	31R	C <sub>34</sub> S	Tm	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

 Table2-3 : The results of mass chromatograms of hopanes (m/ z 191) parameters
 for the studied crude oil samples


Figure2-20: Gas chromatography/mass spectrometry showing terpanes peaks of NS-1 oil sample.



Figure 2-21: Gas chromatography/mass spectrometry showing terpanes

peaks of NS-3 oil sample.



Figure2-22: Gas chromatography/mass spectrometry showing terpanes peaks of NS-4 oil sample.



Figure2-23: Gas chromatography/mass spectrometry showing terpanes peaks of NS-5 oil sample.



Figure 2-24: Gas chromatography/mass spectrometry showing terpanes

peaks of NS-6 oil sample.



Figure 2-25: Gas chromatography/mass spectrometry showing terpanes

peaks of NS-70il sample.



Figure 2-26: Gas chromatography/mass spectrometry showing terpanes

peaks of NS-8 oil sample.



Figure 2-27: Gas chromatography/mass spectrometry showing terpanes

peaks of NS-9 oil sample.



Figure 2-28: Gas chromatography/mass spectrometry showing terpanes

peaks of NS-10 oil sample.



Figure2-29: Gas chromatography/mass spectrometry showing terpanes peaks of NS-12 oil sample.



Figure2-30: Cross plot between  $C_{26}/C_{25}$  tricyclic terpane and  $C_{31}/C_{30}$ hopane



Figure2-31: Relationship between C29/C30hopane andC35/C34 Hopane to predict source-rock depositional environments of the Mishrif crude oils from Nasiriyah oil field (after Zumberg, 2000).



Figure 2-32: The relationship between  $C_{22}/C_{21}$  and  $C_{24}/C_{23}$ .



Figure 2-33 : The cross plot of Oleanane ratios source rock age (Moldowan *etal.*, 1994).

#### 2.3.2.3.Steranes:

Steranes are a class of tetracyclic, saturated biomarkers constructed from six isoprene subunits (approximately  $C_{30}$ ). Steranes originate from sterols, which are important membrane and hormone components in eukaryotic organisms. Most commonly used steranes are in the range  $C_{26}$ -  $C_{30}$  and are detected using m/ z 217 mass chromatograms by SIM/ GCMS rather than TIC for identifying the sterane isomers, such as cholestane ( $C_{27}$ ), 24-methylcholestane ( $C_{28}$ ), 24-ethylcholestane ( $C_{29}$ ), and diasterane (Figures 2-34, 2-35, 2-36, 2-37, 2-38, 2-39, 2-40, 2-41,2-42,2-43).

Many other parameters and ratios can be calculated from these biomarkers (Table 2-4), and could be used as depositional environment, thermal maturity and age related indicators of source rocks and related oils. These parameters are:

#### **1. Regular Steranes (C<sub>27</sub>, C<sub>28</sub>, C<sub>29</sub>):**

The relative abundances of  $C_{27}$ ,  $C_{28}$ , and  $C_{29}$  are given as percentage in Table (2-4), which show that  $C_{29}$  and  $C_{27}$  steranes are generally more abundant than those of  $C_{28}$ . Almost all higher plants have  $C_{29}$  as the dominant, also  $C_{29}$  sterols are dominant in brown algae and same species of green algae. The C<sub>27</sub> sterols tend to be dominant in most plankton, particularly in red algae and zooplankton (Hunt, 1996), while the  $C_{28}$ sterols may have derived from unicellular green algae such as parsiynophytes or chlorophytes (Volkman, 1986). Sterane ternary diagrams (discussed later) are used extensively to show relationships between oils and/ or source rock bitumens. Most oils and their source rock extracts have values located between  $C_{27}$  and  $C_{29}$  sterols (Table2-4). The ratio projected on the triangle  $C_{27}$ - $C_{28}$ - $C_{29}$  sterane as shown in Figure (2-44) represents information for different types of crude oils from different sources, projected on triangle, and from it we can know the depositional environment of source rocks and oil groups (Moldowan *etal.*, 1985).

Sterane ternary diagram is widely used to observe the relation among oils or source rocks bitumen (Peter *etal.*, 2000) .Depending on observations of some researchers, Oils from the hypersaline lacustrine family have very low amounts of diasteranes, which commonly suggests a source rock that has low content of catalytic clays, consistent with carbonate or evaporate source rocks (Mello *etal.*, 1988; Peter and Moldowan, 1993).Values  $C_{27}$ , $C_{28}$  and  $C_{29}$  sterane were calculated of Gas Chromatography –Mass Spectrum of the crude oil in wells of study area and projected them on the sterane ternary diagram and accordingly indicate relation to carbonate marine environment for its source rocks (Figure 2-44).

#### 2. C<sub>28</sub> / C<sub>29</sub> steranes:

The relative content of  $C_{28}$  steranes increase and the  $C_{29}$  steranes decrease in marine *petroleum* through geologic time. The increase in  $C_{28}$  may be related to increased diversification of phytoplankton assemblage, including diatoms, coccolithophares, and dinoflagellates in the Jurassic and Cretaceous periods. Although this approach is not sufficiently accurate to determine the age of the source rock for oil, it is possible to distinguish Upper Cretaceous and Tertiary oils from Paleozoic or older oil (Grantham and Wakefield, 1988 in Peter *etal.*, 2005). These authors observed that  $C_{28}$ /  $C_{29}$  steranes is less than 0.5 for Lower Paleozoic and older oils, 0.4 to 0.7 for Upper Paleozoic to Middle Jurassic oils, and greater than approximately 0.7 for Upper Jurassic to Miocene oils. In general, the Mishrif oils can be accepted to represent the age of Middle Jurassic to Lower Cretaceous (Table 2-4).

#### 3. Diasterane / Steranes:

Diasterane is a rearrangement product from sterol precursors through diasteranes. Diasteranes increase relative to steranes with thermal maturation and they are low in clay-poor carbonate source rocks and related oils. Diasterane / Steranes ratio are commonly used to distinguish petroleum from carbonate versus clastic source rocks (Mello etal., 1988), and can be used to differentiate immature from highly mature oils (Younes and Philp, 2005). Low diasteranes/ steranes ratios (m/z 217) in oils indicate anoxic clay-poor or carbonate source rock (Eglinton etal., 2006). During diagenesis of these carbonate sediments, bacterial activity provides bicarbonate and ammonium ions (Berner etal., 1970), resulting in increased water alkalinity. Under these conditions of high PH and low Eh, calcite tends to precipitate and organic matter preservation is improved (Peter etal., 2005). Low values ratio in Mishrif crude oils indicate that these oils are from anoxic clay-poor or carbonate source rocks, also the closed values

reflect that these samples have a similar level of thermal maturity (Table2-4).

4. 20 S/ (20 S+ 20 R) isomerization:

Highly specific for maturity, measured using m/ z 217 or preferably by GCMS/ MS analysis of C<sub>29</sub> steranes (other than C<sub>27</sub> and C<sub>28</sub> due to the ease of analysis by m/ z 217). Also expressed as %20 S, 20 S/ 20 R, and C<sub>29</sub> 20 S/ R. Isomerization at C-20 in the C<sub>29</sub> 5 $\alpha$ , 14 $\alpha$ , 17 $\alpha$  (H)-steranes causes 20 S/ (20 S+ 20 R) to rise from 0 to approximately 0.5 (0.52 - 0.55 = equilibrium) with increasing thermal maturity (Seifert and Moldowan, 1986). C<sub>29</sub> 20 S/ R ratio can be used to indicate the onset of *petroleum* generation when it is calibrated for each basin and source rock by comparison with other maturity and generation parameters. Mackenzie *etal.*, (1980a) indicate that *petroleum* generation begins at %20 S of approximately 40%, while the ratio ranging from 0.23 to 0.29 refers to low maturity oils (Seifert and Moldowan, 1981). All crude oil samples values range from (0.57 to 0.67) referring to mature samples (Table2-4).

Tab	ole 2-4 : T	The results	of mass	chromatograms	of steranes	( <b>m</b> / z )	217)
for 1	the studie	ed crude oi	l sample	s.			

Sample	Well	Depth	Ø.C	Ø.C	Ø.C		C <sub>29</sub> 20S/
No.	No.	(M)	%C 27	%C 28	%€29	C <sub>28</sub> / C <sub>29</sub>	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



Figure 2-34: Gas GC/MS showing steranes peaks of NS-1 oil sample.



Figure2-35: GC/MS showing steranes peaks of NS-3 oil sample.



Figure2-36: GC/MS showing steranes peaks of NS-4 oil sample.



Figure 2-37: GC/MS showing steranes peaks of NS-5oil sample.



Figure2-38: GC/MS showing steranes peaks of NS-6oil sample.



Figure2-39: GC/MS showing steranes peaks of NS-7oil sample.



Figure2-40: GC/MS showing steranes peaks of NS-8oil sample.



Figure2-41: GC/MS showing steranes peaks of NS-9oil sample.



Figure2-42: GC/MS showing sterane speaks of NS-10oil sample.



Figure 2-43: GC/MS showing steranes peaks of NS-12oil sample.



Figure2-44: Ternary diagram show relation between C<sub>27</sub>-C<sub>28</sub>-C<sub>29</sub>steranes of Mishrif crude oil samples.



Figure 2-45: The relation between  $C_{28}/C_{29}$  steranes and diversity with age.



Figure2-46: The C<sub>28</sub>/C<sub>29</sub>steranes ratios for 150 global petroleum system source rocks for different environments.

# 2.3.2.4. Biomarker Compounds as Geochemical Indicators: 2.3.2.4.1 Source-Related Biomarkers:

Source-Related Biomarkers ratios are particularly useful in order to describe the source rock even when only crude oil samples are available for analysis .Cyclic and acyclic biomarker can be used to provide information on source-rock organic matter input or depositional environment of formations crude oils .The source affinity of Mishrif crude oil is determined by using and comparing different 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. 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 (Figure 2-32). The  $C_{27}$ - $C_{28}$ - $C_{29}$  steranes ternary diagram support the others parameters and referred to marine carbonate source. 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 .  $Pr/nC_{17}$  values is ranged between (0.18 to 0.22), Ph/nC<sub>18</sub> 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 scarcity of higher plant (flowering plant) contributions, while the low concentration of gammacerane indicates 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.

Table	2-5: S	ome	characteristics	of	petroleum	from	carbonate	versus
shale s	source	rocks	(modified from	Pe	eter <i>etal</i> ., 20	)05)		

Characteristics	Shales Carbonates		Mishrif oil	Notes					
Non-biomarker parameters									
API, gravity	Medium-high	Low-medium	23°-26.2°	Carbonates					
Sulfur, wt %	Variable	High (marine)	3.67%- 4.72%	Carbonates					
Saturate/ aromatic	Medium-high	Low-medium	0.57- 0.62	Carbonates					
Naphthenes/ alkanes	Medium-low	Medium-high	Medium-high	Carbonates					
Carbon preference index	> 1	< 1	0.93- 0.99	Carbonates					
$(C_{22}-C_{32})$	_	—							
Biomarker Parameters									
Pristane/ phytane	High $(\geq 1)$	Low $(\leq 1)$	0.76- 0.83	Carbonates					
Phytane/ nC <sub>18</sub>	Low (≥ 0.3)	High $(\leq 0.3)$	0.28- 0.3	Carbonates					
Diasteranes/ steranes	High	Low	0.55- 0.6	Carbonates					
$C_{29}/C_{30}$ hopanes	Low	High (> 1)	1. 41- 1.60	Carbonates					
C <sub>35</sub> homopane index	Low	High	1.07- 1.17	Carbonates					
Ts/ (Ts + Tm)	High	Low	0.16- 0.18	Carbonates					

Table 2-6: Generalized geochemical properties differ betweennon-<br/>biodegradedcrude oils from marine, terrigenous, and lacustrine source-<br/>rockorganic matter (modified from Peters *etal.*, 2005).

Property	Marine	Terrigenous	Lacustrine	Mishrif oil	Notes
Sulfur (wt %)	High (anoxic)	Low	Low	3.67%- 4.72	Marine
Pristane/ Phytane	< 2	> 3	~ 1 - 3	0.76- 0.83	Marine
Pristane/ nC <sub>17</sub>	Low (< 0.5)	High $(> 0.6)$	-	0.18 – 0.20	Marine
Tricyclic diterpanes	Low	High	High	Low	Marine
28, 30-bisnorhopane	High (anoxic)	Low	Low	High	Marine
Oleananes	Low or absent	High	Low	0.00	Marine
V/Ni	High (anoxic)	Low or absent	Low or absent	3.6-4.5	Marine

Table 2-7: Geochemical properties differ between non-biodegraded crude oils from marine carbonate, marine shale, and deltaic marine shale source-rocks (modified from Peters *etal.*, 2005)

Property	Marine carbonate	Marine shale	Deltaic shale	Mishrif oil	Notes			
Bulk								
API, gravity	10 - 30	25 - 40	35 – 45 23°-26.2°		Marine Carb.			
Saturate/ aromatics	0.3 – 1.5	1 - 2	> 2	> 2 0.57-0.62				
Carbonpreference index	< 1	1 – 1.5	> 1.5	0.93-0.99	Marine Carb.			
Biomarkers	Biomarkers							
Pristane/ Phytane	< 1	1.1 – 1.8	2 - 4	0.76-0.83	MarineCarb.			
Phytane/ nC <sub>18</sub>	> 0.3	< 0.3	< 0.1	0.28- 0.3	Marine Carb.			
Diasterenes/ steranes	Low	High	High	0.55-0.6	Marine Carb.			
$C_{29}/\overline{C_{30}}$ hopane	High $(> 1)$	Low	Low	1.48 - 1.67	MarineCarb.			
Gammacerene/ hopane	Low - high	Low	absent	0.33-0.35	Marine Carb.			

#### 2.3.2.4.2. Age dating - related biomarkers:

Various compounds in source rocks show distributions through geological time suggesting their use as age-related biomarkers in crude oil (Figure2-47).

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 (Peter *etal.*, 2005).

The absence of oleanane in all samples of Mishrif crude oils refer that these oils are from a rock older than Early Cretaceous age(Table 2-3) (Figure 2-33). Murray *etal.*,(1994) reported that Oleanane preservation is enhanced by salty water and that fresh water environments are poor in this regard.

The ratio of  $C_{28}/C_{29}$  steranes for oil samples ranged from (0.55 to 0.60)(Table 2-4) (Figure2-46), which roughly represent upper Jurassic to lower Cretaceous oils. Other parameter is the extended tricyclic terpane ratio

(ETR) which has a value less than 1.2 in all oil samples (Table 2-3) and represent oils generated from Middle or upper Jurassic source rocks.



Figure 2-47: Age-related biomarkers to infer the source rocks for crude oils (after Holba *etal.*, 2001).

#### 2.3.3.4.3. Maturity – related Biomarker:

Some transformation of biomarkers occur as result of thermal reactions, whose rates are controlled both by subsurface temperatures and period of exposure to those temperatures. Biomarkers can thus 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 2-3), are referred that these oils are mature. The low ratio of  $T_s/T_m$  (less than one) for all oil samples refer

that these samples are from carbonate sources, and within the stage of maturity according to the relative, amounts of T<sub>s</sub> and T<sub>m</sub> (Table 2-3). Also the T<sub>s</sub>/ hopane ratio shows closed values, are indicated that these oils at the same level of maturation (Table 2-3) (Peter *etal.*, 2005). The steranes isomerization ratios [20 S/ (20 S + 20 R)] in all Mishrif crude oil samples Table( 2-4), indicated 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 are indicated to mature oils and does not reach the postmature range (Table 2-4). Pristane/*n*C<sub>17</sub> and phytane/*n*C<sub>18</sub> decrease with thermal maturity as more *n*-alkanes are generated from kerogen by cracking (Tissot *etal.*, 1971). These isoprenoids/*n*-alkanes ratios can be used to assist in ranking the thermal maturity of related, non-biodegraded oils and bitumens(Table 2-2), 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.

#### 2.3.2.4.4.Biodegradation parameters:

*Petroleum* biodegradation is the alteration of crude oil by living organisms (Cannon, 1984).Numerous eubacteria, fungi, and possible archaic evolves metabolic pathways to consume saturated and aromatic hydrocarbons, (Peter *etal.*, 2005). Biodegradation of crude oils requires molecular oxygen ( $O_2$ ) and temperatures below about 80 °C, with an optimum temperature around 60 °C (Connan, 1984). *Petroleum* biodegradation is primarily a hydrocarbon oxidation process, producing CO2 and partially oxidized species, such as organic acids. Heteroatom compounds are less susceptible to biological attack and increase in relative abundance as biodegradation proceeds. This increase is caused primarily by enrichment of pre-existing petroleum NSO compounds due to selective biodegradation of other compounds, but a secondary cause is the direct production of heteroaromatic compounds (mainly oxidized species) by microbes. *Petroleum* quantity and

net volume thus decreasing with increasing biodegradation. API gravity decreases while non-hydrocarbon gases, viscosity, NSO compounds, and trace metals increase. Although loss of n-alkanes and isoprenoids is the most common molecular transformation that occurs as a result of bacterial attack on crude oil, it is now recognized that in certain cases steranes and triterpanes also can be affected when biodegradation is extremely severe.

Volkman *etal.*, 1983 have proposed a nine-level scale for evaluating the level of biodegradation of any crude oil as in (Table 2-8). The first five levels of biodegradation are based on n-alkanes, isoprenoids, and alkylcyclohexanes, but levels (7-9) can be distinguished only by analysis of sterane and triterpane biomarkers. Prior to level 7, steranes and triterpanes are not affected by biodegradation. The Mishrif crude oil samples show non-biodegradation effect according to the following reasons:

- 1. The crude oils of Mishrif field are of normal class, having medium (API), and the main constituents of these oils are saturated and aromatic, with minor amount of NSO compounds as in (Table 2-1).
- 2. The depth of reservoirs is greater than (2000 m) as in (Figure 2-48), and their temperatures equal or more than 80°C.
- 3. The light hydrocarbons are greater than heavy hydrocarbons with low ratio of Pristane/C17 and Phytane/nC18 as in (Table2-8) .The presence of nalkanes and n-isoprenoid alkanes indicated that the Mishrif crude oil samples are non-biodegraded.

Table 2-8: Stage or absent of crude oils based on the presence or absenceof certain classes of compounds from Vokman *etal.*,1983

Level of Biodegradation	Compounds Removed	Extent of Biodegradation
1	None	Undegraded
2	Short n-alkanes	Minor
3	>90% of n-alkanes	Moderate
4	Alkylcyclohexanes; isoprenoids reduced	Moderate
5	Isoprenoids	Moderate
6	Bicyclic alkanes	Extensive
7	>50% of regular steranes	Very extensive
8	Steranes; hopanes reduced; demethylated hopanes abundant	severe
9	Demethylated hopanes predominate ;diasteranes formed;steranes gone	extreme



Figure 2-48: Pristane/nC17 alkane versus depth for crude oil sample of Nasiriyah oil field ,(after Peter *etal.*,2005)

#### **2.3.2.4.5.Depositional environments- related biomarkers:**

The advantage of biomarkers as indicators of depositional environments arises from the fact that certain types of compounds are associated with organisms, or plants that grow in specific types of depositional environments (Philp, 2004). The relative low concentrations of gammacerane compound presented in Mishrif oils samples (Table 2-3) actually refer to that these oils are from marine depositional environment, with low salinity according to the decrease of the ratio of the concentration of gammacerane to that of hopane (Peter and Moldowan, 1992). The pristane to phytane ratio (Pr/ Ph) was used as an indicator of the oxicity of the depositional environment. Oil studied samples show high concentration of phytane rather than pristane (Pr/ Ph less than one) (Table2-2), indicating anoxic marine depositional environment oils (Figure 2-18) (Freeman *etal.*, 1990).

(CPI) index The carbon preference values (Table 2-2)equals approximately one or around one, exhibited the predominance of marine organic matter during deposition. Low diasteranes/ steranes ratios in Mishrif oil samples indicate anoxic clay-poor or carbonate source rock depositional conditions (Table 2-4). The high  $C_{35}$  homohopane in crude oils of Mishrif reservoir is interpreted as a general indicator of highly reducing (Low Eh) marine conditions during deposition Table (2-4) (Peter and Moldowan, 1991). The high ratios of  $C_{31}$  22R homohopane/ 30 hopane( $C_{31}$  R/  $C_{30}$ > 0.25) in Mishrif crude oil samples Table (2-3) are referred to marine carbonate depositional environments Figure (2-30). The ratio of  $C_{29}/C_{30}$  17 $\alpha$  hopane is greater than 1.0 for all Mishrif oil samples (Table 2-3), represented as anoxic carbonate or marl source rocks and related oils (Figure 2-29).

#### 2.3.2.4.6. Oil- Oil Correlation:

Mishrif reservoir oil samples represent as one group of oils according to the similar bulk parameters composition such as API gravity, percent sulfur, vanadium to nickel ratio, paraffine content and stable carbon isotope. The Pr/ Ph ratios as a correlation parameters refer that all crude oil samples are significantly less than one ranging from( 0.76 to 0.83) (Table 2-3). These values are accompanied by high porphyrins and sulfur content (Table 2-1), indicated an anoxic environment, typical of carbonate source rocks (Peters and Molodwan, 1993). Furthermore the concentrations of vanadyl porphyrins ranging from (57.0 to 99.0) ppm and sulfur contents ranging from( 3.67 to 4.72)% represented as similar group crude oils, which confirm with Mishrif crude oils. The Pr/ nC<sub>17</sub> versus Ph/ nC<sub>18</sub> diagram (Table 2-1) (Figure 2-19) show a good relationship between these oils. The C<sub>27</sub> Ts/ Tm ratio in all oil samples show more intense of Ts than Tm (values range from 0.16 to 0.18) and high concentration of C<sub>29</sub> – nor hopane relative to C<sub>30</sub> hopane (range from 1.48 to 1.67), reflected a good similarity (Table 2-3).

The homohopane index values are ranging from (1.04 to 1.15) and the gammacerene index values ranging from (0.33 to 0.35) for all oil samples (Table2-3) indicated the same reducing marine carbonate environment as well as the lower levels of salinity. The diasteranes/ steranes ratios for oil samples are closed to each other range from (0.55 to 0.60), reflected a good similarity (Table 2-4). These oil samples show a dominance of  $C_{29}$  steranes relative to  $C_{27}$  steranes, and the  $C_{30}$  steranes (indication of marine- derived organic matter) are present in relatively low concentrations compared to the  $C_{27}$ - $C_{29}$  steranes (Table2-4).

These compounds reflect similarity of oils too. The geochemical analysis of crude oil samples of Mishrif oil field show that non major difference in general crude oil composition and also indicate that all oil samples are derived from one source rock that is middle Jurassic to lower cretaceous carbonate marine.

# **2.3.2.4.7.** Correlating Mishrif crude oil samples in Nasiriyah oil field with other crude oils in the surrounding areas:

Mishrif whole crude chromatograms is much similar with Mishrif Formation in the south of Iraq which studied by Al-Khafaji A., 2006, Jafar M.S., (2010), AL-Obaidi Q.A. (2012) and Faisal R.F. (2010). All the chosen crude oil studies show a close values of Pr/Ph and by using the cross plot between the  $Pr/nC_{18}$  and  $Ph/nC_{17}$ it is noticed that all the chosen studies make almost one oil family with Mishrif in Nasiriyah oil (Figure2-49). The calculated  $C_{28}/C_{29}$  regular steranes is also used to correlate between Mishrif oils in Nasiriyah and the surrounding previous studies (Figure2-50).

The  $C_{24}/C_{23}$ terpanes is almost same for all chosen previous studies along with the recent one. However  $C_{22}/C_{21}$ terpanes is slightly different, which make it a good tool to distinguish between crude oils (Figure2-51). As a conclusion Mishrif oil from Nasiriyah oil field is much similar with Mishrif Formation oil in south Iraq. That could indicate that Mishrif oil source from Nasiriyah oil is thought that it is similar to Mishrif source in south of Iraq.According to the geochemical similarities with Sargelu Formation AL-Obaidi Q.A.(2012) ,Al-Ameri *etal.*,(2009, Al-Ahmed, A. A. (2006) ) these oils extracts mainly Sargelu Formation .



Figure 2-49: Cross plot shows the Phytane/nC<sub>18</sub> and thePrstane/C<sub>17</sub> of Mishrif oil with other oils group from the surrounding area.



Figure 2-50: Correlation between the calculated  $C_{28}/C_{29}$  regular steranes between Mishrif oil and known source age oil of the surrounding areas





### 2-4 Results and Discussion:

- According to the bulk geochemical properties, Mishrif crude oils in Nasiriyah oil field can be classified as a one family, represent a typical mid- oil window mature oils. These non-biodegraded, marine, non-waxy oils represent marine anoxic environments.
- 2. Terpane and sterane biomarker parameters provide information, which explain that the Mishrif oils in Nasiriyah oil field also represented as a one family generated from anoxic, marine carbonate source rocks. The most appropriate source for these crude oil extracts mainly Sargelu Formation.

# CHAPTER THREE THE SOURCE ROCKS

# CHAPTER THREE THE SOURCE ROCKS

## 3.1. Preface

A *petroleum* source rock is defined as any rock that has the capability to generate and expel enough hydrocarbons so that when it is buried and heated ,it will produce petroleum (oil and gas). The organic matter tend to accumulated in high concentrations in areas of high organic matter productivity and stagnant water. To preserve organic matter, the oxygen contents of the bottom waters and interstitial waters of the sediments need to be very low to zero. Such conditions can be created by overproduction of organic matter, and that occur in nutrient rich coastal upwelling, swamps, shallow seas, and lakes environments or in environments where poor water circulation leads to stagnation.

The term kerogen originally refers to the organic matter in oil shale that yields oil upon heating. Subsequently the term was defined as all the disseminated organic matter of sedimentary rock that is insoluble in non-oxidizing acids, bases, and organic solvents (Hunt, 1996). The four principle sources of kerogen in rocks are: marine, lacustrine, terrestrial, and recycled. The presence of insoluble organic matter (kerogen) is a primary requisite for an active or a potential source rock. A potential source rock is one that is too immature to generate petroleum in its natural setting but will form significant quantities of petroleum when heated in the laboratory or during deep burial. An effective source rock is one that has already formed and expelled petroleum to a reservoir.

The relative ability of source rock to generate *petroleum* is defined by its kerogen quantity (TOC) and quality (high or low in hydrogen). Whether or not it has generated petroleum is defined by its state of maturation (immature,

mature, or postmature with respect to oil) (Hunt, 1996).Source rock quality is defined in terms of amount, type of kerogen, bitumen, and its stage of maturity. However, while it is possible to recognize whether a source rock is immature, and thus cannot yet have yielded oil, it is yet very difficult, except in special cases, to find out whether or not oil has migrated out of a mature source rock (Tissot and Welte, 1984).

### 3.2. The Origin of Petroleum in Source Rocks:

#### 3.2.1. Organic Matter:

The chemical composition of organic matter is diverse because the organisms from which they are derived are complex. The principle biological components of living organisms are proteins, carbohydrates, lipids and lignin. Animal tissue and enzymes are partly composed of proteins, built from aminoacids. Carbohydrates are also found in animal tissue, being a principle source of energy for living organisms. Lipids are fatty organic compounds, insoluble in water, and found in most abundance in algae, pollen, and spores.

Lipids are rich in hydrogen, and hence yield high volumes of hydrocarbon molecules on maturation. The lipid group contains a special group of compounds called isoprenoids, which are found in chlorophyll and include pristane and phytane. These molecules are preserved during petroleum formation. Their abundance and composition in petroleum can be indicative of the depositional environment in which the organic matter is accumulated (Gluyos and Swarbrick, 2005).

#### 3.2.2. Preservation of organic matter:

The two basic requirements for the generation and preservation of organic matter in sediments are (1) high productivity and (2) oxygen deficiency of the water column and the sea bed .The supply of organic matter to any depositional site is controlled by primary productivity (commonly

within the top 50m of the water column) and the depth of water through which the material must settle.

Preservation beneath the sediment /water interface is a function of the rate of burial and oxygenation of the bottom waters. Both productivity and oxygen deficiency at the site of deposition can combine to produce excellent source rock, although some source rocks may result from a dominance of only one control. Environment of high organic productivity include (1) continental margins, (2) lagoons and restricted seas, (3) deltas in warm latitudes, and (4) lakes (Demasion and Moor, 1980).

#### **3.2.3. Evolution of Organic Matter:**

Tissot, (1977) defined three major phases in the evolution of organic matter in response to burial: The first phase occurs in the shallow subsurface at near normal temperature and pressure. It includes both biogenic decay, aided by bacteria, and a biogenic reaction. Methane, carbon dioxide, and water are given off by the organic matter, leaving a complex hydrocarbon (kerogen). The net result of this phase of organic matter is the reduction of its oxygen content, leaving the hydrogen: carbon ratio largely unaltered, this phase referred as Diagenesis, whereas the phase that occurs in the deeper subsurface as burial continues and temperature and pressure increase. Petroleum is released from kerogen during this phase -first oil and later gas. The hydrogen: carbon declines, with no significant change in the oxygen: carbon ratio, this phase is referred as Catagenesis and third phase is the Metagenesis which occurs at high temperature and pressure limiting on metamorphism. The last hydrocarbon, generally only methane, is expelled. The hydrogen: carbon ratio declines until only carbon is left in the form of graphite. Metagenesis is reached only at great depth. However, this last stage of evolution of organic earlier (vitrinite reflectance matter beings approximately 2%) than metamorphism of the mineral phase (vitrinite reflectance of about 4%)

corresponding to the beginning of the green schist facies (Figure 3-1) (Tissot and Welte, 1984).



Figure (3-1): General scheme of kerogen evolution from diagenesis to metagenesis in the Van Krevelen diagram. Approximate values of vitrinite reflectance are shown for comparison. (after Tissot and Welte, 1984).

### **3.2.4Kerogen Type:**

kerogen is subdivided into four main "types" on the basis of maceral content, that is, original organic source material. The main maceral groups are liptinite, exinite, vitrinite, and inertinite.

• Type I kerogen (liptinite) has a high atomic H/C (~ 1.5) and low O/C(<0.1) .This type is dominated by liptinite macerals, although vitrinites and inertinite can occur in lesser amounts .laboratory pyrolysis or burial maturation of this type results in higher yields of hydrocarbons than other kerogen types .It is oil-prone, with a high yield (up to 80%). It is derived mainly from an algal source, rich in lipids, which is formed in lacustrine and/or lagoonal environments .Kerogen type I has low sulfur content

.Liptinite fluoresces under UltraViolet (UV) light. Type I kerogen is relatively rare.

- Type II Kerogen (Exinite) has high atomic H/C (1.2-1.5) and low atomic O/C ratios compared with type III and IV.This type is dominated by liptinite macerals but like type I kerogen ,vitrinites and inertinite can occur in lesser amounts ,It is oil-and gas prone, with yields of 40-60%. The source is mainly membranous plant debris (spores, pollen, and cuticle), and phytoplankton and bacterial microorganisms in marine sediment with medium to high sulfur content. The presence of sulfur influences the timing and rate of kerogen maturation. Exinite fluoresces under UV light. Type II kerogen are the most abundant.
- Type III kerogen (Vitrinite) has a low atomic of H/C (0.7-1.0) and high ratio of O/C up to ~ 0.3 and therefore forms a low yield kerogen, principally generating gas. The primary source is terrestrial higher plant debris found in coals or coaly sediments. Vitrinite does not fluoresce under UV light, however it is increasingly reflective at higher levels of maturity and therefore can be used as an indicator of source rocks maturity.
- Type IV kerogen (Inertinite) is dead carbon often termed "Residual kerogen" showing low atomic H/C (<0.7) and low to high O/C
- up to ~ 0.3 ,having no effective potential to yield oil and gas, it is the non-fluorescing product of any of above kerogens. (Brook *et al.*, 1987).

The source rocks deposited in anoxic lakes or anoxic shallow marine basins tend to contain a very hydrogen-rich kerogen derived from plankton (type I or II) whereas those deposited in fluvial, deltaic and deep-marine basins tend to contain predominantly hydrogen-lean kerogen (type III) derived from higher land plants (Table 3-1) (Welte *etal.*, 1997).

# Table 3-1: Characteristic features of different settings for petroleum source rock deposition (Welte *etal.*, 1997).

Settings	Contribution to world	Pre dominant	Lateral	Predominant	Characteristic Kerogen	
Settings	petroleum	Rock type	extent	Organic particles	Types	
Marine silled basins, anoxic continental shelves	+++	Marlstones Shales, siltstones, carbonates	* *	Alginite, bituminite	11, 11-111	
Anoxic lacks	++	Shales, marlstones	*	Alginite	I, II	
Fluviodeltaic (coal-bearing) basins	+	Siltstones, shales, coals	*	Vitrinite	III	
Progradational Submarine fans	+	Shales, siltstones, Marlstones, turbidites	* *	Often vitrinite, also inertinite, liptinite	III	
Evaporatic environments	0	Carbonates, sulfates, interlayered, thin shales, salt		Alginite	II or III	
Deep marine Upwelling areas	0	Siliceous shales, Shales, marlstones	*	Predominant unstructured (marine/derived), alginate	II-III	

+++, Extremely important; ++, very important: +, important especially for gas generation; 0, less important or unknown; \*\*, extensive to very extensive; \*, small to extensive.

### 3.2.4.2. The Quantity and Quality of kerogen:

The quantity of kerogen in source rock is determined from the total organic carbon (TOC) and reported as a weight percentage of the rock. The quality of kerogen in a rock determines the hydrocarbon yield-that is, the volume of hydrocarbon generated for each volume of source rock-which is usually expressed in kilograms of hydrocarbon per ton of rock (kg HCt<sup>-1</sup>). A range of techniques is used to evaluate potential source samples, including visual inspection of the kerogen type, elemental analysis, and pyrolysis.

### 3.3. Maturation of Source Rocks:

The quantity of generated hydrocarbons related to the maturity of the source rocks that buried in a restricted basin and due to thermal burial the whole organic content will convert to kerogen ,otherwise immature source rock cannot generate oil unless it attains to the reliable transformation ratio that convert it to HC .Exceeding of thermal burial more than 150°C already transfer the organic matter to gas due to over maturation. The transformation of kerogen is controlled by the reaction kinetics and the most important control is temperature (Tissot *et al.*, 1987). Lesser controls are the nature and abundance of the kerogen in the source rock and pressure. Significant oil generation occurs between temperatures approximately 60°C and 120°C, and significant gas generation between 120°C and 225°C, above 225°C the kerogen is inert, having expelled all hydrocarbons; only carbon remains as graphite (Selley, 1998). The maturation of kerogen can be measured by several techniques as maturation indicators (Figure 3-2). Miscellaneous parameters have used for estimating source rock maturation. These parameters include Vitrinite reflectance  $(\mathbf{R}_0)$ , the temperature at which the kerogen yields maximum hydrocarbons (T<sub>max</sub>), and Production index (PI)by Pyrolysis.



Figure 3-2: Correlation between hydrocarbon generation, temperature, and some Paleothermometers.

# 3.4 The analytical program subdivided into Screening analysis and detailed analysis:

### 3.4.1 Screening analysis:

The most effective screening method for large number of rock samples from well and outcrops usually combine lithological description, quantity of organic matter by Total organic carbon(TOC) ,quality and source potential by Rock-Eval pyrolysis.

# 3.4.2 Detailed analysis:

Detailed analysis focus in more specific geochemical aspects, they include Kerogen isolation and typing, elemental analysis, and maturity analysis (Vitrinite reflection, thermal alternation index ,fluorescence ,etc).

### 3.5. Method to Determine Kerogen Type:

In this study Van Krevelen Diagrams were depend on specifying the kerogen type, these Diagrams were developed by Van Krevelen in 1961, It provides indirect methods for kerogen, More recently, modified Van Krevelen diagrams use the hydrogen index (HI) versus oxygen index (OI) generated from Rock- eval pyrolysis and TOC analysis. HI versus OI data can be generated more rapidly and at less expense than atomic H/C versus O/C data. HI versus Tmax plots (Espitalie *etal.*, 1984) may be used also.

# **3.6.** Source Rock Richness: Total Organic Carbon (TOC)

The quantity of organic matter is usually expressed as total organic carbon (TOC). It is also called organic carbon (Corg). It measures the quantity but not the quality of organic carbon in the rock or sediment samples (Peter et al.,2005). Nearly all service laboratories and several oil companies define a minimum TOC for oil expulsion usually ranges between (0.4-1)% (Hunt 1996) .Dow (1978) mentioned that, most acknowledged source rock must contain (0.2 - 0.8 %) organic carbon .Thomas (1979) classified the potentiality of source rocks based on their weight percentage of organic carbon into poor source (<0.5 wt %), fair source (0.5 - 1.0 wt %), good source (1.0 - 2.0 wt %) and excellent source (>2.0 wt %). TOC is determined by direct combustion of source rock sample in a LECO analyzer. (1-2 grams) is weighted and in order to remove carbonates ; the sample treated with concentrated HCl, and vacuum filtered on glass filter paper then in a ceramic crucible the residue and paper are placed, dried and combusted with pure oxygen in a LECO carbon analyzer to about 1000°C and from the free (organic) carbon in the rock carbon dioxide will form. A laboratory standard is run every certain number of samples for quality control.
## **3.7.Quality and Hydrocarbon Potential:Rock-Eval Pyrolysis 3.7.1.(Pyrolysis)**

Pyrolysis is the best rapid- screening technique for source rock evaluation, and has a huge advantage over elemental analysis because it is simple, rapid ,and inexpensive . Samples can be analyzed in about 20 minutes , making it relatively easy , In this method a rock sample is subjected to controlled heating in an inert gas to or past the point of generating hydrocarbons in order to assess its quality as a source rock, the abundance of organic material in it, its thermal maturity, and the quality of hydrocarbons it might generate or have generated. Pyrolysis breaks large hydrocarbon molecules into smaller molecules. This process is used to determine the quality of shale as a source rock and is instrumental in evaluating shale gas plays (Hunt , 1996) .

## 3.7.2. (Rock-Eval Parameters):

The pyrolysis technique provides different parameters to evaluate directly the amount of free hydrocarbons present in the rock and the amount of hydrocarbons that the source rock can generate with more maturity and indirectly the Kerogen type and its maturity (Figure 3-3). A small portion of the dried core is crushed to fine sand particle size (0.125-0.25mm). A smaller size is not recommended because powdered samples can result in anomalous Rock-Eval pyrolysis where every of twentieth sample is a rock standard.

- Initially the samples is heated to 300°C to determine the amount of free hydrocarbons (S1 Peak) that is thermally distilled and can be volatilized out of the rock without cracking the kerogen.
- (S2 Peak) is measured next when the sample is progressively heated in an inert environment, which rises from 300 to 550°C at a heating rate of 25°C/minute and S2 measures the hydrocarbon yield from cracking of kerogen and heavy hydrocarbons and represents the existing potential of a

rock to generate petroleum .At last, carbon dioxide generated during the S2 pyrolysis, an indicater of kerogen oxidation, is collected up to a temperature of 390°C and reported as S3 Peak in units of mg CO2/g sample.

- S1: the already generated oil in the rock. These are the free hydrocarbons (oil and gas) already present in the sample, and they are distilled out of the sample at initial heating of the sample to a temperature of 350 ° C. Free hydrocarbons increase with depth. These values may be anomalously high from migration and contamination by drilling fluids and mud.
- S2: The amount of hydrocarbons generated through thermal cracking of nonvolatile organic matter (Kerogen) when the sample temperature is increased to 550 °C.S2 is an indicator of the quantity of hydrocarbons that the rock may potentially produce should burial and maturation continue. This parameter normally decreases with burial depths >1Km.

 $S2 \ge 5.0 \text{ mg HC/dry rock}$  -- Minimum value for good source rocks.

S3: The trapped CO<sub>2</sub> released during pyrolysis up to a temperature of 390 °C. This value is proportional to the oxygen present in the kerogen. Carbonate rocks may increase S3 values.

### **3.7.2.1 Vitrinite Reflectance (R<sub>o</sub>):**

The use of vitrinite reflectance as a technique for determining the maturation of OM in the sedimentary rocks was first described by Marlies Teichmuller (1958). Today Vitrinite reflectance is the most widely used indicator of thermal stress, because it extends over a longer maturity range than any other indicator. Vitrinite is composed of clusters of condensed aromatic rings linked with chains and stacked on top of one another. With increasing maturity the clusters fuse in to larger, condensed- aromatic ring structure. Eventually they form sheets of condensed rings that assume an orderly structure. Both the increase in the size of the sheets and their preferred orientation cause greater reflectivity (Hunt, 1996).

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This reflectance can be measured optically. Empirically there is a relationship between vitrinite reflectance and hydrocarbon generation. Waples (1985) considered a Vitrinite reflectance (Ro %) of 0.6% to mark the early stage of oil generation, while the peak of oil generation is at Ro  $\approx$ 0.8%, and the late stage or the end of oil generation is marked at Ro  $\approx$  1.35%.

 $R_0\%$  in this study is calculated theoretically according to the following equation:

 $R_0 = (T_{max}, 0.0180) - 7.16... (Jarvie$ *etal.*, 1991)

### 3.7.3.2. T<sub>max</sub>:

It is a Rock-Eval pyrolysis thermal maturity parameter based on the temperature at which the maximum amount of pyrolyzate (S<sub>2</sub>) is generated from the kerogen in a rock sample. The  $T_{max}$  is influenced by the type of organic matter during the diagenetic stage and the beginning of catagenesis. It is lower in the terrestrial kerogen of type III and higher in the marine or lacustrine type I and II. The beginning and end of the oil-generative window approximately correspond to  $T_{max}$  of 430°Cand 470°C, respectively (Figure3-4a and b) (Peter *etal.*, 1986).Hunt(1996) reported that sometimes these values oscillates back and forth as much as 20 C°.



Figure 3-3: General diagram showing the different fractions of the total organic matter of rocks analyzed ,the corresponding parameters and their recordings (after Espitalie *et al.*, 1977).



Figure 3-4a : Cycle of analysis and example of record obtained by the pyrolysis method of Espitalie *etal.*,(1977) (after Tissot and Welte, 1984).



Figure 3-4b : Characterization of source rock maturity pyrolysis methods. Transformation ratio and / or peak temperature:  $T_{max}$  may be used as indicators of thermal evolution (Modified by Tissot and Welte, 1984 after Espitalie *et al.*, 1977).

#### 3.7.3.3. Production Index (PI):

The production index  $(S_1/S_1+S_2)$  can be used to estimate thermal maturity. When PI value is less than 0.1, it indicates immature organic matter that generates little or no *petroleum* and when reaches 0.4at the bottom of the oil window (beginning of the wet gas zone) and can increase to as high as 1.0 when the hydrocarbon-generative capacity of the kerogen has been exhausted (Peter *etal.*, 2005).PI is meaningless, if the S<sub>2</sub> is below 0.2. Many high PI values above 1mg HC/g TOC indicate migrated oil, especially if the T<sub>max</sub> decreases and the TOC increases at the same time (Hunt, 1996).

## 3.8. Derived measurements:

## **HI**:Hydrogen index $[HI = (S2/TOC) \times 100]$ :

It is a measure of the hydrogen richness of the source rock, and when the kerogen type is known, it can be used to estimate the thermal maturity of the rock(Peters and Moldowan, 1993). The number of hydrogen atoms per unit volume is divided by the number of hydrogen atoms per unit volume of pure water at surface conditions. The hydrogen index (HI) is thus the density of hydrogen relative to that of water. It is a key factor in the response of a neutron porosity log.

## **OI**: Oxygen index $[OI = (S3/TOC) \times 100]$ :

This parameter measures the oxygen richness of a source rock and can be used in conjunction with the hydrogen index to estimate the quality and thermal maturity of source rocks. This index is unreliable in rocks with high carbonate content. High OI values (>60 mg/g) are characteristic of immature hydrocarbons (Hunt ,1996).

## **3.9. Source Rocks Evaluation:**

The total organic carbon (TOC), Rock-Eval pyrolysis, Vitrinite Reflectance ( $R_o$ ), and kerogen atomic hydrogen/carbon (H/C) parameters can be used to evaluate the rock samples. Table 3-2 shows the source rock characterization in global context by pyrolysis. Also Table (3-3) shows the generally accepted criteria for describing the quantity, quality, and thermal maturity of organic matter in source rocks standards on earth (Peters and Cassa, 1994 in Peters *etal.*, 2005). This classification is applied for classifying the samples .Geochemical parameters, TOC values, and pyrolysis analysis for thirty-one (31) selected rock samples in this study. Table 3-4 represents analyzed samples in the laboratories of the oil exploration company (OEC) in Baghdad, Iraq.

## Table 3-2: Source Rock characterization by Pyrolysis (after Hunt, 1996)

### Definitions:

 $S_0$  (P<sub>0</sub>) Free Hydrocarbons  $C_1$  to about  $C_9$  thermally liberated at

a 90 °C isotherm.

 $S_1 \left( P_1 \right)$  Free Hydrocarbons  $\, C_1 \mbox{ to about } C_{23} \mbox{ thermally liberated at }$ 

a 300°C isotherm.

 $S_{2}\left(P_{2}\right)$  Hydrocarbons cracked from Kerogen or from  $C_{24+}$ 

bitumens by heating to 550°C. Units with TOC go to 600°C.

 $S_3$  (P<sub>3</sub>) Organic carbon dioxide released between 300 and 390 °C.

 $T_{max}$ The temperature at the highest yield of  $S_2$  hydrocarbons.

 $S_4$ Total organic carbon in weight percent (TOC). TOC= pyrolysis

carbon (PC) + residual carbon (RC). PC=  $0.82 (S_1 + S_2)/10$ . RC =  $S_4/$ 

10, where  $S_4 = mg C/g rock$ .

## **Quantity:**

 $S_1$  = Migrated hydrocarbons if immature sediments (oil and gas shows).

 $S_2$  = Generated or migrated hydrocarbons or contaminants if mature

sediments. The migration index,  $S_1 / TOC$ , is high, and the  $T_{max}$  is

low if migrated.  $S_1 / TOC = 0.1$  to 0.2 for oil expulsion.

 $S_2$  = Potential to generate hydrocarbons if buried deeper.  $S_1 + S_2$  is the

total genetic potential in mg HC/ gm rock. It is < 2 for poor source

rocks, 2- 5 for fair, 5- 10 for good, and > 10 for very good.

## Quality (Kerogen types I, II or III):

 $(S_2 / TOC) \times 100$ = Hydrogen index (mg HC/g TOC).

 $(S_3 / TOC) \times 100$ = Oxygen index (mg CO<sub>2</sub>/g TOC).

 $S_2/S_3$  = Hydrocarbon type index. It is < 2 for gas and > 5 for oil.

## Maturation State:

 $S_1/(S_2 + S_2)$  = Production index. Oil window = 0.08- 0.4. Higher values are often due to migrating hydrocarbons or contaminants.

 $T_{max}$ = S2peak temperature. Oil window = ~430 to 470  $^{0}$ C.

## **Reservoir Studies:**

Oil and gas recovery from sands has been monitored by the  $S_1/S_2$ , with the best recoveries from horizons with values greater than 5. It is normally used with mud logging and wireline logs. Also, the  $S_1/TOC$  can be used.

 Table 3-3: Geochemical parameters guidelines used in source rock

 evaluation.

Geochemical parameters describing the petroleum potential (quantity) of an immature source rock (after Peters and Cassa, 1994 in Peter *etal.*, 2005).

Petroleum Potential	TOC	Rock-Eval Pyrolysis		Bi	tumen	Hydrocarbons (ppm)	
Totentia	(	<b>S</b> <sub>1</sub>	S <sub>2</sub>	(wt %) (ppm)			
Poor	0- 0.5	0- 0.5	0-2.5	0-0.05	0-500	0-300	
Fair	0.5-1	0.5-1	2.5-5	0.05-0.1	500-1000	300-600	
Good	1-2	1-2	5-10	0.1-0.2	1000-2000	600-1200	
Very Good	2-4	2-4	10.20	0.2-0.4	2000-4000	1200-2400	
Excellent	> 4	> 4	> 20	> 0.4	> 4000	> 2400	

Geochemical parameters describing kerogen type (quality) and the character of expelled products (after Peters and Cassa, 1994 in Peter *et al.*, 2005).

Kerogen Type	H1 (mg HC/g TOC)	S <sub>2</sub> /S <sub>3</sub>	Atomic H/ C	Main Expelled Product at peak Maturity
Ι	> 600	> 15	> 1.5	Oil
II	300-600	10-15	1.2-1.5	Oil
II/ III	200-300	5-10	1.0-1.2	Mixed oil and gas
III	50-200	1-5	0.7-11.0	Gas
IV	< 50	< 1	< 0.7	None

Geochemical parameters describing level of thermal maturity (after Peter and Cassa, 1994 in Peter *etal.*,2005)

Stage of		Maturation		Generation			
Thermal Maturity	$\mathbf{P}_{\alpha}(\mathcal{O}_{\alpha})$	$T_{\alpha}(\mathcal{O}_{\alpha}) = T_{\alpha}(\mathcal{O}_{\alpha})$		Bitumen/	Bitumen	PI St/	
for Oil	$\mathbf{K}_0(n)$	I <sub>max</sub> (C)	IAI	TOC	Rock g	$(S_1 + S_2)$	
Immature	0.2-0.6	< 435	1.5-2.6	< 0.05	< 50	< 0.1	
Mature							
Early	0.6-0.65	435-445	2.6-2.7	0.05-0.1	50-100	0.11-015	
Peak	0.65-0.9	445-450	2.7-2.9	0.15-0.25	150-250	0.25-0.4	
Late	0.9-1.35	450-470	2.9-3.3	-	-	> 0.4	
Postmature	> 1.35	> 470	> 3.3	-	-	-	

Chapter Three

Sample No.	Depth (M)	Formation	TOC %	S <sub>1</sub>	$S_2$	S <sub>3</sub>	T <sub>max</sub>	PI S <sub>1</sub> /(S <sub>1</sub> +S <sub>2</sub> )	HI S <sub>2</sub> /TOC	OI S <sub>3</sub> /TOC	PP S <sub>1</sub> +S <sub>2</sub>	S <sub>2</sub> /S <sub>3</sub>	S <sub>1</sub> /TOC	R <sub>O</sub> (calcu.)
1	3229	Yammama	0.86	0.15	0.6	0.56	419	0.2	70	65	0.75	4.0	0.17	0.38
2	3236	Yammama	0.62	0.12	0.5	0.48	421	0.19	80	77	0.62	1.04	0.19	0.41
3	3266	Yammama	0.52	0.09	0.3	0.45	423	0.23	57	86	0.39	0.66	0.17	0.45
4	3274	Yammama	0.34	0.53	0.61	0.7	433	0.46	179	206	1.14	0.87	1.55	0.63
5	3279	Yammama	0.65	0.05	0.05	0.15	424	0.5	8.0	23.0	0.1	0.33	0.07	0.47
6	3320	Yammama	0.18	0.15	0.46	0.1	432	0.25	256	56	0.61	4.6	0.83	0.61
7	3351	Yammama	0.16	0.26	0.39	0.28	428	0.4	244	175	0.65	1.39	1.62	0.54
8	3443	Sulaiy	1.11	0.21	0.32	0.62	432	0.4	29	47	0.53	0.50	0.189	0.61
9	3450	Sulaiy	0.68	0.2	0.38	0.28	432	0.34	56	41	0.58	1.35	0.294	0.61
10	3455	Sulaiy	0.68	0.33	0.48	0.6	428	0.41	70	88	0.81	0.8	0.485	0.54
11	3461	Sulaiy	0.8	0.39	0.53	1.03	430	0.42	66	129	0.92	0.5	0.487	0.58
12	3469	Sulaiy	0.84	0.3	0.6	0.16	428	0.33	71	90	0.9	3.73	0.357	0.54
13	3478	Sulaiy	0.59	0.48	1.04	0.61	433	0.31	176	103	1.62	1.7	0.813	0.63
12	3484	Sulaiy	0.8	0.3	0.41	0.37	431	0.42	51	46	0.71	1.1	0.375	0.59
13	3491	Sulaiy	0.68	0.33	0.38	0.65	429	0.46	56	95	0.71	0.5	0.485	0.56
14	3498	Sulaiy	0.27											
15	3504	Sulaiy	0.75	0.5	0.6	0.37	429	0.45	80	49	1.1	1.6	0.666	0.56
16	3509	Sulaiy	0.8	0.48	0.71	0.41	429	0.4	89	51	1.19	1.73	0.6	0.56
17	3524	Sulaiy	0.81											
18	3544	Sulaiy	0.8	0.33	1.18	0.42	434	0.15	226	52	2.14	4.3	0.412	0.65
19	3556	Sulaiy	0.6	0.45	1.13	1.17	428	0.28	188	195	1.58	0.9	0.75	0.54
20	3564	Sulaiy	0.82	0.75	1.72	0.37	432	0.3	210	45	2.47	4.6	0.914	0.61
21	3569	Sulaiy	0.64	0.79	1.55	0.64	433	0.34	242	100	2.34	2.4	1.234	0.63
22	3575	Sulaiy	0.52	0.69	1.19	0.55	431	0.37	229	106	1.88	2.1	1.326	0.59
23	3578	Sulaiy	0.72	0.89	1.4	0.74	433	0.39	194	103	2.29	1.8	1.236	0.63
24	3583	Sulaiy	0.4											
25	3588	Sulaiy	0.72	1.64	2.72	1.64	430	0.38	378	228	4.36	1.9	2.277	0.58
26	3592	Sulaiy	0.42											
27	3595	Sulaiy	0.59	0.93	1.11	0.68	430	0.45	188	204	2.04	1.6	1.576	0.58
28	3606	Sulaiy	0.45	0.8	2.09	2.44	424	0.28	464	542	2.8	0.8	1.777	0.47
29	3612	Sulaiy	0.44											

## Table 3-4: Rock-Eval Pyrolysis data of the studied samples from the (NS-1)(OEC Laboratories)

### **3.10. The Results:**

#### • Yamama Formation:

Total organic carbon (TOC wt %), Vitrinite reflectance (Ro) and Pyrolysis analyses were conducted on seven core samples (Table 3-4) in order to measure the generation capability, organic matter type and state of maturity of Yamama Formation within the study area. Total organic carbon (TOC, wt%) content is generally used as an indicator of the kerogen and bitumen amount (as weight percent) in a source rock. The TOC content of Yamama Formation is between 0.15- 0.86 wt% indicating fair source rock potentials (Table 3-4)(Figure 3-5). S1 hydrocarbons in the whole rock are found in Free State, and they can be disintegrated under heat. S1 hydrocarbon peak values (0.05-0.53) indicate poor generating potential (Table 3-4). The relatively low S1 values may suggest that hydrocarbons are not yet produced from source rocks because of the low thermal maturity, and the cross plot between S1 and TOC indicates that the most hydrocarbons contained in the sediments are indigenous (Figure 3-6). The cross plot of the S1/TOC with the depth indicate bring closer to oil expulsion (Figure 3-7). Pyrolysis S2 yields (0.05-0.61) mg HC/g rock indicate poor generating potential (Table 3-4). $S_2/S_3$ , average values ranges from (0.33 to 4.6), show that the OM in the Yamama Formation can be determined as type III kerogen and the gas will be the main expelled product when the OM reach the maturity peak (Table 3-4). The cross plot of PI values with Ro values (Figure 3-8) and the cross plot of PI vs. Tmax(Figure 3-9) suggest immature stage. The temperature at maximum hydrocarbon generation is the Tmax. Tmax together with the vitrinite reflectance (Ro) indicate immature to early stage source rocks, since the values range from (419-433) C<sup>0</sup> and (0.38 - 0.63), respectively (Figure 3-10), also the same figure indicates the type II/III of kerogen. The ratio of S2 to the TOC of the rock is the hydrogen index (HI). HI is a key source rock parameter used in quantitative modeling of the phase and volume of expelled hydrocarbons and the classification of kerogen type. In the present work, HI values are typically range from (8 - 256) mg HC/g TOC suggest type II/ III(Table3-4).

## • Sulaiy Formation:

Twenty –four core samples were taken from Sulaiy Formation within the study area (Table 3-4) ,and according to the analyzed methods ,the TOC content is between (0.45to 1.11) wt% indicating poor to good source rock potentials(Table 3-4)(Figure3-5).Rock-Eval S<sub>1</sub> value range from(0.2 to 1.64) mg HC/g rock indicate poor to good potentiality (Table 3-4)and the cross plot between S1 and TOC indicates that the most hydrocarbons contained in the sediments are indigenous (Figure 3-6). The cross plot of the S1/TOC with the depth Figure(3-7) indicate oil expulsion. S<sub>2</sub>,values range from 0.32 to 2.7 mg HC/g rock, indicate poor to fair potentiality of hydrocarbon (Table 3-4). S<sub>2</sub>/S<sub>3</sub>, value range from (0.8-4.6), shows that the OM in this Formation can be determined as type III kerogen and the gas will be the main expelled product when the OM reaches the maturity peak (Table 3-4).The cross plot of PI vs. Tmax suggest oil zone (Figure 3-9).

 $T_{max}$  value for all samples(424-434)°C indicating that the OM of source rock reaches the immature to early stage of maturation for oil ,in agreement with the values of vitrinite reflectance at same stage of maturation which range from (0.47-0.65)(Table 3-4). Figure3-10 show that the kerogen type is mixed between II and III. HI values range from (56-464) mg HC/g TOC, which suggest kerogen type II /III except two samples indicate type II kerogen (Table 3-4).



Figure3-5:Petrolum potential and total organic matter of studied samples in NS-1well (OEC analysis).



Figure 3-6: Total organic matter (wt%) and  $S_1(mgHc/grock)$  of studied samples in NS-1well (OEC analysis).



Figure 3-7 :The relation between the depth(m)and  $S_1$ /TOC of the studied samples in NS-1well (OEC analysis).



Figure3-8:Kerogen conversion and Maturity based on Ro%of studied samples in NS-1well (OEC analysis).



Figure 3-9: Kerogen conversion and Maturity based on Tmax c<sup>0</sup>of samples in NS-1well (OEC analysis).



Figure 3-10 : Hydrocarbon generation and Kerogen types of the studied samples in NS-1well (OEC analysis).

#### **3.11. Jurassic Source rock Formations:**

Several studies document the stratigraphy and sedimentology of Jurassic source rocks (Al-Sharhan and Nairn, 1997; Sadooni, 1997; Sadooni and Aqrawi, 2000; Sharland *et al.*, 2001; pitman *et al.*, 2004), and burial-temperature histories have been published for a few wells (Ibrahim, 1983); however, a regional analysis of source- rock maturation is only available in the northern part of Iraq for the Sargelu Formation (AL-Ameri *et al.*, 2006).

Kerogen facies of upper Jurassic rocks is similar to type II kerogen in terms of organic potential, this type of kerogen is favorable for oil production at the thermal maturity level diagnosed as late stage maturation. The important Jurassic source Formations are expected to be Sargelu, Naokelekan and Najmah Formations in the studied area based on the studies of Jafar (2010) and Al-Kafaji (2006). These source rocks are generally associated with carbonate and are interpreted to have been deposited during both transgression and regression, when restricted marine environments were present within the intra-shelf basin (MoO and JAPEX, 2006). The kerogen type in the upper Jurassic belongs in facies for which active oil generation may have continued up to vitrinite reflectance level of 1.5% (extremely oil generative type). It is expected that the oil in the Jurassic trap probably may not be cracked into gas under the situation of this type of kerogen (Pitman etal., 2004 and MoO and JAPEX, 2006).

Jurassic source rocks (Sargelu, Naokelekan and Najmah Formations) have passed through the oil window and into the kerogen-to-gas generation zone. Minor gas generation from oil-prone kerogen with trace amounts of gas derived locally from the thermal cracking of oil. Most of the source rocks have reached or exceeded peak of oil generation and completed oil generation and expulsion (Pitman *etal.*, 2004).

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#### **3.12. Migration of Hydrocarbons:**

Commercial accumulations of oil and gas do not occur in source rocks, but in more coarse grained and permeable (reservoir rocks) that contain little or no organic matter. The formation of oil and gas accumulation in reservoir rocks requires some kind of hydrocarbon transport from source rock to trap positions. This transport is known as hydrocarbon or (*petroleum*) migration (Verweij, 1993).

The process of *petroleum* migration has been divided into two parts : primary migration has been considered to be the movement of oil and gas within and out of the non-reservoir source rock into the permeable reservoir rocks , whereas secondary migration has been described as the movement within carrier rocks and reservoir type rocks , leading to a *petroleum* accumulation . Today it is recognized that the process is more complicated because there is extensive movement through many fractured source rock ,which can act in some cases as both source and reservoir .also migration occurs along faults and joints that are neither source nor reservoir rocks Consequently , primary migration is more correctly defined as any movement within the fine-grained portion of the mature source rock, and secondary migration is any movement outside of it .Tertiary migration is the movement of a previously formed accumulation (Hunt ,1996).

Seismic sections in Nasiriyah area show the occurrence of fractures and faults in Nasiriyah oil field which act as pathways for vertical and horizontal migration of hydrocarbon from Middle Jurassic Najmah and Sargelu Formations to Cretaceous-Miocene traps such as Yamama, Nahr Umr and ,Mishrif reservoirs (Figures3-11,3-12, 3-13 ,and 3-14).The trapped oil of all sources is preserved between the highest regional seal of early Cretaceous, and the lowest seal of early Jurassic, including other local seals of non-permeable shale and limestone.

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Figure 3-11:Seismic Section in Nasiriyah oil field show migration pathways of hydrocarbon accumulation.



Figure 3-12: Inline base map in NS-7,NS-10 and NS- 12wells shows the direction of the seismic section .



Figure 3-13: Seismic Section in Nasiriyah field shows migration pathways of hydrocarbon accumulation.



Figure 3-14:Inline base map in NS-3 well shows the direction of the seismic section .

## **3.13. Discussion:**

- 1. The early Jurassic late Cretaceous Yammama Sulaiy Formation yield most of the oil that charged reservoir rocks in the south Mesopotamian Basin (Beydoun, 1991). The TOC content for Yamama Formation, is fair generally for oil expulsion with poor generation potential ;the other parameters indicate that the maturity of this Formation is between the immature to early stage and the type of kerogen is typeII/ III, thus it is considered less in contribution with the hydrocarbon production in contrast to other studied Formation of the (Sulaiy Formation) (Al-Ameri *etal.*, 2009).Sulaiy Formation has poor to good content of TOC with poor to fair potentiality and reached the immature to early stage of oil generation and expulsion with kerogen type II/III, it is considered as an effective source rock than Yamama Formation for oil generation in the studied area.
- 2. The oil occurrences in Nasiriyahal oil field are high while in the source rocks of Sulaiy is low . Accordingly, these oils could have been mainly migrated oils from the Sarglu Formation source rocks by vertical migration and some from the Mesopotamian by the horizontal migration through fractures and faults along Gotnia Anhydrite regional seal (figure 3-11) and may be with some indigenous oil from the Sulaiy Formation.
- 3. The above mentioned results point out the importance of the Middle Jurassic Formation rocks, in addition to the smaller share of Sulaiy (Tithonian-Early Valanginian) as an effective potential source rocks in the studied area. The hydrocarbons which are produced from these source rocks must be charging the Cenomanian-Early Turonian reservoir rock (Mishrif and Yamama Formation) through the migration pathways simultaneously with trap formation and accumulation.

### 3.14.PalynofaciesAnalysis

#### 3.14.1 Preface

Facies analysis was used in this study to evaluate the palaeoenvironment, and potentiality to generate hydrocarbons. Combaz (1964) introduced the term " palynofacies "to refer to the total organic content of a palynological assemblage (e.g. pollen, spore, microplankton, woody tissues, cuticle, etc.) or to encompass the total complement of acid -resistant organic matter recovered from a sediment or sedimentary rock by palynological processing techniques using HCL and HF, as seen under microscope. Nowadays is accepted to be the a body of sediment of a specified character that represents a particular environment of deposition (Batten, 1996) . The data of Palynofacies can generate for more numerous and diverse parameters than bulk geochemical data, permiting the analysis of much more detailed and suitable variations in sedimentary environment and organic matter source or preservation state .Palynofacies microscopic test results are represented as percentage ratio, then values were projected on diagrams of triangles which were prepared by Tyson (1995), Table 3-4 represents the Palynofacies defined on the triangle(Amorphous –Phytoclast – Palynomorph) (APP).

The importance of these diagrams come from their ability to determine the environmental of locations in addition to the detail environment explanations, e.g., paleoclimate conclusions and changes in the marine surface level, as well as the potentiality to generate hydrocarbons .In the recent study, sixteen core samples from Yamama Formation from Nasiriyah oil field ( NS-1, NS-2, NS-4 ,NS-5 ), samples were subjected to palynological kerogen preparation slides. All samples were examined by using the transmitted light microscope .

**3.14.2 The palynological analysis**: Its applied to different core samples of the formations and source rocks and performed according to published standard methods (Tyson ,1995).

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#### 3.14.3. Organic Matter Groups:

The four major organic matter categories identified by Tyson (1993& 1995) include the following:

#### **A- Phytoclast Group**

It represents fragments of strongly lignified mechanical support and vascular tissues of the secondary xylem ('wood') of arborescent gymnosperms and angiosperms.

The most conspicuous lignified structures seen in palynological preparations are fragments of xylems elements, comprising tracheids and vessels. Tracheids may be recognizing by their bordered, scalariform or other types of pits, pores by which the elements communicate with adjacent cells. Each trachea may have 50-300 pits, mostly located on the radial walls, and arranged in single or multiple rows (uniseriate, biseriate or multiseriate). The vessels are analogous structures to tracheids but are longer and often somewhat greater diameter (25-500  $\mu$ m).

The woody tissue as a category of phytoclasts is most typical of the swamp facies and other sediments rich in terrestrial organic matter. The cuticle layer is the outermost part of the epidermis of those tissues of the aerial parts of higher plants that do not show secondary growth. Most cuticles are derived from leaves, because these are also produced and shed in great numbers and their surface area is very large(Tyson, 1987, 1995) (Plate3-1).

#### **B-Palynomorph Group**

The term palynomorph refers to all discrete acid- resistant ,organic walled microfossils that may be encountered in a palynological preparation ,the following are considered to be palynomorphs: small spores ( isospores, microspores ,megaspores , sporangia ,pre-pollen and pollen grains, small seeds ( seed cuticle ) and seed like bodies ,fruiting bodies spores and other reproductive parts of fungi , cysts of prasinophyte algae dinocysts , and foraminiferal test linings (Batten ,1996).

The presence of foraminiferal test linings is a reliable indicator of marine conditions. In recent sediments, the abundance of linings declines sharply at the head of estuaries, and their size decreases as salinity falls (Tyson, 1995). The abundance of linings in recent sediments also decreases with increasing water depth. The foraminiferal linings are absent in most deltaic sediments and in the major part of the prodeltaic sediments littoral zone; modern shallow-water shelf sediments contain a

high percentage (15-45% from all palynomorphs) of foraminiferal linings (Plate 3-2,3-3,3-4).

#### **C-Amorphous Group**

The term (amorphous) refers to organic matter that lack of a distinct shape outline(traditionally referred to as 'AOM'). The amorphous group consists of all particulate organic components that appear structureless at the scale of light microscopy, including phytoplankton- or bacterially derived amorphous organic matter, large proportion of living or dead bacteria higher plant resins, and amorphous products of the diagenesis of macrophyte tissue (Plate3-5,3-6,3-7).

The high value of the AOM point to reducing (dysoxic and anoxic) environments with high preservation potential of planktonic organic matter or benthic microbial mat material(Tyson, 1995).

An abundance of AOM in recent marine sediments appears to be especially diagnostic of dysoxic to anoxic facies and is typical of most dysoxic–anoxic source rock facies. The oxygen deficient bases are ideal for AOM preservation (Jones and Demaison, 1982;Jones, 1983).

#### **D-Opaque Group**

The term refers to all structured brownish black-to-black color oxidized or carbonized particles .Once particulate organic matter particles have undergone sufficient maturation or alteration they become opaque. This category of grains appears as mostly homogeneous highly corroded opaque fragments of an elongated shape with sharp angular outlines. The presence or absence of the oxidized or carbonized woody tissue in sediments is very important in environmental interpretation and source rock evaluation.

Inertinite is the product of oxidation of structured materials, generated by the alteration of wood in an oxidizing environment at normal or elevated temperature; sedimentary charcoal is widely accepted to be primarily the product of Pyrolysis of mainly land plant matter during wildfires. Wild fires are important biologically because they occur in abroad range of terrestrial environments including swamps and bogs, where accumulated peat may also burned most argillaceous deposits, regardless of environment of deposition; contain at least a few minute oxidized and/or reworked black particles (Batten, 1996). Fragment of woody material inorganic residues from semioxidizing environment range from dark brown to black in color and from translucent at the edges to completely opaque in aspect. Inertinite cannot, however, be produced by bacterial decay in a reducing environment. Inertinite is chemically very stable and is frequently preserved as a product of recycling. Being composed of carbon, it has no source rock potential. Although Inertinite is chemically inert and not potential for hydrocarbon in undertaken project is a good parameter to indicate the pre-depositional environment recognized in determination of palynofacies types (Pocock *et al*, 1987).

#### **3.14.4. RESULTS AND DISCUSSION**

It's obvious from previous presentation of the palynofacies that the main contents are amorphous organic matters, phytoclast and palynomprph(Plate 3-1,3-2,3-3,3-4,3-5,3-6,3-7) and from their statistical treatments ;the sedimentary paleoenvironment is diagnosed according to the percentages of organic matters on Tyson (1995) triangle (APP).From the AOM-Phytoclast Palynomorph ("APP") ternary plot (Figure 3-15) ,it is clear that most of the samples plotted in AOM dominated the field IX-field that is usually associated with distal suboxic-anoxic basin(Tyson, 1995) .This facies is characterized by the dominance of amorphous organic matter assemblages and low abundance of palynomorphs partly due to masking, frequently alginate-rich. Deep basin or stratified shelf sea deposits, especially sediment starved basins. Spores and pollens are low and microplanktons are generally low and prasionphytes are often dominant. Table 3-5 represents the percentages of the three groups (Amorphous- Phytoclast –Palynomorph ) in the studied wells . In the studied formation, the sedimentary organic matter is amorphous up to 93% due to degradation caused by bacteria and its distal marine environment (offshore).The organic matter is preserved in good way because it is far from water circulation with the presence of bacterial activity in the previously mentioned facies, which made the percentage of amorphous organic matter very high.

According on the indications gathered from geochemical and palynological analyses for Yamama Formation, the (TOC) fair and kerogen type (II/III) according to (Tissot and Welte, 1984).

The mentioned results lead to the interpretation of gas and oil generation ability of Yamama Formation.

Table 3-4: Distribution of the various particulate organic matter (P	OM)
recorded from the Nasiriyah oil field.	

Sample	Well	Douth(m)	AOM	Phytoclast	Palynomorph	Opaques
No.	Name	Deptn(m)	%	%	%	%
1	NS-1	3228.4	95	3	2	0
2	NS-1	3285.2	95	4	1	0
3	NS-1	3378.2	97	2	1	0
4	NS-1	3385	100	0	0	0
5	NS-2	3371.1	94	4	2	0
6	NS-2	3346.5	96	3	1	0
7	NS-2	3186.2	95	2	3	0
8	NS-2	3277.55	95	4	1	0
9	NS-3	3366.8	97	2	1	0
10	NS-3	3291	98	1	1	0
11	NS-3	3404.6	99	1	0	0
12	NS-3	3210.7	96	2	2	0
13	NS-5	3196.6	93	5	2	0
14	NS-5	3291.3	95	4	1	0
15	NS-5	3378.4	98	2	0	0
16	NS-5	3303.55	100	0	0	0

Plate 3-1: Sedimentary Organic Matters of Yamama Formation Palynomorph (Dinoflagellates).



**(a)** 





(c)



**(d)** 

- a) NS-2, depth 3404 m, Dinoflagellates
- b) NS-3, depth 3291 m, Dinoflagellates
- c) & d) NS-1, depth 3285 m, Dinoflagellates

Plate 3-2: Sedimentary Organic Matters of Yamama Formation ,Palynomorph (Spore).



**(a)** 





(c)



**(d)** 

- a) NS-3, 3404 depth m, Verrucosisporites sp.
- b) 2&4NS-2, depth 3346m, depth 3277.5m, Verrucosisporites sp.
- c) 3 NS-2, 3371 depth m, Cyathidites australis

Plate 3-3: Sedimentary Organic Matters of Yamama Formation Palynomorph (Pollen).



**(a)** 





(c)



**(d)** 

(a) & (b) & (d) NS-3, depth 3404, depth 3210 m,Cycalapites pollen (c) NS-2,depth 3182m , Pollen Plate 3-4: Sedimentary Organic Matters of Yamama Formation (Phytoclast).









**(c)** 

- a) NS-1, depth 3228.2 m, Phytoclast (Cuticle)
- b) NS-3, depth 3366 m, Phytoclast (Cuticle)
- c) NS-5, depth 3378.5m, Phytoclast (Trachied)

Plate 3-5: Sedimentary Organic Matters of Yamama Formation (Amorphous).



**(a)** 

**(b)** 



(c)



**(d)** 

- a) NS-1, depth 3385 m, Amorphous
- b) NS-2, depth 3186 m, Amorphous
- c) NS-3, depth 3404.6 m, Amorphous
- d) NS-5, depth 3303 m, Amorphous

Plate 3-6: Sedimentary Organic Matters of Yamama Formation (Degraded organic matter).





- a) NS-1, depth 3285.2 m, degraded organic matter
- b) NS-5, depth 3291.3 m, degraded organic matter
- c) NS-2, depth 3277.55m, degraded phytoclast

Plate 3-7: Sedimentary Organic Matters of Yamama Formation (Foraminifera test lining)FTL.









(c)



- a) NS-2, depth 3346.5 m, Foraminiferal test lining.
- b) NS-2, depth 3277.55 m, Foraminiferal test lining.
- c) NS-3, depth 3291 m, Foraminiferal test lining.
- d) NS-5, depth 3196.6 m, Foraminiferal test lining.



Figure 3-15: The Palynofacies of Yamama Formation in NS-1, NS-2, NS-3and NS-5 (after Tyson, 1995).

# **CHAPTER FOUR**

# WELL LOG ANALYSES AND INTERPRETATION

## **CHAPTER FOUR**

## WELL LOG ANALYSES AND INTERPRETATION 4.1 Preface

The chapter discusses how different log types measure various properties in the boreholes and surrounding formations, what factors affect these measurements, where on a standard log display a particular curve is recorded, and how interpreted information is obtained from the logs using both charts and mathematical formulas.

As logging tools and their interpretation methods are developing in accuracy and sophistication, they are playing an expanded role in the geological decision- making process. Today, petrophysical log interpretation is one of the most useful and important tools available to petroleum geologist (Asquith and Krygowski, 2004)

Many parameters or different parameters can be recorded such as, formation resistivity, Sonic velocity, density and Radioactivity. The recorded data can then be interpreted to determine the lithology and porosity of the penetrated formation and also the type and quantity of fluids ( oil , gas or water ) within pores. The various log can be used to defined these parameters and to analysis the Stratigraphic Relations .The porosity and oil saturation addition to lithology and subdivision of the reservoir units were estimated in the current study. Gamma ray, self-potential , neutron, density , sonic and resistivity logs were studied in Nasiriyah oil field for fourteenth boreholes :(NS-1, NS-2, NS-3, NS-4, NS-5, NS-6, NS-7, NS-8, NS-9, NS-10, NS-11, NS-12, NS-13, NS-14 ) .The parameters of log interpretation are determined directly or inferred indirectly and measured by one of three types of logs:
#### 1. Electric

- Spontaneous Potential
- Resistivity

### 2. Radioactive

- Gamma Ray
- Density
- Neutron

# **3.** Acoustic or sonic logs

The most common log types that are routinely employed for log analyses (lithology, porosity, fluid evaluation) and stratigraphic correlations are summarized in Table 4.1 (Catuneanu, 2006).

Table 4.1: Types of well logs , properties they measure, and their use for geologic interpretations (Catuneanu, 2006).

Log	Property measured	Units	Geological interpretation
Spontaneous potential	Natural electric potential (relative to drilling mud)	Millivoits	Lithology, correlation, curve shape analysis, porosity
Conventional resistivity	Resistance to electric current flow (1D)	Ohm-metres	Identification of coal, bentonites, fluid types
Micro resistivity	Resistance to electric current flow (3D)	Ohm-metres and degrees	Borehole imaging, virtual core.
Gamma ray	Natural radioactivity (e.g., relater to K, Th, U)	API units	Lithology (including bentonites, coal), correlation, shape analysis
Sonic	Velocity of compressional sound wave	Microseconds/metre	Identification of porous zones, tightly cemented zones, coal
Neutron	Hydrogen concentration in pores (water, hydrocarbons)	Per cent porosity	Porous zones, cross plots with sonic and density for lithology
Density	Bulk density (electron density) (includes pore fluid in measurement)	Kilograms per cubic metre (g/cm <sup>3</sup> )	Lithologies such as evaporites and compact carbonates
Dipmeter	Orientation of dipping surfaces by resistivity changes	Degrees (azimuth and inclination)	Paleoflow (in oriented core), stratigraphic, structural analyses
Callper	Borehole diameter	Centimetres	Borehole state, reliability of logs

#### 4.2 Basic Principles of used well logs

It is important to understand the fundamental principles of well logs used in this study.

#### **4.2.1Electrical Logs**

#### 1. Spontaneous Potential(SP):

The Spontaneous Potential (SP) log was one of the earliest electric log used in the petroleum industry, and has continued to play a significant role in well log interpretation. Primarily the Spontaneous Potential log is used to identify impermeable zones such as shale , and permeable zones such as sand. However the sp log has other uses perhaps equally important which are : detect permeable beds , detect boundaries of permeable beds , determine formation water resistivity  $R_w$  and determine the volume shale impermeable beds(Asquith and Gibson,1982).

The Sp log records the electric Potential setup between an electrode in a sonde drown up the bore hole and fixed electrode at the earth surface (Selley, 1998). It can only be used in open holes filled with conductive mud (Asquith and Gibson, 1982). The electric charge of the SP. is caused by the flow of ions (largely Na and Cl) from concentrated to more dilute solutions. Generally this flow is from salty formation water to fresher drilling mud (Selley, 1998). The factors that are essential to produce an SP current involve : a conductive fluid in the borehole ,a porous and permeable bed surrounded by an impermeable formation, and a difference in salinity (or pressure) between the borehole fluid and the formation fluid. The shale volumes can be calculated mathematically from the self-potential log by the following Schlumberger (1972) formula:

$$Vsh = 1 - \frac{(SP - SPsh)}{(SPcl - SPsh)}$$
(4-1)
Where:

Where:

SP: SP log reading.

SP<sub>sh</sub>: SP log reading in the shale.

SPcl: SP log reading in the clean rock.

The determination of shale volume from self-potential log is unacceptable in the formations that contain hydrocarbons (oil and gas) because this method gives high values of ( $V_{sh}$ ) (Asquith and krygowski, 2004). The Spontaneous Potential in current study is used to determined water resistivity of formation water , formation contact and determine the upper and lower contact of the Mishrif Formation in Nasiriyah oil field .

#### 2. Resistivity Logs

Resistivity is one of the most useful physical properties measured in the borehole. Formation resistivity measurements, in conjunction with porosity and water resistivity, are used to obtain values of water saturation and consequently, hydrocarbon saturation. They are also used in conjunction with lithology logs to identify hydrocarbon bearing intervals and to estimate the net pay thickness.

Resistivity is the degree to which a substance "resists" or impedes the flow of electrical current. It is a physical property of the material, independent of size and shape. In well logging, both resistivity and conductivity are used frequently. One is the reciprocal of the other.

Resistivity (ohms  $m^2/m$ ) = 1×1000/conductivity (millimhos/m) ...... (4.2)

The resistivity unit used in well logging is ohm-meter<sup>2</sup>/meter, which is usually shortened to ohm-meter. Electrical conductivity is expressed in mhos per meter. In order to avoid decimal fractions, in electrical logging, it is expressed in millimhos per meter.

The three main ways of measuring the electrical resistivity of formations penetrated by boreholes are the normal log, lateral and Induction log techniques (Selley, 1998). The electrical resistivity of a formation varies greatly: solid rock is highly resistivity as is porous rock saturated in fresh water, oil or gas, Shale on the other hand and porous formations saturated with salty or brine has very low resistivity. When run simultaneously  $S_P$  and resistivity logs enable qualitative interpretation of lithology and nature of pore fluids to be made. There are two types of resistivity logs to be used:-

- Induction logs used to measured true resistivity from formation (R<sub>t</sub>) or un invaded zone. This log was used to compute water or oil saturation from the un invaded zone, (S<sub>w</sub>,S<sub>h</sub>) by Archi formula.
- 2. Short normal log was used to measured resistivity from flushed zone ( $R_{xo}$ ). These values of resistivity were used to compute water and oil saturation from flushed zone ( $S_{xo}$ ,  $S_h$ ).

#### 4.2.2. Radioactive logs

#### 1. Gamma Ray log:

Gamma ray logs measure natural radioactivity in formation and because of this measurement, they can be used for identifying lithology and for correlating zones. Beside that it provides information for calculating the volume shale in a sandstone or carbonate (Asquith and Gibson, 1982) . Abrupt changes in gamma-ray logs response are commonly related to sharp lithological breaks associated with unconformities and sequence boundaries (Krassay,1998).

Shale-free sandstones and carbonates have low concentrations of radioactive material and give low gamma ray readings. As shale content increases, the gamma ray log response increases because of the concentration of radioactive material in shale. The volume of shale expressed as a decimal fraction or percentage is called V shale (Larionov, 1969).

#### 2. Density log

The formation density log is a porosity log that measures electron density of formation. It can assist the geologist to:

1. Identify evaporate minerals.

- 2. Detect gas bearing zones.
- 3. Determine hydrocarbon density.
- 4. Evaluate shaly sand reservoirs and complex lithologies .

Density is measured in grams per cubic centimeter, g/cm3 (or Kg/m3 or Mg/m3), and is indicated by the Greek letter  $\rho$  (rho). Two separate density values are used by the density log: the bulk density ( $\rho$ b or RHOB) and the matrix density ( $\rho$ ma). The bulk density is the density of the entire formation (solid and fluid parts) as measured by the logging tool. The matrix density is the density of the solid framework of the rock. It may be thought of as the density of a particular rock type (e.g., limestone) that has no porosity. Porosity is derived from the bulk density of clean liquid-filled formations when the matrix density  $\rho$ ma and the density of the saturating fluids  $\rho f$  are known (Asquith and Krygowski, 2004):

Where:

 $\Phi \rho$ = Porosity by density log  $\rho b$  = Formation bulk density (the log reading) f = fluid density (Saltwater mud 1.16)  $\rho$ ma=matrix density

#### 3. Neutron Log:

Neutron logs are porosity logs that measure the hydrogen concentration in a formation. In clean formations (i.e., shale-free) where the porosity is filled with water or oil, the neutron log measures liquid filled porosity ( $\phi$ N) (Asquith and Krygowski, 2004).Older neutron logs were scaled in counts, but modern neutron logs are recorded in apparent porosity units with respect to a given mineralogy (Doveton, 1999).Whenever pores are filled with gas rather than oil or water , neutron porosity will be lowered ,this occurs because there is less concentration of hydrogen in gas compared to oil or water .Neutron log responses vary depending on :

- 1. Differences in detector types.
- 2. spacing between source and detector
- 3. Lithology i.e. sandstone , limestone and dolomite(Asquith and Gibson, 1982).

#### 4.2.3. Acoustic or Sonic logs

The sonic tool measures the interval transit time (t) or the time in microseconds for an acoustic wave to travel through 1 feet (or 1 m) of a formation along a path parallel to the borehole. The interval transit time ( $\Delta$ t) is dependent upon both lithology and porosity .In this technique interval transit time are recorded of clicks emitted from one end of the sonde travelling to one or more receivers at the other end . The sound waves generally travel faster through the formation than through the borehole mud (Selley , 1998) .To calculate porosity Wyllie time-average equation can be used (Wyllie *etal.*, 1958):

$$\Phi_{s} = (\Delta t - \Delta t_{ma}) / (\Delta t_{f} - \Delta t_{ma})$$
(4-4)

Where:

 $\Phi_s$ = sonic-derived porosity

 $\Delta t_{\rm f}$ = interval transit time of the formation fluid ( salt water mud= 185 µsec/ft).  $\Delta t_{\rm ma}$ = interval transit time of matrix , $\Delta t$ = interval transit time in the formation, we can get the matrix velocity values by using Table (4-2) (Schlumberger, 1972). Table 4-2: Sonic Velocities and Interval Transit Times for Different Matrixes. These constants are used in the sonic porosity formulas above (Schlumberger, 1972).

Lithology/Fluid Matrix Velocity ft/sec		Δt <sub>matrix</sub> orΔt <sub>fluid</sub> (Wyllie) μsec/ft[μsec/m]	Δt <sub>matrix</sub> (RHG) μsec/ft[μsec/m]
Sandstone	18,000 to 19,500	55.5 to 51.0 [182 to 186]	56[184]
Limestone	21,000 to 23,000	47.6[156]	49[161]
Dolomite	23,000 to 26,000	43.5[143]	44[144]
Anhydrite	20,000	50.0[164]	
salt	15,000	66.7[219]	
Casing(iron)	17,500	57.0[187]	
Freshwater mud filtrate	5,280	189[620]	
Saltwater mud filtrate	5,980	185[607]	

The interval transit time ( $\Delta t$ ) of a formation is increased due to the presence of hydrocarbons (i.e., hydrocarbon effect). If the effect of hydrocarbons is not corrected, the sonic-derived porosity is too high (Selley,1998). Hilchie (1978) suggests the following empirical corrections for hydrocarbon effect:

$\Phi = \Phi_{\rm s} * 0.7$	(gas)	(4-5)
$\Phi = \Phi_{\rm s} * 0.9$	(oil)	(4-6)

 $\Phi = \text{porosity}$ 

 $\Phi_s$  =sonic-derived porosity.

# 4.3 Interpretation of log and their reservoir applications:

The interpretation of results is made through direct reading as well as through established relationships in order to find the important lithological and petro physical properties.

#### **4.3.1.** The Direct Applications:

#### 4.3.1.1. The Stratigraphic Boundaries:

The recent study depends on many log types to determine the upper and lower boundaries of the studied formations Table (4-3,4-4).

- **SP log :**The Sp log is a reading or recording of positive values (right side) in the upper and the lower part of Mishrif Formation(Figure4-1).In Yamama Formation the reading record negative values (left side) in the upper boundaries , and positive deflection (right side ) in the lower boundaries(Figure4-2)
- **Resistivity log :**  $R_{xo}$  and  $R_t$  log of Mishrif Formation deflect toward the right (high resistivity) in the upper contact, the decreasing in readings (low resistivity) occurs in the lower contact. In Yamama Formation the  $R_{xo}$  and  $R_t$  log deflect (right side) "increasing in recording at the upper and lower contact".
- **Porosity log** ( **Neutron , density and sonic** ): low porosity is observed in the upper and lower contact in Mishrif and Yamama Formations .
- **Gamma ray log:** gradual deflection (decrease to left) is observed in the upper Mishrif and Yamama Formations ,and the recording increases (right side ) at the lower parts of these formations( Figure4-1,4-2).

Wells	Тор	Bottom	Mean of Phi	Mean of SW
NS-1	1915	2086	0.23	0.28
NS-2	1908	2076	0.23	0.32
NS-3	1916	2088	0.21	0.31
NS-4	1913	2090	0.25	0.32
NS-5	1905	2085	0.27	0.20
NS-6	1906	2080	0.2	0.27
NS-7	1904	2076	0.23	0.21
NS-8	1897	2039	0.23	0.24
NS-9	1897	2065	0.25	0.22
NS-10	1893	2073	0.23	0.18
NS-11	1909	2075	0.23	0.21
NS-12	1910	2075	0.22	0.23
NS-13	1911	2085	0.21	0.22
NS-14	1904	2083	0.24	0.2

# Table 4-3: Top , bottom, Phi ,and Sw of Mishrif Formation in the Present

Study.

Table 4-4: Top, Bottom, Mean of Phi and Sw of Yamama Formation in
the Present Study.

Wells	Тор	Bottom	Mean of Phi	Mean of Sw
Ns-1	3178	3420	11.1%	47.5%
Ns-2	3158	3386	12.45%	48%
Ns-3	3179	3422	9.45%	47%
Ns-4	3165	3391	12.55%	41%
Ns-5	3170	3390	11.58%	46.5%



Figure 4-1 : Types of logs that show the stragraphic boundaries of Mishrif Formation.



Figure 4-2 : Types of logs that show the stragraphic boundaries of Yamama Formation NS-3.

#### 4.3.1.2. Primary and Secondary Porosity

Porosity can be defined as the percentage of voids to the total volume of rock. It is measured as a percent and expressed as the symbol ( $\phi$ ) Phi. Porosity ( $\phi$ )= Volume of pores /total volume of rock ×100% ......(4-7) The primary porosity is the amount of pore present in the sediment at time of deposition. It is usually a function of the amount of space between rock – forming grains (Halliburton, 2001) .The sonic porosity represents the primary (intergranular) porosity ( Asquith and Gibson, 1982 ) .Secondary porosity (vuggy , moldic , channels and fracture ) are the result of geological processes (diagenesis) after the deposition of sediments (Tiab and Donaldson, 2004 ). It computed by this formula (Schlumberger, 1997). SPI=  $(\Phi_{n,d} - \Phi_s)$  ......(4-8)

Where:

SPI = secondary porosity index

 $\Phi_{n,d}$  = neutron-density properties combination

 $\Phi_s$  = sonic-derived porosity.

The secondary porosity index (SPI) may be computed as the difference between total porosity as determined from Neutron and/or Density logs, and primary porosity obtained from sonic log.

When sonic properties are compared with neutron and density properties the total porosity can be subdivided between primary recorded by the sonic log, and secondary porosity .The type of porosity in the Mishrif and Yamama Formations in Nasiriyah field is mainly a primary porosity with less effect of secondary porosity (Table 4-3,4-4) .The low values of secondary porosity means absence of the effect of digenesis processes on the porosity of these formations such as dolomitization and dissolution. The recognized types of porosity from available core sample from Mishrif Formation are Moldic , Fracture, dolomitic ,Vuggy and intragranular (Plates 1,2,3,4) appendix , whereas the porosity types in Yamama Formation involved : Moldic, Stylolite, Channal and Intragranular (Plates 5,6,7,8) appendix .The porosity value in Mishrif Formation increase in NS-5,NS-14,NS-9 and decrease in NS-1, NS-2,NS-6( Table4-3) . In Yamama Formation the porosity increases in NS-2,NS-4 ,NS-5 and decrease NS-1 and NS-3( Table4-4) .

#### 4.3.1.3 Water and hydrocarbon Saturation

Fluid saturation is usually obtained from resistivity logs. Different resistivity logs with variable fluid saturation occur at different distances from the borehole wall. A micro resistivity log is used to obtain the resistivity in the flushed zone behind the borehole wall while deep resistivity device (induction or lateral logs) is used to obtain the resistivity in the virgin (un invaded) zone. Fluid saturation is estimated from resistivity measurement by the Archi equation. This equation relates the resistivity of the formation to the porosity, water saturation and resistivity of the water formation (Archie, 1942).Archie determined experimentally that the water saturation in the following formula:

$$S_w = (F R_w/R_t)^{1/n}$$
 .....(4-10)

 $S_w$  = water saturation of un-invaded zone F= Formation factor  $R_w$ = resistivity of water ohm-m<sup>3</sup>/m  $R_t$ =resistivity of the un invaded zone ohm-m<sup>3</sup>/m n=usually taken as 2

The water saturation could be calculated for the invaded zone in the following formula:

$$S_{xo} = (F R_{mf}/R_{xo})^{1/n}$$
 .....(4-11)

 $S_{xo}$ = water saturation of the un-invaded zone

F= Formation factor

 $R_{mf}$  = resistivity of mud infiltrate ohm-m<sup>3</sup>/m

 $R_{xo}$  = resistivity of invaded zone ohm-m<sup>3</sup>/m

n= usually taken as 2

 $R_t$  is obtained from the deep resistivity log, and  $R_{xo}$  is obtained from the microsferical resistivity log.

Formation factor is the constant of proportionality of resistivity of clean formation with the resistivity of the brine with which is fully saturated. Archie proposed the formula (Schlumberger., 1972):

 $F = a/\phi^m$  .....(4-12)

Where m is the cementation factor, it equal to 2 in carbonate, and (a) is constant and equal to 1 in compacted formation.

The  $R_{mf}$  is known for bottom hole temperature and it should be corrected for formation temperature. The temperature gradient is required in order to calculate formation temperature:

Where G is temp gradient, BHT is bottom hole temp., ST is surface temp., and TD is total depth. Now Formation temp. Could be calculated: FT= G\*Fd+ST .....(4-14)

Where FT is formation temp., and Fd is formation depth. The  $R_{mf}$  could be corrected for the Formation temp. Using the following equation:

 $R_{mf Formation} = R_{mf temp} * (BHT.+6077)/(FT+6.77)$  .....(4-15)

Where  $R_{mf temp}$  is the resistivity of  $R_{mf}$  at known temp., which is the BHT. The  $R_w$  could be calculated in more than one way. The recent study calculates the  $R_w$  from the SP log. (Shlumperger., 1997).  $R_w$  at 75°F=(77\* $R_{we}$ +5)/(146-377\* $R_{we}$ ) .....(4-16)

Where  $R_{we}$  is the equivalent water resistivity and it could be calculated using:

$R_{we} = R_{mfe} / (10 - SSP/K)$	(4-17)
Where:	
K = 60 + (0.133 * ST)	(4-18)

SSP is the static SP curve and it could be calculated by knowing the difference between the maximum negative deflection and the opposite positive deflection (shale base line) for thick permeable bed (Shlumberger, 1972).

 $R_{mfe}$  is the equivalent resistivity of mud infiltrate, and it`s could be calculated by computing the  $R_{mf}$  at 75°F then:

$$R_{mfe} = R_{mf} * 0.85$$
 .....(4-19)

After calculating  $R_w$  at 75°F it is converted to the formation temperature using equation (4-16)

After calculating  $S_w$ , the saturation of hydrocarbon could be calculated using:

```
S_{h}=1-S_{w} .....(4-20)
```

Where  $S_h$  is the hydrocarbon saturation.

The figures 4-3, 4-4 show the values of  $S_w$  and  $S_h$  in NS-3, NS-5 in Mishrif Formation. Figure 4-5 show the values of  $S_w$  and  $S_h$  in NS-3 in Yamama Formation.



Figure 4-3: The  $S_{\rm w}$  and  $S_{\rm h}$  of Mishrif Formation in NS-3



Figure 4-4: The  $S_{\rm w}$  and  $S_{\rm h}$  of Mishrif Formation in NS-5



Figure 4-5: The  $S_{\rm w}$  and  $S_{\rm h}$  of Yamama Formation in NS-3

#### 4.3.1.4 Bulk Volume Water

The product of a formation's water saturation (Sw) and its porosity ( $\Phi$ ) is the bulk volume of water (Asquith and Gibson,1982). On the other hand, the bulk volume of water can be computed in the flushed zone using the following formula (Schlumberger, 1984) :

$BV_W = S_W * \Phi$	(4-21)
$BV_{Xo} = Sxo * \Phi$	(4-22)
Where:	
BV <sub>w</sub> = bulk volume water of un-invaded zone	
$BV_{Xo}$ = bulk volume water of flushed zone	
Sw= water saturation of un-invaded zone	
Sxo = water saturation in the flushed zone	
$\Phi = \text{porosity}$	

If values for bulk volume water, calculated at several depths in a formation, are constant or very close to constant, they indicate that the zone is of a single rock type and at irreducible water saturation ( $S_{wirr}$ ). When a zone is at irreducible water saturation, water in the un-invaded zone ( $S_w$ ) does not move because it is held on grains by capillary pressure (Morris and Biggs, 1967). Therefore, hydrocarbon production from a zone at irreducible water saturation should be water free (Morris and Biggs, 1967). Because the amount of water formation can hold by capillary pressure increases with decreasing grain size, the bulk volume water also increases with decreasing grain size. The bulk volume water values for carbonates should be used only as a very general guide to different types of porosity (Asquith and Krygowski, 2004).

Bulk volume of hydrocarbon represents the moveable hydrocarbon saturation  $(S_{hm})$  and residual hydrocarbon saturation  $(S_{hr})$  (unmovable) (Figure4-6). The bulk volume of hydrocarbon is calculated from the following equation (Asquith and Krygowski, 2004):

Where:

 $Bv_o$  =bulk volume of hydrocarbon S<sub>h</sub>=hydrocarbon saturation

 $\Phi$ =porosity

To calculate residual hydrocarbon saturation  $(S_{hr})$  (unmovable) the following equation should be used (Asquith and Krygowski, 2004):  $S_{hr} = 1-S_{xo}$  ......(4-24)

Where:

 $S_{hr}$  = residual hydrocarbon saturation  $S_{xo}$  = water saturation in the flushed zone To calculate a moveable hydrocarbon saturation  $(S_{hm})$  the following equation should be used (Asquith and Krygowski, 2004):

$$S_{hm} = S_{xo} - S_w$$

.....(4-25)

The restricted place between  $BV_w$  and  $BV_{xo}$  represents the moveable hydrocarbons but between  $\phi$  and ( $\phi$ .  $S_{xo}$ ) represents the residual hydrocarbons and between the  $\phi$  and ( $\phi$ . $S_w$ ) represents the bulk hydrocarbons (Schmidt *etal.*, 1971)



Figure 4-6:  $S_{hm}$  and  $S_{hr}$  of Mishrif Formation in NS-14

#### 4.3.1.5 Volume of Shale (Vshale ):

The volume of shale very importance on water saturation but must be greater 10-15% (Hilchie, 1978)(Asquith,1982).The Gamma ray index IGR is computing by Shlumberger (1978)

I GR = Gamma ray index

 $GR \log = Gamma ray recorded by \log (API)$ 

GR max = Maximum value of Gamma ray.

GR min = Minimum value of Gamma ray.

The Volume of shale (V. Shale) computing by :- (Dresser Atlas, 1979)

 $V_{sh} = 0.33 (2 \times (2 \times IGR) - 1)$  .....(4-27)

Figures 4-7, 4-8,4-9, 4-10 show that the volume of shale , from these figures remark that there is a unit barrier shale rock in all studied wells in the Mishrif Formation .In Yamama Formation there is three barriers of shale rock.



Figure 4-7 : The shale volume of Mishrif Formation in NS-3



Figure 4-8 : The shale volume of Mishrif Formation in NS-5



Figure 4-9 : The shale volume of Mishrif Formation in NS-1



Figure (4-10) : The shale volume of Mishrif Formation in NS-2

**4.3.2** The indirect applications of well logs (from the equations and the Cross plots),the Determination of Lithology using Density vs. Neutron cross plot:

The employment of the cross plot of the different logs is used in determination of various parameters including the lithology and the active zone. The neutron-density cross plot is one of the oldest quantitative interpretation tools, this is considered important and very frequently used which provides satisfactory resolution of porosity, good lithological resolution for quartz, calcite, and dolomite (Ellis and Singer, 2008).

From figures (4-11, 4-12) most points fall on limestone line, only a few points fall on the dolomite line and in (NS-8) there is few points in sandstone line that indicate that the lithology of Mishrif Formation is limestone.



Figure 4-11: Density vs. Neutron cross plot for Mishrif Formation in NS-8



Figure 4-12: Density vs. Neutron cross plot for Mishrif Formation in NS-13

#### 4.4. Evaluation of the Units of Mishrif Reservoir

Mishrif Formation in Nasiriyah oil field consists mainly of porous limestone (ranging from mudstone to grainstone), chalky limestone and thin beds of shale.

Figures (4-13, 4-14,4-15,4-16,4-17,and 4-18) show the computer interpretation (CPI) of NS-4, NS-5, NS-7, NS-10, NS-11,NS-12, NS-13,andNS-14 that are deduced using Interactive Petro physics (IP)software. These figures show the petrophysical properties and fluids analysis of Mishrif Formation which has been deduced by interpretation of well logs.

From figures of (CPI) for Nasiriyah wells, Mishrif Formation is divided into three units separated by barrier beds (seal rock) according to the reservoir characteristics (porosity and saturation). Table 4-3 represents unit tops and barrier beds of Mishrif Formation.

The reservoir includes the following units:

- CRI: consists mainly of compact limestone, which is significant of large ratio of muddy materials. In spite of the high porosity ,this unit lack the characteristics of a good reservoir .The thickness of this unit in Al-Nasiriyah oil field ranged from (2-13)m.
- MA : consists of Mudstone, Wackstone and Packstone ,it also has a good porosity (15)%,but abominable permeability due to the existence of the micrite facies ,the thickness of this unit in Al-Nasiriyah oil field ranges from (52-63)m. it extend in all of the studied wells.
- CRII: it's a good seal rock (barrier bed) between MA and MBI unit. Mainly composed of Shale, it has abominable reservoir characteristics with about(9-13)m in thickness with regional extension .
- MB1 : it is considered the main reservoir of the Mishrif Formation in Nasiriyah oil field, formed of limestone with good reservoir characteristics ,Grainstone and Wackstone .The porosity of this unit is about 20% and about (54-71)m in thickness (Figure 4-19).
- MB2: generally composed of Mudstone and Micrite, the abominable permeability made it a bad reservoir in spite of its good porosity (23)%. This unit is subdivided in to two parts: the upper part is saturated with hydrocarbons, with a thickness of (36-52)m .There is no clear barrier between this part of this unit and MB1 ,So this part is connected in reservoir with MB1 , the lower part of MB2 saturated with water and with thickness of about (30-40.5)m. (Figure4-20). Figure 4-21 shows the correlation of the previous units in the studied wells.

Main focus of this study is on the MB1 unit, This reservoir unit represents oil bearing unit in the Mishrif Formation and characterized by good oil show due to high porosity and low water saturation. The reservoir unit MB2 is characterized by moderate hydrocarbon shows but tends to have good oil shows where the porosity increases and water saturation decreases. The MA unit is not a reservoir because of the presence of the Micrite facies which made the oil unable to remove the intermediate water.



Figure 4-13: Mishrif Formation units in NS-4



Figure (4-14) : Mishrif Formation units in NS-5



Figure 4-15 : Mishrif Formation units in NS-7



Figure 4-16 : Mishrif Formation units in NS-10



Figure 4-17: Mishrif Formation units in NS-11



Figure 4-18: Mishrif Formation units in NS-12



Figure 4-19:Isopach Map of(MB1) unite of Mishrif Formation .



Figure 4-20:Isopach Map of(MB2) unite of Mishrif Formation .



Figure 4-21 :Correlation of Mishrif Formation units in the studied wells.

# 4.5 Evaluation of Yamama Reservoir units:

Figures (4-22, 4-23, 4-24) show the computer processes interpretation (CPI) of NS-1, NS-2, and NS-3 that are deduced using Interactive Petro physics (IP) software.

From figures of (CPI) for Nasiriyah wells, Yamama Formation is divided into four units separated by three barrier beds (seal rock) according to the reservoir characteristics (porosity and saturation).Tables 4-4 & 4-5 represent unit tops and barrier beds of Yamama Formation.

The reservoir including the following units:

- YA: Poor to good reservoir rock type possibly mud-packstone dominated .It varies laterally.Its thickness in the studied fields is about (45-47) m and the porosity is 9%.
- **YB1**: Good to best reservoir rock type zone reservoir, its thickness in all the studied fields is about (26-28) m and the porosity is 10%.

- **YB2:**Good to best reservoir rock type zone, dominant in NS-1 and NS-2 Reservoir.It varies laterally. Its thickness in all the studied fields is about (40-42)m and the porosity is 15%.
- **YB3:**Good to best reservoir rock type zone, Worse reservoir quality In NS-3.It varies laterally; its thickness in all studied fields is about (29-59) m and the porosity 13%.

The main focus in the studied wells is on the unit YB2and YB3 since they have good porosity and permeability (Table 4-5).

Yamama units	Thickness (m)	Porosity %	SW %
Yamama A	47	9	29
Yamama B1	26	10	44
Yamama B2	40	15	44
Yamama B3	45	13	37

Tabl 4-5 : Thickness, Porosity, Permeability and SW of Yamama units

				MovedHycrocarbon	Gas
				Water	Cerbonate
			PHOB	OI	BoundWater
			NPH 045. or cm015	Gas	Clay 1
GR	MD 1:1200	SFL WELLEDITS	DT	Elan Fluid Analysis	PVP_FINAL_OUTPUTS E
u (gAPI) iuu	m	uz (chm.m) ≥uuu	(us/ft) 40	· (V/V) ·	(V/V) u
TOP VARIANT		- had	A ANTANA		
Anna	3200	Relative Autom		Arthony a	
BEP YAMAMA_BI	3280				
	3300			MIN MANA	
DP VAMAMA_BS	3350		A CONTRACTOR		
	3400	A WWW WWWW		Mary Anna Anna Anna Anna Anna Anna Anna Ann	

Figure 4-22: Yamama Formation units in NS-1

			8	MovecWate	OI
				MovadHychocarbon	Gas
				Water	Certonati
	weshout		RHOB	0	BoundWate
	CALI WE 6 (in) 16	SFLSFL@GEOSHA	NPH 0.45(m3/m2) <sup>-0.15</sup>	Ges	Cisy 1
GR 0 (gAPt) 100	HD 1:1500 m	LLD 02 (ohmm) 2000	DT 140 (us/ft) 40	Elan Fluid Analysis 1 (V/V) 0	VP_FINAL_OUTPUTS E
9					
			-	3	
- THE AMAINA A	3150				
the	ile:				
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Mary In	¥250				
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we have a second	3300				
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	3350	and the second s	- Carl	4	
BATTOM YAMAMA_BS				1	

Figure 4-23 : Yamama Formation units in NS-2



Figure 4-24 : Yamama Formation units in NS-3

# **CHAPTER FIVE**

# CONCLUSIONS AND RECOMMENDATIONS

# **CHAPTER FIVE**

# **CONCLUSIONS AND RECOMMENDATIONS**

# **5.1. Conclusion:**

- The geochemical analyses of Mishrif reservoir crude oils of Nasiriyah Oil Field show that oil samples could be rated to one family, and these oils are non-biodegraded, marine, and non-waxy derived from carbonate deposited in marine environment.
- 2. Rock-Eval Pyrolysis data analysis of Sulaiy Formation in the studied well (NS-1) has reached the immature to early stage of maturation to generate hydrocarbons and has capability to produce oil (type II/III kerogen).Sulaiy Formation lies within the oil window while the rocks of Yamama Formation have low thermal maturation, and contain fair total organic matter, and depending on the face study in NS-1, Yamama Formation has kerogen type II/III.
- 3. The source of all oil samples of Nasiriyah oil Field are from Middle Jurassic-late Cretaceous source rocks. Hence the most appropriate source for this crude oil mainly Sargelu Formation.
- 4. Study of seismic sections in Nasiriyah area illustrates minor occurrence of fractures in the Cretaceous Formations and faults in the Jurassic Formations that reached to Gotnia; these faults act as pathways for vertical and horizontal migration of hydrocarbon from Middle Jurassic Sargelu Formation to Cretaceous-Miocene traps such as Yamama, Nahr Umr and Mishrif, reservoirs.
- 5. Interpretations of logs refer to an important of Mishrif and Yamama Formations as reservoirs in Nasiriyah oil field. The oil bearing unit in Mishrif Formation is MB1 while it is YB2 and YB3 in Yamama Formation
#### **5.2. Recommendations:**

1- Making seismic imaging to get more information about the fault systems in the studied area and their contribution as a migration pathway to predict new traps.

2- Employ studies to correlate the analyzed crude oil with the surrounding oil fields of Al- Karaff , Al-Raffiden ,Al-Samawa and Diwan oil field and correlated them with the crude oil of the current study.

3- Studies about the burial and tectonic history of this interested area in order to give more clear picture for other oil pays.

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# APPENDIX

# **Porosity Slides**

**Plate 1: Mishrif Formation** 

a: Wackestone ,Moldic Porosity Well:NS-1 Depth :2033.5 m **4**x **b:** Wackestone , Moldic Porosity Well:NS-1 Depth :2024.3 m **4**x c:: Wackestone ,Moldic Porosity Well:NS-1 Depth :2047.8 m **4**x

**Plate 1: Mishrif Formation** 



**(a)** 





#### **Plate 2: Mishrif Formation**

a: Wackestone ,Dolomitic Porosity Well:NS-1 Depth :2033.5 m **4**x **b:** Wackestone , Dolomitic Porosity Well:NS-1 Depth :2024.3 m **4**x c: : Wackestone , Grainstone , Dolomitic Porosity Well:NS-1 Depth :2024.3 m **4**x d: Wackestone, Dolomitic Porosity Well:NS-1 Depth :2047.8 m **4**x





**(a)** 







**(d)** 

#### **Plate 3: Mishrif Formation**

a: Wackestone ,Vuggy Porosity with oil show Well:NS-1 Depth :2033.5 m **4**x b: Wackestone, Vuggy Porosity with oil show Well:NS-1 Depth :2047.8 m **4**x c:: Wackestone, Vuggy Porosity with oil show Well:NS-1 Depth :2047.8 m **4**x d: Wackestone, Vuggy Porosity Filled with fossils Well:NS-1 Depth :2033.5 m **4**x





**(a)** 







**(d)** 

## **Plate 4: Mishrif Formation**

a: Wackestone, Intergranular Porosity Well:NS-1 Depth :2033.5 m **4**x **b:** Wackestone , Intergranular Porosity Well:NS-1 Depth :2024.3 m **4**x c: : Wackestone Intergranular Porosity Well:NS-1 Depth :2033.5 m **4**x

# Plate 4



**(a)** 





#### **Plate 5 : Yamama Formation**

a: Wackestone ,Stylolites Porosity Well:NS-5 Depth :3175 m **4**x **b:Mudstone**, Stylolites Porosity Well:NS-3 Depth :3262 m **4**x c: Mudstone ,Stylolites & Moldic Porosity Well:NS-2 Depth :3249 m **4**x d: Mudstone ,Stylolites & Moldic Porosity Well:NS-1 Depth :3240 m

**4**x

**Plate 5:Yamama Formation** 



**(a)** 







(**d**)

#### **Plate 6 : Yamama Formation**

a: Packstone, Grainstone, Intergranular Porosity Well:NS-5 Depth :3270 m **4**x b: Packstone, Grainstone, Intergranular Porosity Well:NS-5 Depth :3175 m **4**x c: : Packstone , Grainstone , Intergranular Porosity Well:NS-3 Depth :3219.7 m **4**x d:: Packstone, Grainstone, Intergranular Porosity Well:NS-1 Depth :3240 m **4**x

# Plate 6



**(a)** 







**(d)** 

## **Plate 7 : Yamama Formation**

a: Wackestone , Sandstone ,Fracture simple rupture Porosity Well:NS-2 Depth :3361 m 4x b: Wackestone , Sandstone ,Fracture simple rupture & Vuggy Porosity Well:NS-2 Depth :3342 m 4x

# Plate 7



**(a)** 



# **Plate 8: Yamama Formation**

a: Wackestone ,Moldic Porosity
Well:NS-5
Depth :3175 m
4x
b: Wackestone , Moldic Porosity
Well:NS-1
Depth :3240 m
4x
c: : Wackestone , Grainstone , Channel & Moldic
Porosity
Well:NS-3
Depth :3262m
4x
d: Wackestone, Moldic Porosity
Well:NS-1
Depth :3240 m
4x

XXI

# Plate 8



**(a)** 







**(d)**
المستخلص

يقع حقل الناصرية في محافظة ذي قار في جنوب العراق إلى الشرق من نهر الفرات ويبعد حوالي ٣٨ كيلومتر شمال غرب مدينة الناصرية . تم اكتشاف الحقل من قبل شركة النفط الوطنية العراقية عام ١٩٧٥ . يتضمن الحقل اربعة عشر بئرا وجميع تلك الأبار تصل إلى تكوين المشرف بينما خمسة منها تصل إلى تكوين اليمامة العميق (بئر الناصرية ١، ٢، ٣، ٤، ٥) وبئر واحد فقط (الناصرية ١) يصل إلى تكوين سلي .

استخدمت تقنية ( الغاز كروماتوغراف والغاز كروماتوغراف الطيف الكتلي) لتحليل نماذج النفط الخام الماخوذة من (١٠) ابار منتجة والتي تضمنت (الناصرية – ١، ٢، ٣، ٤، ٥، ٦، ٧، ٨، ٩، ١٠، ١٢) من تكوين المشرف وبينت التحاليل ان نماذج النفط تعود الى عائلة واحدة ، غير متاكلة حيويا ، غير شمعية ، تولدت من ترسبات صخور مصدرية كاربونية ترسبت في بيئة بحرية غير متهوية .

تم اخذواحد وثلاثون انموذج من اللباب الصخري من البئر ( ناصرية - ١ ) من تكوين اليمامة وسلي لأجراء تحاليل التكسر الحراري واشارت النتائج الى ان صخور تكوين سلي ذات محتوى كاربوني عضوي يتراوح من فقير الى جيد وبجهد توليد من فقير الى مناسب وكيروجين من نوع III/II . بينما المحتوى الكاربوني العضوي لتكوين اليمامة مناسب وبجهد فقير لتوليد النفط . التحليل السحني لتكوين اليمامة بين وجود بيئة واحدة فقط هي بيئة الحوض شبه المؤكسد - الاخترالي البعيد ومن نتائج تحليل التكسر الحراري والسحني للتكوين السابق الذكر تبين ان نوع الكيروجين هو III/II.

المقاطع الزلزالية لمنطقة الدراسة اظهرت وجود فوالق في تكاوين الجوراسي تخترق تكوين القطنية ووجود تكسرات في تكاوين الكريتاسي وهذه الفوالق والتكسرات قد تكون هيات الظروف لهجرة النفط المتولد الى الاعلى مما يشير الى ان اصل الصخور المصدرية للنفط في حقل الدراسة بشكل رئيسي من تكوين ساركلو.

باستخدام برنامج (IP) Interactive Petrophsyics (IP) تم تفسير قراءات المجسات لمنطقة بالسراسة في تكويني المشرف واليمامة واظهرت التفسيرات ان تكوين المشرف يتكون بشكل اساسي من المحر الجيري وقليل من الدولومايت وينقسم هذا التكوين الى اربع وحدات هي MA, MB1, الحجر الجيري وقليل من الدولومايت وينقسم هذا التكوين الى اربع وحدات هي MB2, MB3 وان الوحدة الاساسية المنتجة للنفط هي MB1، بينما التفسير للمجسات في تكوين اليمامة بين ان هذا التكوين يتكون بشكل اساسي من MB2, MB3 وان الوحدة الاساسية المنتجة للنفط هي MB1، بينما التفسير المجسات في تكوين اليمامة وان الوحدة الاساسية المنتجة للنفط هي MB1، بينما التفسير المجسات في تكوين اليمامة بين ان هذا التكوين يتكون بشكل اساسي من الحجر الجيري وقليل من الوحدة الاساسية المنتجة للنفط هي MB3، بينما التفسير للمجسات في تكوين اليمامة بين ان هذا التكوين يتكون بشكل اساسي من الحجر الجيري وقليل من الحجر الرملي وينقسم اليمامة بين ان هذا التكوين يتكون بشكل اساسية من الحجر الجيري وقليل من الحجر الرملي وينقسم اليمامة بين ان هذا التكوين يتكون بشكل اساسية من الحجر الجيري وقليل من الحجر الرملي وينقسم اليمامة بين ان هذا التكوين يتكون بشكل اساسية من الحجر الجيري وقليل من الحجر الرملي وينقسم اليمامة بين ان هذا التكوين يتكون بشكل اساسية من الحجر الجيري وقليل من الحجر الرملي وينقسم اليمامة بين ان هذا التكوين يتكون بشكل الساسية من الحجر الجيري وقليل من الحجر الرماي وينقسم اليمامة بين ان هذا التكوين يتكون بشكل الساسية من الحجر الجيري وقليل من الحجر الرماي وينقسم اليمامة بين ان هذا التكوين يتكون بلحقل الناصرية.



وزارة التعليم والبحث العلمي جامعة بغداد كلية العلوم قسم علوم الأرض

## عائدية وتوزيع النفط الخام في حقل الناصرية

رسالة مقدمة إلى عمادة كلية العلوم - جامعة بغداد كجزء من متطلبات نيل درجة ماجستير في علم الأرض

۲۰۱۳ م

<u>ما ۲۲</u>٤