
***Petroleum system analysis of the Lower
Jurassic-Upper Cretaceous source rocks
and Miocene reservoirs in the NE of Iraq***

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Contents

Contents	iii
List of Figures	v
Abstract	vii
Zusammenfassung.....	xi

Chapter 1 Introduction

1. Regional and Geological Setting of Arabian Plate.....	1
2. The Zagros Orogeny and Zagros basin development	3
3. The Gotnia Basin depositional environment during Lower Jurassic- Early Cretaceous.....	5
4. Geological and tectonic setting of the Arabian Plate and Iraq.....	6
5 Generalized sedimentation history.....	8
6. Paleogeography during Jurassic- Lower Cretaceous.....	10
7. Petroleum Systems in Iraq.....	11
7.1 Jurassic Petroleum System in Iraq	14
7.2 Cretaceous Petroleum System in Iraq.....	15
8. Petroleum system North Iraq.....	16
9 Objectives.....	18

Chapter 2 Geology, paleogeography, well logs, organic geochemistry of the Lower Jurassic-Upper Cretaceous NE Iraq.

1. Stratigraphic and Geological setting	20
2. Paleogeography during the Early Jurassic - Lowermost Cretaceous in the Middle East.....	27
3. Material and Methods.....	35
3.1 Organic geochemical Analysis.....	35
3.2 Analysis of the soluble organic matter.....	36
4. Relation between rock properties and wire line logs.....	37
4.1 Principles of well log data interpretation.....	38
4.2 Method of computing TOC from Wireline Logs	41
5. Distribution and composition of organic matter.....	42
5.1 Total Organic Carbon (TOC) content.....	44
5.2 Source rock generative potential.....	48

6. Bitumen bulk geochemical parameters.....	50
7. Conclusion remarks.....	52

Chapter 3 Biomarkers features of the Lower Jurassic- basal Early Cretaceous source rocks NE Iraq

1. Stratigraphic and Geological setting.....	62
2. Molecular Ratio or Biomarkers.....	65
3. Carbonate-Anhydrite sequence facies of a sabkha environment for Gotnia Formation: molecular approach.....	65
3.1 Introduction	65
3.2 Gotnia Formation Carbonate-Anhydrite sequence facies	65
4. Samples analyzed.....	68
4.1 Bulk geochemical analyzed.....	68
4.2 Molecular parameter.....	70
5. Conclusion remarks.....	79
6. Aliphatic and aromatic hydrocarbons.....	80
7. Maturity Parameters.....	91
7.1 Maturity parameters based on aromatic hydrocarbons.....	91
7.2 Maturity parameters based on saturated hydrocarbons.....	92
8. Type of source rocks	96
9. Environment and deposit conditions.....	98
10. Origin of Organic Matter and quality of source rocks.....	102
11. Age of the source rock.....	105
12. Different in the Biomarker distribution and behaviors and preservation condition in the central and margin of the Sedimentation basin.....	106
13. Sulfur content and Biodegrading.....	109
14. Conclusion remarks.....	111

Chapter 4 Geochemical, biomarkers distribution for the reservoirs solid bitumen and crude oils of the Miocene reservoirs NE Iraq and comparison with source origins.

1 . Geological background.....	113
2. Harmin oil field and relationship between Ajeel oil field and Harmin oil field structures...	118
3. Methods.....	121
4. Bulk geochemical parameters result and soluble organic matter extraction	122
5. Biomarker distribution of the saturated fraction.....	124
6. Biomarker distributions of the aromatic fraction.....	128
7. Conclusion remarks.....	130
8. Geochemical Correlation.....	132
9. Solid bitumen-Source rocks correlation.....	133
9.1 Correlation basis of bulk properties.....	133
9.2 Biomarker ratios for correlation	134
10. Conclusions remarks.....	144
11. Characterization, maturity, origin and correlation of selected crude oils from Ajeel and Hamrin oil fields.....	144
11.1 Oil-oil correlation	146
11.2 Solid bitumen – Crude Oil correlation	147
11.3 Crude Oil -Source rocks Correlation	149
11.4 Crude Oil - Solid bitumen - Source rocks Correlation	152
12. Conclusions remarks.....	153

Chapter 5 conclusion

Synthesis conclusion and outlook	154
Erklärung.....	174

List of Figures

Chapter 1

Fig. 1. 1 (A) Arabian Plate site with other continents. (B) A simplified map showing Iraq site with the Arabian Plate, (C) Arabian Plate with plate boundaries and principal geologic features..... 2

Fig. 1. 2: Pale-plate reconstruction of the Mesozoic-Cenozoic Period showing the position and tectonic evolution of the Arabian and Iranian Plates..... 3

Fig 1.3 (A) Regional tectonic map of northeast Iraq showing Zagros Orogen and study Area.(B) Map showing the Zagros suture in Iran and Iraq..... 5

Fig 1.5 Tectonic and structure elements of the Arabian Plat and rounding areas..... 6

Fig 1.6: Schematic of the Tectonic evolution of Northeast Iraq..... 8

Fig 1.7 Geological evolution of Iraq during the LateTriassic-Early Jurassic (a) Mid-Late Jurassic (b) and Early Cretaceous (c)..... 10

Fig 1.8 Map showing the extent of total petroleum systems in Iraq..... 12

Fig 1.8 Map showing the extent of total petroleum systems in Iraq..... 16

Chapter 2

Fig.2.1 Simplified map showing Iraq site with the Arabian plate (b) Regional tectonic setting of Iraq (c) Location map showing oil fields and wells where the crude oil samples are collect.(d) structure contour map for Ajeel oil field and location map for Hamrin oil field showing the wells where the source and reservoir samples where collect..... 21

Fig.2.2 Lithostratigraphic correlation chart of Jurassic-Early Cretaceous in Iraq and surrounding countries 26

Fig. 2.4 Palynofacies map of the Early Jurassic showing deposition of the Formations in Iraq and In Middle East 29

Fig. 2.5 Palynofacies map of the Middle Jurassic showing deposition of the Formations in Iraq and In Middle East	30
Fig. 2.6 Palynofacies map of the Middle -Late Jurassic showing deposition of the Formations in Iraq and In Middle East	31
Fig. 2.7 Palynofacies map of the Late Jurassic showing deposition of the Formations in Iraq and In Middle East	32
Fig. 2.8 Palynofacies map of the Very Early Cretaceous showing deposition of the Formations in Iraq and In Middle East	33
Fig. 2.9 Palynofacies map of the Early Cretaceous showing deposition of the Formations in Iraq and In Middle East	34
Fig. 2.10 Plot of sonic log vs. measured TOC for the Najmah and Sargelu Formations	39
Fig. 2.11 Cross-plots of the measured TOC(wt%) vs. digitized values from well logs (Gamma ray API, CNL%, FDC g/cm ³)	40
Fig. 2.12 Cross plot for well Aj-12 comparing core TOC versus Log-Derived TOC (wt %)	41
Fig. 2.13 Pictures for core samples studied collected from Najmah Formation.....	45
Fig. 2.14: Cross- Plot of S2 and TOC (wt %) for Ajeel oil field	46
Fig. 2.15 Cross plots for the Tmax vs. HI for the samples studied.....	47
Fig. 2.16. Genetic cross plot maturity based on T _{max} and PI for samples studied.....	48
Fig. 2.17. Cross Plot for the TOC(wt%) versus hydrocarbon genetic potential from (S1+S2) for the studied.....	50
Fig. 2.18. Cross plots of the TOC(wt%) versus extraction in ppm for the Formations studied...	51
Fig. 2.19. Pictures for core samples studied collected from Gotnia Formation.....	54
Fig. 2.20. Pictures for core samples studied collected from the Chia Gara Formation.....	55
Fig. 2.21 Vertical variation of the TOC(wt%) and logs digitized values from well Aj-12.....	56
Fig. 2.22 Vertical variation of the TOC(wt%) and Rock-Eval parameters infrom well Aj-12....	57
Fig. 2.23 Vertical variation of the Extraction in (ppm) and Rock-Eval parameters infrom well Aj-12.....	58

Fig. 2.24 Vertical variation of the TOC(wt%), TS(wt%) and Gamma ray log values infrom well Aj-8.....	59
Fig. 2.25 Vertical variation of the TOC(wt%) and Rock-Eval parameters(T_{max} , HI and S_2) values infrom well Aj-8.....	60
Fig. 2.26 Vertical variation of the Extraction in (ppm) and Rock-Eval parameters values infrom well Aj-8.....	61

Chapter 3

Fig 3.1 (a) a simplified map showing Iraq site with the Arabian plate (b) Regional tectonic setting of Iraq (c) Location map showing oil fields and wells where the crude oil samples are collect.(d) structure contour map for Ajeel oil field and location map for Hamrian oil field showing the location of wells studied.....	63
--	----

Fig 3.2 :(a) Lithostratigraphy of the Low Folded Zone in Iraq (b)Lithostratigraphy of one of the wells studied the well is (Aj-12 well) from Ajeel oil field.	64
--	----

Fig. 3. 3 Palynofacies map of the Late Jurassic showing deposition of the Formations in Iraq and surrounding countries.....	66
--	----

Fig 3.4 Lithostratigraphic correlation chart of Jurassic-Early Cretaceous in Iraq and surrounding countries	67
--	----

Fig. 3.5 Cross-Plot of (TOC%wt) with different bulk geochemical analysis and extraction in ppm samples studied from Gotnia Formation	69
---	----

Fig.3.6 photo show mixing between the Carbonate and Anhydrite layers in Gotnia Formation.....	70
--	----

Fig. 3.7 Representative total ion chromatogram of saturated hydrocarbon fractions showing distribution of n-alkanes from 85 m/z and isoprenoids from Tic samples from Gotnia Formation inform well Aj-8.....	72
---	----

Fig. 3.8 Representative total ion chromatogram of saturated hydrocarbon fractions showing distribution of n-alkanes from 85 m/z and isoprenoids from Tic samples from Gotnia Formation inform well Aj-8.....	73
---	----

Fig. 3.9 Representative total ion chromatogram of saturated hydrocarbon fractions showing distribution of n-alkanes from 85 m/z and isoprenoids from Tic. Samples from Gotnia Formation inform well Aj-12.....	74
---	----

Fig.3.10. Representative total ion chromatogram of aromatic fractions showing distribution 178m/z)phenantherene,(192m/z)methylphenantherene,(184m/z)diobenzothiophene and (198m/z) methylphenantherene. Samples from Gotnia Formation inform well Aj-12.....	75
Fig 3.11 Stable variations of calculated ratios with facies changes and clearly separation between Carbonate and Anhydrite layers. Samples from the wells (Aj-12 and Aj-8) Gotnia Formation.....	76
Fig 3.12 Stable variations of calculated ratios with facies changes and clearly separation between Carbonate and Anhydrite layers. Samples from the wells (Aj-12 and Aj-8) Gotnia Formation.....	77
Fig.3.13 Cross plots between two stereans parameters show the good and poor source rocks in Gotnia Formation	78
Fig 3.14 Representative saturate fraction gas chromatograms showing distribution of isoprenoids (pristane and phytane) for the Formations studied in well Aj-12.....	82
Fig. 3.15 Representative saturate fraction gas chromatograms showing distribution of isoprenoids (pristane and phytane) for the Formations studied in well Aj-8.....	83
Fig.3.16 Representative saturate fraction gas chromatograms showing distribution of n-alkanes for the Formations studied in well Aj-12.....	85
Fig 3.17 Representative saturate fraction gas chromatograms showing distribution of n-alkanes for the Formations studied in well Aj-8.....	86
Fig.3.18 Representative saturate fraction gas chromatograms of the distributions of trepans(191 m/z) with identification peak. The sample from Ajeel oil field.....	88
Fig. 3.19 Representative saturate fraction gas chromatograms of the distributions of the steranes (217 m/z) with identification peak. The sample from Ajeel oil field.....	88
Fig 3.20 The m/z 191(left) and m/z 217 mass fragmentogram (right) of saturated hydrocarbon fractions of two select samples studied.	89
Fig 3.21 Representative aromatic fraction gas chromatograms.	90
Fig 3.22 Relation between methylphenantherene index PP-1 and sulfur abundance (weight %) for samples studied from Aj-12 and Aj-8.	92
Fig 3.23 Relationship between two maturity parameters based on steranes parameter	94
Fig. 3.24 Relationship between two maturity parameters (MPI-1) from aromatic fraction and C29 $\beta\beta / (\beta\beta + \alpha\alpha)$ steranes parameter	94

Fig. 3.25 Cross plot of C29 $\beta\beta / (\beta\beta + \alpha\alpha)$ sterane and hopane/sterane ratio showing maturity for the source rocks.	94
Fig. 3.26 Cross-Plot of trepan maturity parameters indicating high maturity of maturation of rock samples.	96
Fig. 3.27 Relationship between Pr/ (Pr + Ph) and C ₂₇ diasterane / (dia+ reg) sterane to show type of the source rocks	97
Fig. 3.28 Cross-Plot of tricyclic terpane ratios (C ₂₂ /C ₂₁ versus C ₂₄ /C ₂₃)	98
Fig. 3.29. Cross-Plot of tricyclic terpane ratios (C ₂₆ /C ₂₅ versus hopane C ₃₁ R/C ₃₀ ratio)	98
Fig. 3.30 Cross-Plot of dibenzothiophene/ phenanthrene-(DBT/P) vr.Pr./Ph. samples inform Aj-12 and Aj-8 wells	100
Fig. 3.31 Relationship between Pr/n-C ₁₇ and Ph/n-C ₁₈ for rocks samples.....	101
Fig. 3.32 Hopane and isoprenoid Pr./Ph. ratios of extracts sediments from the well Aj-12 and Aj-8	101
Fig. 3.33 Different triplot providing the composition of the %C27-C29 regular steranes of the samples studied	103
Fig. 3.34 . Pristane/Phytane ratio versus %C27/C29 regular steranes plot for the samples studied..	104
Fig 3.35 Two steranes parameters from saturated hydrocarbon (217m/z) show the poor and rich source rocks for the samples studied.....	104
Fig. 3.36. Simple couture map show the location of the wells studied (Aj-12 and Aj-8)	107
Fig. 3.37 Cross plots for different calculates ratios show different in biomarkers distribution related to the location of the wells studied	108
Fig.3.38 Sulfur content (wt%) plotted against (TOC wt%) for samples studied in wells(Aj-12 and Aj-8).	110
Fig 3.39. C29/C30 hopane ratio versus different calculate ratio: (a and b) aromatic ratios P/MP and (4+1)/(2+3) MDBT. (c) versus hopane/regular sterane ratio.(d) TOC/TIC ratio from bulk analysis. ...	112

Chapter 4

- Fig 4.1** (a) a simplified map showing Iraq site with the Arabian plate (b) Regional tectonic setting of Iraq.(c) Location map showing oil fields and wells studied (d) structure contour map for Ajeel oil field and location map for Hamrin oil field. 114
- Fig 4.2** Lithostratigraphy for Hamrin oil field from the well Hr. 39 studied. the photos are core collected samples from the Hamrin oil field..... 115
- Fig 4.3** Paleogeographic maps for the study Formations (a) Euphrates Formation (b) Dhiban Formation and (d) Jeribe Formation..... 117
- Fig 4.4** Distribution of extract yield in ppm for the Formations studied 123
- Fig 4.5** Distribution of extract yield in ppm for the Formations studied in Ajeel and Harmin oil fields for all the wells studied 123
- Fig 4.6** Distribution of some biomarker composition in Ajeel and Harmin oil fields 126
- Fig 4.7** Distribution of some biomarker composition in Ajeel and Harmin oil fields 127
- Fig 4.8** Distribution of BNH/ (BNH+C29 hopane) biomarker composition in Ajeel and Harmin oil fields 128
- Fig 4.9** Distribution of DBT/P average ratio in Ajeel and Harmin oil fields 128
- Fig 4.10** Distribution of calculated vitrinite reflectance values, R_c and R_m obtained from MPI-1 and MDR aromatic maturity parameters respectively 129
- Fig 4.11** Cross Plots between calculated vitrinite reflectance values, R_c and R_m obtained from MPI-1 and MDR aromatic maturity parameters respectively. 130
- Fig 4.12** Bar chart show the high extraction in(ppm)from the Euphrates Formation in Ajeel and Hamrin oil fields 131
- Fig 4.13** Bar chart show the extraction from Jeribe Formation in Hamrin and Ajeel oil fields..... 131
- Fig 4.14** Bar chart DBT/P ratio for the Jeribe Formation and Euphrates Formation in Ajeel and Hamrin oil fields 132
- Fig 4.15** Plot of pyrolysis T_{max} versus production index PI showing the maturity and nature of hydrocarbon products of the solid bitumen and source rocks samples. 133

Fig 4.16 Plot of two steranes parameters to correlated the maturity of the solid bitumen and the extract from the source rocks studied.	134
Fig 4.17. The m/z 191 mass fragmentograms of saturated hydrocarbon fractions of the solid bitumen and the source rock extracts.	135
Fig 4.18 The m/z 217mass fragmentograms of saturated hydrocarbon fractions of the solid bitumen and the source rock extracts.	136
Fig4.19 Mass chromatograms of phenanthrene, methylphenanthrenes and dibenzothiophenes and methyl dibenzothiophenes for source rock select extract sample from Gotnia Formation Ajeel oil field	137
Fig4.20 Mass chromatograms of phenanthrene, methylphenanthrenes and dibenzothiophenes and methyl dibenzothiophenes for source rock select extract sample from Najmah Formation Ajeel oil field	138
Fig4.21 Mass chromatograms of phenanthrene, methylphenanthrenes and dibenzothiophenes and methyl dibenzothiophenes for source rock select extract sample from Dhiban Formation Hamrin oil field	139
Fig4.22 Mass chromatograms of phenanthrene, methylphenanthrenes and dibenzothiophenes and methyl dibenzothiophenes for source rock select extract sample from Dhiban Formation Hamrin oil field	140
Fig 4.23 Triplot providing the composition of the % C27-C29 regular steranes of the source rock and bitumen from the reservoir Formations showing the strong relationship between them. .	141
Fig 4.24 Plots of different calculate ratios for correlation between the source rock extract and bitumen studied	142
Fig 4.25 Plots of different calculate ratios for correlation between the source rock extract and bitumen studied	143
Fig4.26 Plots for two steranes parameters comparing the maturity of the crude oils studied and extract from the core reservoir samples	145
Fig4.27 Plots for two steranes parameters comparing the maturity of the crude oils studied and extract from the core reservoir samples.....	146
Fig4.28 Plots of different calculate ratios for correlation between the source rock extract and bitumen studied	147

Fig4.29 Plots for two steranes parameters comparing the maturity of the crude oils studied and extract from the core reservoir samples	148
Fig 4.30 Different cross plots from different calculate ratios to study the characteristic of the crude oils samples studied	149
Fig 4.31 Plots of the BNH/(BNH+C29 hopane) ratio versus the %C27/C29 sterane ratio for correlation the crude oils with the extract source rocks studied	150
Fig 4.32 Different calculate correlation ratios comparing the crude oils studied and extract from the core reservoir samples.	151
Fig 4.33 .Plots of the BNH/(BNH+C29 hopane) ratio versus the %C27/C29 sterane ratio for correlation the crude oils with the extract source rocks studied.....	152
Fig 4.34 Correlation ratios plot for the oil samples studied and source rocks studied.	153

Abstract

Sediments deposited under hypersaline conditions within carbonate/evaporitic cycles have high preservation potential for organic matter and are recognized as important potential oil source rocks. For this reason the carbonate/evaporitic cycles in the Northern Iraq for the Lower Jurassic to the Early Cretaceous time interval were studied to investigate their source rock intervals as well as residual bitumen and crude oils in Miocene reservoirs.

This study is the first to report that the Gotnia Formation acts as both as source rock as well as cap rock. The carbonate organic-rich sedimentary layers sandwiched between gypsum anhydrite beds of the sabkha-type like Gotnia Formation were found to contain substantial indigenous petroleum source potential. In order to characterize their source rock potential, sediments of the Gotnia Formation were studied by bulk geochemical and molecular parameters. The carbonate layers in the Gotnia Formation have high source rock potential with TOC contents around 6.59% and extractable organic matter (EOM) up to 6376 ppm, which is sufficient to generate petroleum hydrocarbons. Terpane biomarkers and aromatic geomarkers for sediments of the Gotnia Formation were found in residual bitumen and crude oils in Miocene reservoirs. The oil generated from the Gotnia Formation was shown to contribute to the petroleum system of the Ajeel and Hamrin Fields of the study area and can be assumed to have done so in other reservoirs of Northern Iraq.

To investigate the Lower Jurassic-Upper Cretaceous age source rock intervals 195 rock samples (covering the Lower Sarmond, Chia Gara, Gotnia, Najmah, Sargelu, Alan and 2 samples from the Mus Formation) have been studied. The following analysis were conducted for bulk geochemical parameters (i.e. total organic carbon, total carbon, total inorganic carbon, sulfur content and Rock-Eval) and 57 samples were selected for biomarker and geomarker analysis. Terpane biomarker and aromatic geomarker signatures reveal an origin from similar source and facies regimes indicating similar depositional environments for the source in a restricted setting on the margin of the Arabian platform, which led to the accumulation of quasi-invariant kerogen types. Analytical result shows that the Formations studied were deposited in a marine, carbonate rich, anoxic environment with more oxygenated conditions during deposition of the upper Chia Gara and Lower Sarmond Formations thus reducing kerogen quantity and quality. The kerogen is predominantly derived from cyanobacterial and algal sources, whereby the cyanobacterial contributions increase in sediments deposited under higher salinity (anhydrite in Gotnia and Alan Formation). Decreased early diagenetic preservation of cyanobacterial structures in the shallower site for well Aj-12 (type II kerogen) versus excellent preservation of cyanobacterial biomass and high sulfurization of kerogen (type II-S) in the basinal setting of the well Aj-8 can be differentiated. Thermal maturity of the source rocks is within the oil window but they have not yet reached the main generation phase. Triterpanes show low abundance of tri- vs. pentacyclic terpanes and a predominance of the C₂₉-hopanes. A highly source and environment-specific biomarker were found in 29,30-bisnorhopane, which rarely occurs in other source rocks and the relative proportion of dibenzothiophene versus phenanthrene. Bulk geochemistry and geomarkers were used to understand the origin of sulfur in kerogen and the environment conditions and to signify to early diagenetic incorporation of H₂S into the organic matter. Most sulfur in the samples studied originates from Anhydrite in the Gotnia and Alan Formations, which produced sulfides via the activity of sulfate-reducing bacteria under highly anoxic condition, such as the condition for (Najmah/Naokelekan and Sargelu) Formations.

This work demonstrates that only the basal 30 m of the entire Chia Gara Formation has an excellent source rock potential. This basal part is the main source within this formation and the main source interval in the area whereas the much thicker middle and upper part is organic lean, thus not contributing to the source potential of the Chia Gara Formation.

The geochemistry and molecular compounds of 108 residual oils and from 6 production oil samples from Miocene reservoirs in the Northern Iraq from (Euphrates, Dhiban, Jeribe and Transition bed Formations) were evaluated and were used for oil-source rock correlation. Results show that the oils were generated by carbonate source rocks which were deposited under highly anoxic conditions and which contain mainly marine derived type II-S kerogen. The molecular composition of aliphatic terpane biomarkers and aromatic hydrocarbons in residual reservoir bitumen are equivalent to what was found in the Ajeel and Hamrin production oils. All the oils possess a high sulfur content with a high ratio of dibenzothiophene versus phenanthrene, which indicates that these oils were generated from source rocks deposited in hypersaline environments. Expressed in salinity and sulfurization, oil compositional gradients are reflected in samples on field scale and relate to a more basinal character at the Hamrin oil field compared to Ajeel oil field with mixing between the oils studied in Ajeel and Hamrin oil fields related to structural control. The bitumen in the Euphrates Formation shows higher maturity in the Hamrin oil field compared to the Ajeel oil field and relates to different sources charging this formation in these oil fields.

Based on molecular analysis for the residual oil (in a solid bitumen phase) and production oil in the study area, which shows low abundance of tri- vs. pentacyclic terpanes, a predominance of the regular C₂₉-hopanes and the presence of highly source specific 29,30-bisnorhopanes and aromatic tracers as well as bulk properties from Rock-Eval pyrolysis, the result indicate that these oils are derived from mixing of charges from multiple source rocks at variable maturity levels. Various discrimination diagrams for bio/geomarker ratios show that a reliable oil-source-correlation could be established based on molecular aliphatic and aromatic tracers. These data show that the Chia Gara Formation is the main source rock in the study area together with the Najmah/Naokelekan and Sargelu Formations and also with additional input from carbonate intervals intercalated into the Gotnia Formation.

Wire line logs have been used in the Ajeel oil field (for the Lower Sarmond, Chia Gara, Gotnia, Najmah, Sargelu and Alan Formations) to establish a quantitative correlation between well logs (gamma ray, density, neutron and sonic in short interval) and total organic carbon. Comparison of log-derived TOC values with measured TOC values from core and cutting samples was employed to improve evaluation of source rock potential. TOC% wt. had a positive relation to Gamma ray, neutron and sonic logs showed an inverse relationship with density logs. The Schmoker method used to derive TOC wt% from rocks via logging also showed a positive relationship. However, in this study logging response in source rocks was not sufficient to evaluate source rock potential

Zusammenfassung

Sedimente, die unter hypersalinen Bedingung innerhalb von Karbonat/Evaporit-Zyklen abgelagert wurden, weisen ein hohes Potential für die Erhalten von organischem Material auf und stellen somit wichtige Erdölmuttergesteine dar. In diesem Zusammenhang wurden Karbonat/Evaporit-Zyklen, die während des Unterjuras bis zur Unterkreide im heutigen Nordirak abgelagert wurden, untersucht. Besonderer Fokus lag hierbei auf potentiellen Erdölmuttergestein Intervallen als auch auf der Analyse von residualem Bitumen und Rohölen, die in Reservoirformationen Miozänen Alters angetroffen werden.

Im Rahmen dieser Arbeit konnte gezeigt werden dass die Gotnia Formation sowohl als Muttergestein als auch als Cap Rock in fungiert. Karbonat-reiche Intervalle, die in Anhydrit-Lagen der in einem Sabkha-Milieu abgelagerten Gotnia Formation eingeschaltet sind, zeigen hierbei ein besonders hohes Generierungspotential für Kohlenwasserstoffe. Um das Erdölgenerierungspotential der Gotnia Formation genauer zu charakterisieren wurden entsprechende Sedimente mittels pauschal- und molekular-geochemischer Parameter untersucht. Karbonathorizonte der Gotnia Formation zeichnen sich durch einen hohen Anteil organischen Kohlenstoffs von etwa 6.50% (TOC: total organic carbon) aus. Des Weiteren werden sehr hohe Anteile organischen Materials angetroffen (bis zu 6376 ppm), die mittels organischer Lösemittel extrahierbar sind (EOM: extractable organic matter). Den Karbonathorizonten der Gotnia Formation kann somit ein hohes Potential zur Generierung von Kohlenwasserstoffen zugesprochen werden. Charakteristische Biomarker, wie z.B. Terpane als auch Geomarker der aromatischen Kohlenwasserstofffraktion, welche in den Sedimenten der Gotnia Formation angetroffen wurden, konnten ebenso in residualen Bitumen und Rohölen Miozäner Reservoirs nachgewiesen werden. Es kann somit gefolgert werden, dass Öle die aus der Gotnia Formation generiert wurden und bedeutende Ölfelder im Nordirak, wie das Ajeel und das Hamrin Felder, speisen.

Insgesamt wurden 195 Proben aus potentiellen Erdölmuttergesteins-Intervallen unterjurassischen bis oberkretazischen Alters untersucht (untere Sarmond, Chia Gara, Gotnia, Najmah, Sargelu, Alan und Mus Formation). Für alle Proben wurden pauschal-geochemische Parameter erhoben, welche die quantitative Bestimmung des organischen und anorganischen Kohlenstoffs als auch des Gesamt-Schwefelgehaltes umfassten. Des Weiteren wurden für alle Proben Rock Eval Pyrolysen durchgeführt. An 57 Proben wurden zudem molekular-geochemische Untersuchungen durchgeführt. Biomarker, wie Terpane, und Geomarker der aromatischen Kohlenwasserstofffraktion deuten auf eine weitestgehend einheitliche Fazies und damit ähnliche Quellen des organischen Materials hin. Dies spiegelt sich auch in der wenig variablen Zusammensetzung des Kerogens wider. Der Ablagerungsraum kann als ein restriktiver, flach-mariner Ablagerungsraum, auf der Arabischen Platte beschrieben werden. Potentielle Erdölmuttergesteine kamen in einem flach-marinen, karbonatischen Milieu unter vorzugsweise anoxischen Bedingungen zur Ablagerung. Eine verbesserte Sauerstoffverfügbarkeit kann für die obere Chia Gara Formation und die untere Sarmond Formation dokumentiert werden, was sich in einem geringeren Kerogen-Anteil schlechterer Qualität widerspiegelt. Das Kerogen stammt vorwiegend aus Cyanobakterien und Algen-stämmigen organischem Material, wobei Cyanobakterien-stämmiges Material in Sedimenten dominiert, die unter erhöhter Salinität zur Ablagerung kamen (Anhydrite der Gotnia und Alan Formation). Eine verminderte Erhaltung des Cyanobakterien-stämmigen Materials kann in Proben aus dem Kern Aj-12 dokumentiert werden, der einen vorzugsweise flach-marinen Ablagerungsraum repräsentiert. Sehr gute Erhaltungsbedingungen könne dagegen für organisches Material aus Proben von

Kern Aj-8 nachgewiesen werden, der ein tieferes Ablagerungsmilieu repräsentiert. Höhere H₂S Konzentrationen führten hier zur Bildung eines Typ II-S Kerogens.

Der Diageneseegrad des organischen Materials der Erdölmuttergesteine entspricht dem Ölfenster, die Hauptgenerierungsphase wurde allerdings noch nicht erreicht. Triterpane zeigen niedrige Konzentrationen von tri- gegenüber pentazyklischen Komponenten. Zudem wird eine Dominanz des C₂₉ Hopane dokumentiert. Quellen-spezifische Biomarker wie das 29,30-Bisnorhopan wurden ebenso wie Dibenzothiophen und Phenanthren nachgewiesen. Ursprung des im Kerogen gebundenen Schwefels als auch Ablagerungsbedingungen konnten anhand pauschal- und molekular-geochemischer Daten nachvollzogen werden und ein frühdiagenetischer Einbau von H₂S in das organische Material bestätigt werden. Hohe Schwefelgehalte im organischen Material in den Anhydriten der Gotnia Formation können mit erhöhten Sulfatreduktionsraten durch Bakterien unter stark reduzierenden Bedingungen in Verbindung gebracht werden. Ähnliche Bedingungen werden auch in den Najmah, Naokelekan und Sargelu Formationen angetroffen. Die Arbeit konnte weiterhin zeigen, dass nur die untersten 30 m der Chia Gara Formation ein erhöhtes Erdölgenerierungspotential aufweisen. Der obere Teil der Formation zeigt nur niedrige Gehalte organischen Materials und kann somit nicht als effektives Muttergestein klassifiziert werden.

Eine Korrelation der Öle, die in Miozänen Reservoirs in Nordirak angetroffen werden (Euphrates, Dhiban, Jeribe Formationen als auch deren Übergangsbereiche), wurde anhand der molekular-geochemischen Untersuchung von 108 residualen und 6 geförderten Ölen durchgeführt. Die Ergebnisse belegen, dass die Öle karbonatischen Muttergesteinen entstammen, die unter stark reduzierenden Bedingungen abgelagert wurden (Typ II-S Kerogen). Verteilungsmuster der Terpane als auch aromatischer Kohlenwasserstoffe decken sich mit denen, die in den Ajjel und Hamrin Ölen angetroffen werden. Alle Öle haben einen hohen Schwefelgehalt und hohe Dibenzothiophen/Phenanthren Verhältnisse, was auf einen hypersalinen Ablagerungsraum hindeutet. Im Vergleich mit dem Ajeel Ölfeld zeigt das Hamrin Ölfeld einen stärkeren Bezug zur Beckenfazies was sich in einem geochemischen Gradienten der Ölzusammensetzung äußert. Unterschiede sind hierbei vorwiegend strukturkontrolliert. Bitumen, welches in der Euphrates Formation angetroffen wird zeigt eine höhere Reife im Hamrin als im Ajeel Ölfeld an was auf unterschiedliche Quellen hindeutet. Residuale Öle und geförderte Öle zeigen niedrige Konzentrationen von tri- gegenüber pentra-zyklischen Terpanen als auch eine Dominanz von C₂₉ Hopanen. Zudem konnten 29,30-Bisnorhopanen nachgewiesen werden. Diese molekular-geochemischen Daten in Verbindung mit weiteren aromatischen Geomarker-Verteilungsmustern und Daten aus der Rock Eval Pyrolyse implizieren, dass die Öle aus der Vermischung verschiedener Quellen unterschiedlichen Reifegrades resultieren. Eine verlässliche Öl-Muttergestein-Korrelation konnte auf Basis diverser Bio-/Geomarker Proxies aliphatischer und aromatischer Kohlenwasserstoffe erfolgen. Die Daten belegen, dass die Chia Gara Formation, neben den Najmah/Naokelekan und Sargelu Formationen, das wichtigste Erdölmuttergestein im Arbeitsgebiet ist. Öle werden zudem auch aus Karbonathorizonten der Gotnia Formation geliefert.

Im Ajeel Ölfeld erfolgte eine Korrelation unterschiedlicher Formationen (untere Sarmond, Chia Gara, Gotnia, Najmah, Sargelu und Alan Formationen), die in verschiedenen Bohrungen angetroffen wurden, mittels Wire Line Logs and Konzentrationsänderungen des organischen Kohlenstoffs (TOC). Der Vergleich von aus Wire Line Logs abgeleiteten TOC Werten mit tatsächlichen TOC Werten erlaubte eine verbesserte Einschätzung des Kohlenwasserstoffgenerierungspotentials. Eine positive Korrelation wurde

zwischen TOC Werten und Gamma Ray Daten dokumentiert, wohingegen der TOC gegenüber Neutron und Sonic Logs eine inverse Korrelation zeigt. Die Schmoker Methode, die angewendet wurde, um TOC Gehalter von Log Daten abzuleiten, zeigte ebenso eine positive Korrelation mit tatsächlichen TOC Werten. Allerdings konnte im Untersuchungsgebiet das Kohlenwasserstoffgenerierungspotential nicht eindeutig von Wire Line Log Daten abgeleitet werden. .

Chapter 1

Introduction

1.1 Regional and Geological Setting of Arabian Plate

The Arabian Plate formed part of the northern margin of Gondwana and one of three tectonic plates: the African, Arabian and Indian crustal plates which have been moving northward over millions years. The Red sea, the Gulf of Aden, and the Arabian Sea bounded the Southwest and South of Arabian Plate Fig. (1.1).

The Arabian Plate consists of two major tectonic provinces. The first one is Arabian Shield which covers about one third of Arabian plate and consists of Precambrian gneiss and Metamorphosed sedimentary and volcanic rocks that have been intruded by granites .The second one is the Arabian Platform which is a large sedimentary basin that comprises about two third of the Arabian plate and consists of Paleozoic and Mesozoic sedimentary layers that unconformably overlap the basementrocks and gently dip to the east (Powers et al ., 1966, Mokhtar et al., 2001). During the Late Precambrian, a number of basic and dense volcanic sutures brought together to make the Arabian Plate.

During the Late Ordovician times, the western part of the Arabian Plate was affected by a glacial event occurred, and the Arabian Plate was in high southern part latitudinal position. The Hercynian Orogeny which is a term commonly used for Late Devoinan to Permian diastrophic movements in Europe and North America was the first main tectonic event that broadly affected the Arabian Plate (Haq and Al-Qahtani, 2005; Konyuhov and Maleki, 2006) and in the Carboniferous time, the Arabian Plate was extensively uplifted by the Hercynian Orogen which made a break and erosion of most Paleozoic sequence in the area (Ahlbrandt, 2000). In the Early Permian The Neo–Tethys Ocean began to open in two stages, the first began when Iranian Plate moved away from Arabian Plate toward the Eurasian Plate, and the second stage was in when the Neo-Tethys reached its maximum width of 400 km during the Late Triassic to Middle Jurassic (Sadooni and Alsharhan, 2004). In the Early Jurassic, the Indian Plate first began to split from Gondwana (Grabowski and Norton, 1995), and by next tectonic events, completed its separation from Arabia in the Late Jurassic (Fig.1.2). The Mediterranean rifting which began in the Early Jurassic continued into the Early Cretaceous and the Neo-Tethys started to close, creating a belt of junction from Turkey to Oman. This belt is Taurus –Zagros belt. During Miocene times, significant plate boundary tectonics included the opening of the Red Sea, the Zagros continental collision and the formation of the associated Mesopotamian foredeep (Barazangl et al., 1993). In the late Eocene, the Plate began to collide with Asia, and the closure of the Neo-Tethys was essentially completed by the Late Oligocene (Haq and Al-Qahtani, 2005). The collision of the continental segments of the Eurasian margin with the continental Arabian Plate created the Zagros Mountain as a result of subduction of the Oceanic Arabian Plate crust under the Eurasian Plate (Beydoun et al., 1992). This Continent-to-continent collision started during the late Eocene time and the junction continues at present (Beydoun et al., 1992).

Verma et al., 2004 have summarized the tectonic evolution of the Arabian Plates to five distinct phases. The first is a Precambrian compression phase, when island and micro-continent terrines accreted and assembled to form the Arabian Plate from in this period many of the structural elements formed controlled later sedimentation, structural development, and petroleum accumulation (Al-Husseini, 1997, 2000; Sharland et al., 2001). The second phase which involved the Late Precambrian to the Late Devonian sedimentation and was associated with the Najd Fault System (Al-Husseini, 2000), with evaporates and carbonates accumulating and a major source rock sequence was deposited. The Third phase occurred during the Late Devonian to mid-

Permian and included the Mid-Carboniferous Hercynian Orogeny. The opening of the Neo-Tethys Ocean started in the fourth tectonic phase after the glaciations ended with rifting and associated passive margin setting. Carbonates and evaporates rocks largely cyclic during the Triassic and Jurassic while Lower Cretaceous strata were dominantly open marine and a mixture of clastic and carbonates. The Zagros Orogeny extended from Late Cretaceous to the present day and this resulted in the closing of the Neo-Tethys and foredeep development that was the five stages.

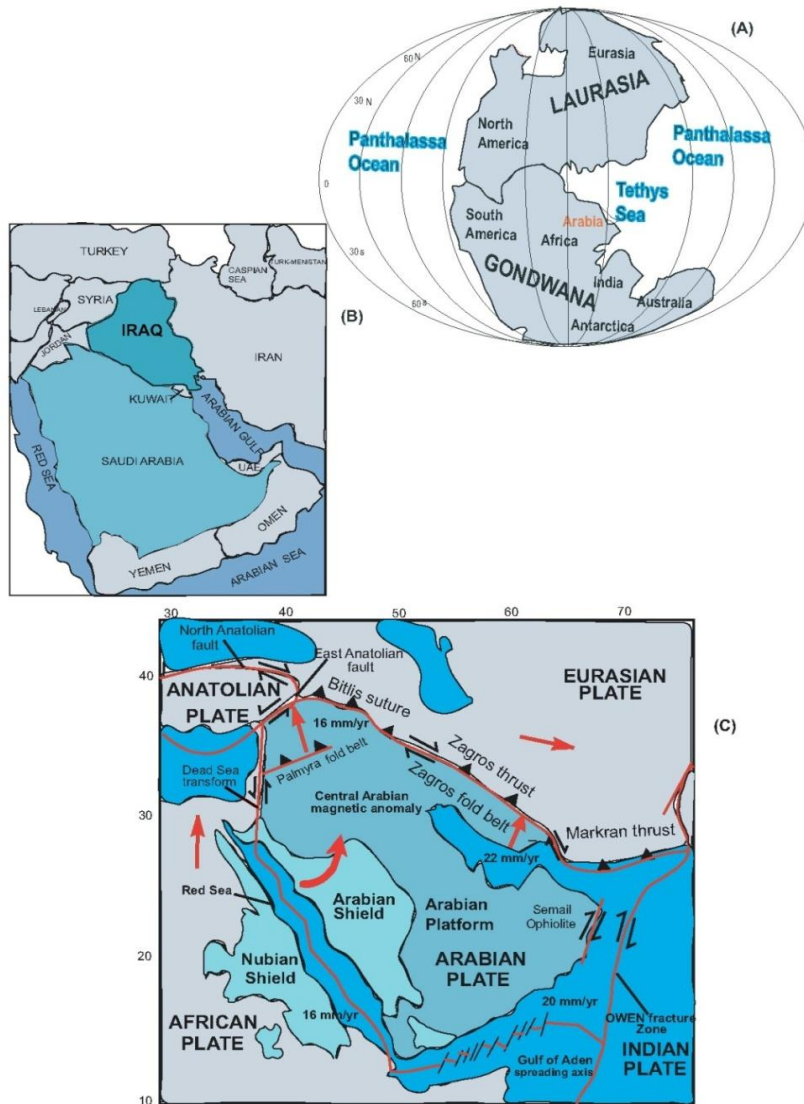


Fig. 1. 1 (A) Arabian Plate site with other continents. (B) A simplified map showing Iraq site with the Arabian Plate, (C) Arabian Plate with plate boundaries and principal geologic features (modified after Stern and Johnson, 2010).

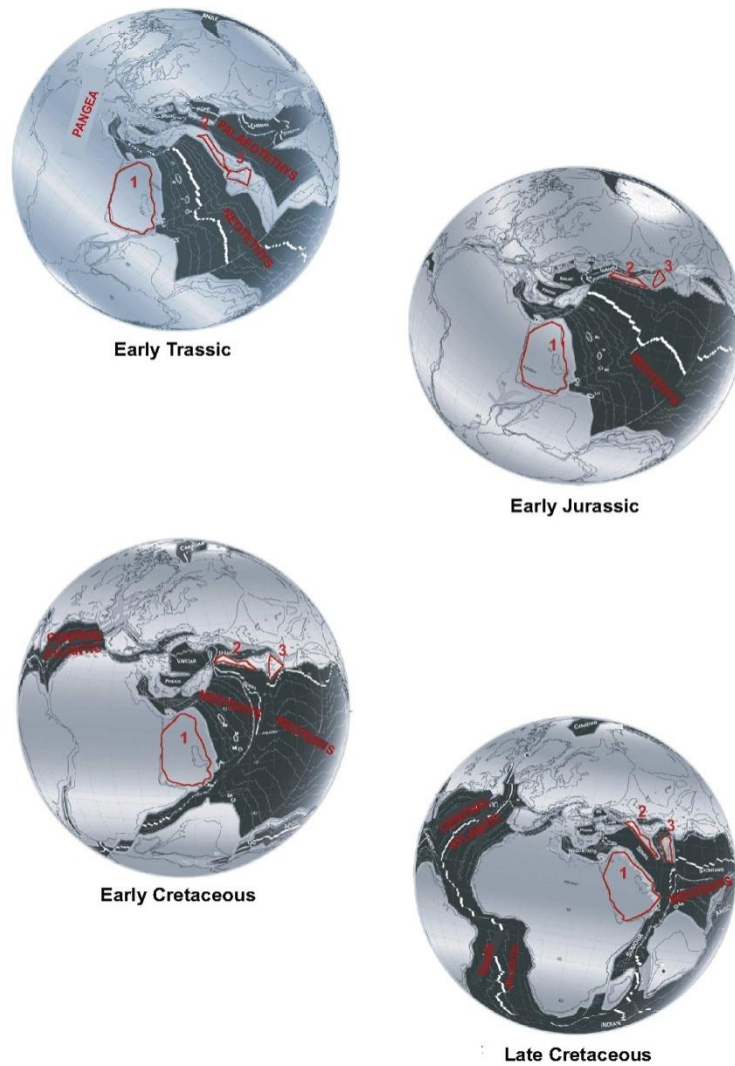


Fig. 1. 2: Pale-plate reconstruction of the Mesozoic-Cenozoic Period showing the position and tectonic evolution of the Arabian and Iranian Plates (modified after Stampfli and Borel, 2002 and Hadi, 2008).1=Arabian Plate, 2=Sanandaj Sirjan block, 3=Central Iranian block. See Fig A1 in Appendix for a color version.

1.2 The Zagros Orogeny and Zagros basin development

The Zagros Orogeny extends about 2,000 Km from Anatolian Fault of southeastern Turkey to the Markran Zone in the southern Iran and into northern Iraq and is part of the Alpine-Himalayan Mountain Chain (Al-Qayim et al.,2012) Fig(1.3) and it is created by collision of the continental Arabian Plate with continental segments of the Eurasian margin. Within the Zagros belt two main zones can be recognized: (1) the thrust zone; and (2) the folded zone (Buday, 1980; Ameen, 1992; Jassim and Buday, 2006a). The thrust zone is located next to the border between Iraq and Iran in the northeast and outside the border between Iraq and Turkey in the north (Buday, 1980; Ameen, 1992; Jassim and Buday, 2006a) and the folded zone can be subdivided into two parts based on the intensity of folding these are the imbricates (crushed) folds zone, which is extremely deformed and the simply folded zone which occurs as distorted smaller fold zone Ameen (1992). The northwestern segment of the Zagros Orogenic Belt of the Kurdistan Region of Iraq includes the Zagros Suture Zone which is consisting of allochthonous Tethyan Triassic-Eocene thrust sheets (Al-Qayim et al.,2012).

Zagros Basin is defined as an area located at the northeastern margin of the Arabian Plate bounded by the Central Iranian Plate to the northeast, the Arabian Platform to the southwest and the Turkish Plate in the northwestern direction (Bahroudi and Talbot, 2003) and it was part of the stable supercontinent of Gondwana in Paleozoic times, a Passive margin in Mesozoic times, and became a convergent orogeny in Cenozoic times and it is defined by a 7–14 km thick succession of cover sediments deposited over an extraordinary, along the north–northeast edge of the Arabian plate (Bahroudi and Koyi, 2004). Zagros Basin can be divided depending on the presence of salt deposits into two main sub-basins and they are southeastern Zagros Basin (Zagros Hormuz Salt Basin) and the Northwestern Zagros Basin. Koop and Stoneley, 1982 summarized the evolution of the Zagros Basin as follow: during the Mid–Permian a major Hercynian tectonic phase of block-faulting and regional arching resulted in complex palaeogeological surface that was unconformable blanketed by marine carbonate-evaporate platform. Unconformity marks during Late Triassic –Early Jurassic the onset of drift separation along the Zagros Suture forming the southern or Neo-Tethys ocean and Oceanic sediments from seaway of Triassic age were emplaced on the shelf margin. In the Late Jurassic sedimentation in the eastern segment of the Zagros Basin was characterized by deep-water deposits accumulating on the continental slope to the north, with erosion not far to the south and deposits accumulating on the continental slope to the still further south. During the Late Jurassic to middle Cretaceous subsidence and sedimentation patterns became more complex and the shelf edge along the present Zagros Suture was alternately depressed or raised led to widespread restricted sub-basins. During the Late Cretaceous was beginning of plate margin tectonics along the Zagros suture as the Neo-Tethys closed. In Oligocene or early Miocene closure of the Neo-Tethys was complete and the Zagros Basin was reduced to a single trough. Very pronounced subsidence during the Miocene to Pleistocene preceded and was partly contemporaneous with Zagros Orogeny, creating an enclosed redded-evaporite trough. The NE flank of this deep trough became the scene of thrusting and folding as the continent-continent collision continued along the complex Zagros Suture zone and the Zagros Basin migrated to its present position in the Gulf .

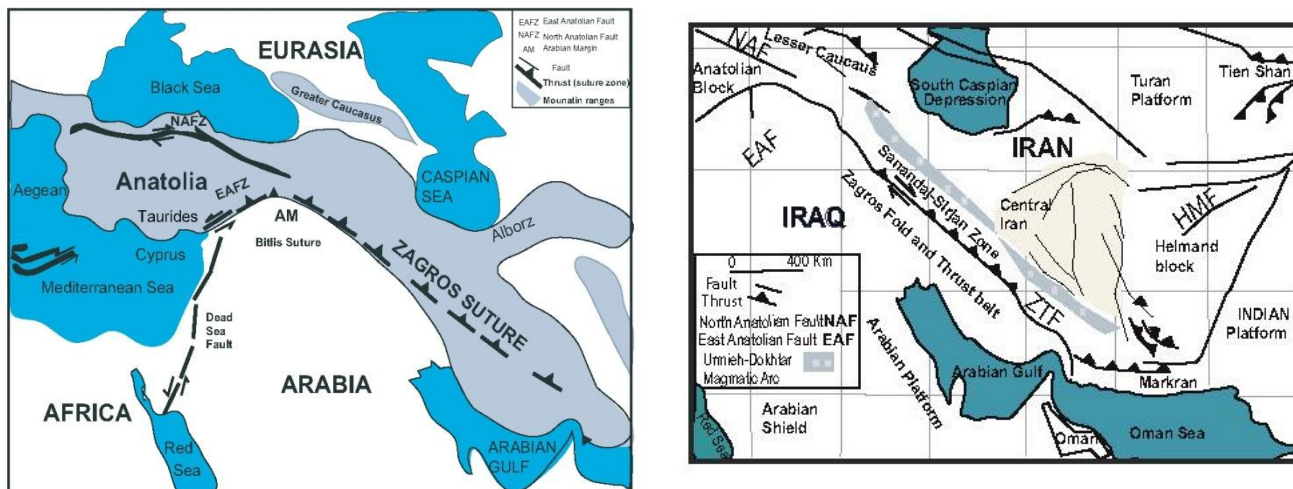


Fig 1.3 (A) Regional map showing Zagros suture extend and (Arabian, Africa, Eurasia) plats. (B) Map showing the Zagros suture in Iran and Iraq (modified after Bahroudi and Talbot 2003)

1.3 The Gotnia Basin depositional environment during Lower Jurassic- Early Cretaceous

During the late Alenian ,arestricted intershelf basin developed and covered most of eastern Iraq and gulf region known as the Gotnia Basin (Saad Z. Jassim and Jeremy C. Gogg, 2006), and other intershelf basin deveoped in the gulf region to the south evolution of Gotnia Basin and have age-equivalent to Gotnia Basin in the gulf countries (subappandix1Fig1a). The margins of Gotnia Basin are not well known because of subsequent erosion and the SW basin margin was aligned roughly parallel with the frontier between Iraq and Saudi Arabia .The western basin margin follows the eastern side of the eastern side of the Rut bah high, probably along the western margin of the Salman Zone to the north, this margin then changes course and approximately follows the line of the river Euphrates. The eastern basin margin is not known in northern Iraq since it was over thrust during convergent margin tectonics in the Cretaceous. It can be inferred that barrier must have separated the euxinic Iraqi portion of the Gotnia Basin from the open-marine waters of Neo-Tethys, which lay to the NE (Jassim and Goff, 2006b).This is consistent with the presence of Silt and plant debris in outcrops of the Bajocian-Bathonian Sargelu Formation in Iraqi Kurdistan. During the subsequent Early Jurassic, carbonate deposition became gradually more widespread, and by late Liassic time there was again a vast carbonate

evaporate conditions were platform limited to the northwestern half of the carbonate platform. (subappandix1Fig2b) ((Murriss, 1980). During the Middle-Late Jurassic evolution of the Gotnia Basin has some similarities with that of age-equivalent basins in Gulf countries to the south. The Rutbah- high in western Iraq was re-activated in the Middle Jurassic and it is continuation in SE Syria. In the Middle Jurassic to Turonian Near the end of the Early Jurassic a major change in

the regional depositional pattern occurred, The climate became more humid, so that the evaporates deposit became rare (subappendix1 Fig2.c). The depositional pattern during the Bathonian-a wide carbonate platform with an intrashelf basin in its northwestern part. Clastic material was supplied from the west and also from the south, where the Gulf of Aden area. The carbonates deposited on the platform during this period are good examples of the ramp model. The higher energy, cleaner carbonate rocks form oil and gas reservoirs in the central part of the basin. The environment of deposition by Late Oxfordian –Early Kimmeridgian time is depicted in (subappendix1Fig2.d) classic was absent and the Lurestan basin had been extended southward by flooding of the platform (Murriss, 1980). During Tithonian the climate again became arid, so that extensive evaporates were deposited on the very shallow southern platform in a sabkha environment, in the Gotnia Basin and Lurestan basin as basin salt and laminated anhydrite and shale which is represent by(Gotnia Formation) (Murriss, 1980) (subappendix1 Fig2.e).

1.4 Geological and tectonic setting of the Arabian Plate and Iraq

The stable platform interior of Arabian plate is surrounded by tectonically active margins Fig(1.4). Compression terranes define the northern and eastern margins of the plate and from the Taurus thrust suture zone of southeastern Turkey and the Zagros thrust suture zone that trends from Iraq to Oman(Ahlbrandt, 2002)

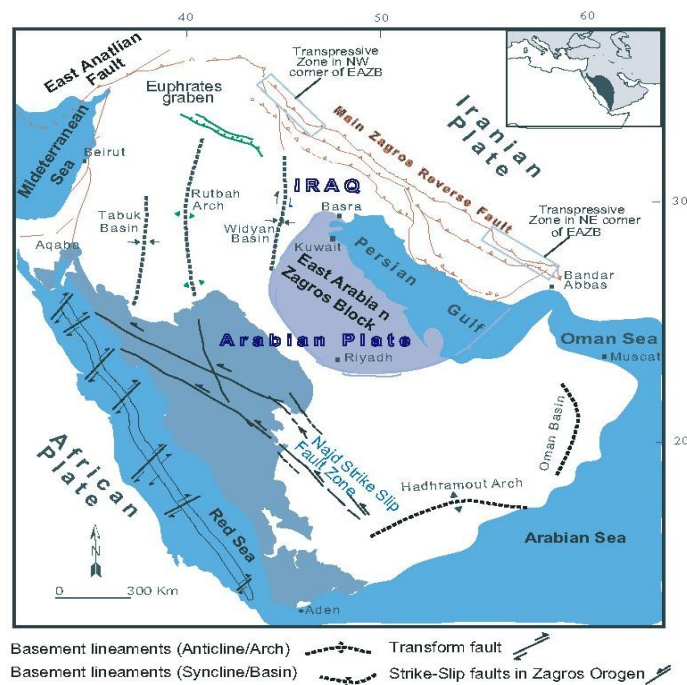


Fig 1.4 Tectonic and structure elements of the Arabian Plat and rounding areas (modified from Bahroudi and Talbot 2003).

During Middle-Late Triassic time Iranian Plate separated from the Arabian Plate and Neo-Tethys Ocean formed between these two plates according to the Glennie (2005) and Bordenave and Hegre (2005). The restricted lagoon facies was changed to the carbonate-evaporate inner shelf facies across the High Zagros Fault. During Norian–Early Jurassic time the Iranian Plate was divided into the Sanandaj –Sirjan Zone and Iranian Micro plate (Glennie, 2005). The Avroman Limestone was deposited on the Bisitoun shoal at the SW margin of the Sanandaj-Sirjan Zone. The Middle Jurassic–Early Tithonian time was characterized by rifting and differential subsidence processes (Jassim and Goff, 2006). In the Jurassic Period the Neo-Tethys Ocean attained maximum width and this time according to Numan (1997) represents the time of incipient subduction. The Sargule Formation was deposited in a euxinic environment and the Naokelekan Formation was deposited in a euxinic environment and the Barsarin Formation was deposited in restricted basin to the east and west of Zagros high fault which beyond the Zagros Foredeep Fault a sabkha environment was dominant which led to the deposition of the Gotnia Formation. During the Late Tithonian–Early Cretaceous the Avroman Limestone was still depositing in front of Sanandaj-Sirjan Zone in the Neo-Tethys Ocean. The Balambo Formation was deposited on the Arabian plate in deep environment during the Turonian –Early Campanian the Neo-Tethys 2 opened between the Bisitoun micro plate and SSZ. In the Late Cretaceous the Neo-Tethys 1 was finally closed and the Upper Cretaceous foreland basin was formed in front of the obducted shoals which became a main source. During Eocene time subducting of the passive Arabian continental margin under the active Iranian continental margin was about to be ceased, and the Neo-Tethys Ocean 2 was about closed finally (Fig 1.5). The compression and collision between the Arabian and Iranian Plates marks in the Oligocene.

The regional geological structure of Iraq in the NE of the Arabian Plate is known as a result of surface geological mapping, seismic surveys, exploration drilling and from the interpretation of regional gravity and magnetic data. In the northern Iraq two large blocks have been recognized Mosul block and Kirkuk block these blocks separated from one another by NE-SW lines and the boundaries of the blocks were regarded as the surface expression of folds or faults in the basement. The Mosul block was less stable and more uplifted relative to Kirkuk block which led to poor development of Middle Jurassic –Upper Cretaceous potential source rocks and in hydrocarbon resources which apparent from the estimated reserves of Oil and Gas in the Northern Iraq (Ameen, 1992) (subappendix 1 Fig 3). The southern part of Iraq is believed to be underlain by an Infra-Cambrian salt basin, which originated during Najd wrench faulting (Alsharhan and Nairn, 1997; Sharland et al., 2001). Furthermore, in Iraq four main structural zones have been defined within the boundaries of Iraq. The first two are the Near Geosynclinal Flank of the Mesopotamian Foredeep and the Central Faulting zones (Buday and Jassim, 1987; Verma et al., 2004). They are tectonically related to the Zagros Belt, and are characterized by a thick, strongly-folded sedimentary cover. This belt includes the Nappe Zone to the east, where

more complex folding occurred, including thrust-folded structures and over-thrusted blocks consisting of both basal strata and magmatic rocks. (Verma et al., 2004).

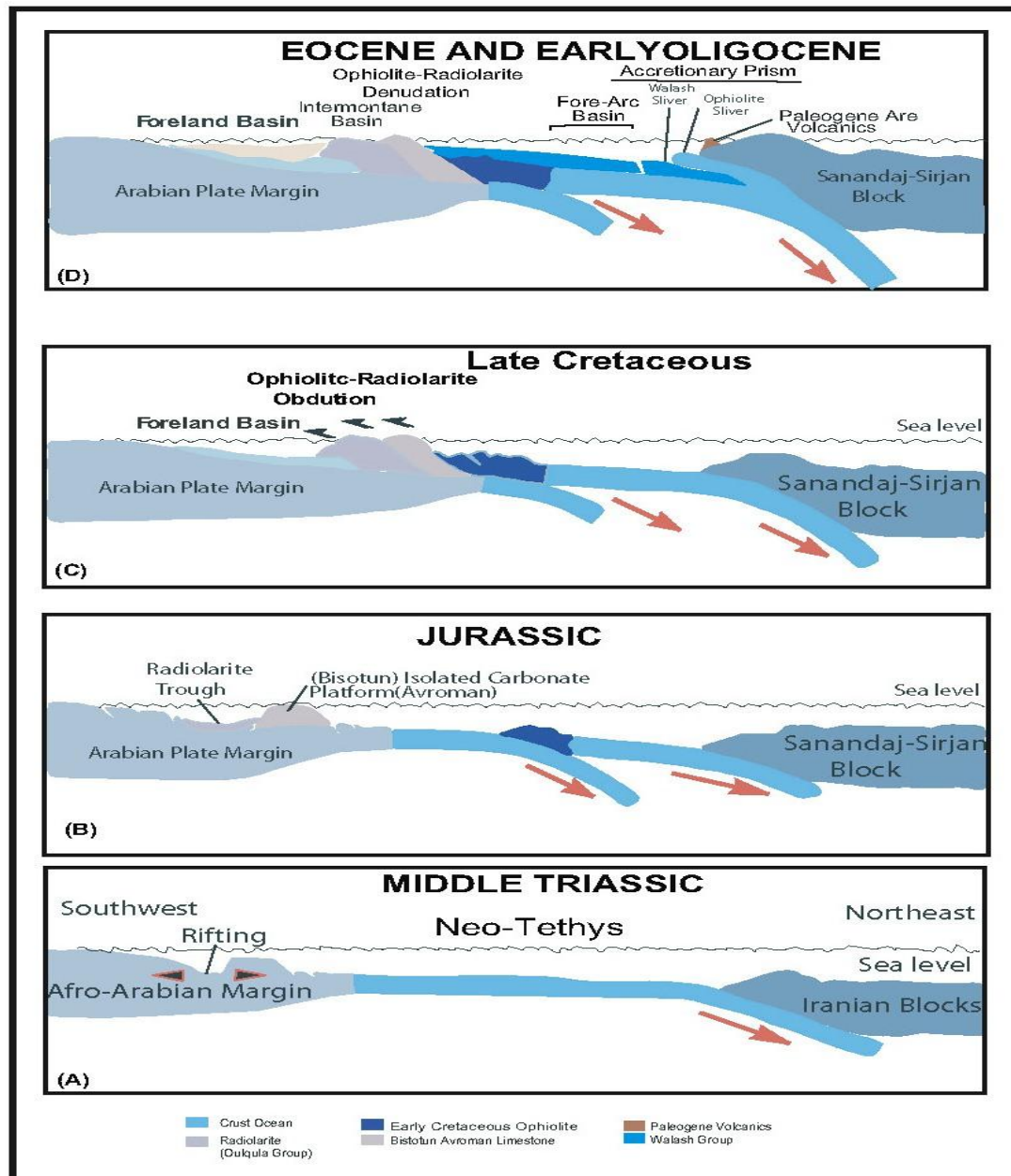


Fig 1.6: Schematic of the Tectonic evolution of Northeast Iraq (adopted from Agard et al., 2005).

1.5 Generalized sedimentation history

The passive margins are very important areas in the world because they represent areas of petroleum accumulation and thick stratigraphic column of sedimentary rocks. For Mesopotamian zone the passive margin formed by two tectonic phase: opening and closing Phase, Opening tectonic phase (Permian-Jurassic) represents the beginning of Wilson Phases. This phase includes

three stages: pre-rifting, rifting and post-rifting. In opening phase the passive margin was beginning in formation when the Iranian and Turkish phase split off from Arabian plate with opening of the Neo-Tethys Ocean. Closing tectonic phase (Cretaceous-Recent), include three stages: pre-collision, initial collision and collision stages. In these tectonic phases the plates moved together so Neo-Tethys became narrow (Condie, 1989). In Mid Triassic –Early Jurassic time, further tectonic extension occurred within the north-facing continental margin of northern Gondwana. The rate of subsidence on the northern Arabian Plate slowed and relatively uniform marginal marine clastics, evaporites and shallow water lagoon carbonates were deposited across the Mesopotamian Basin. Deposition of megalodon limestone occurred on the Bitlis-Bisitoun ridge on the north NE margin of the Arabian plate (Fig) (Aqrave et al., 2010, Jassim and Goff, 2006).

An important phase of rifting in Mid-Late Jurassic time around southern margin of Neo-Tethys extending from Oman (Rabu et al., 1990; Pratt and Smewing 1990), to the Mediterranean (Schettion and Scotese, 2002). Jassim and Goff (2006) consider that this phase of rifting probably extended further north along the margin of the Arabian Plate separating an outer carbonate ridge along the edge of Arabian Plate from the restricted Mesopotamian Basin. A transtensional NW-SE oriented salt basin developed in Yemen. In Iraq, a large –scale intrashelf basin termed the Gotnia Basin formed at the end of the Early Jurassic. (Fig) (Aqravi et al., 2010, Jassim and Goff, 2006). During Mid Tithonian age there is an important regional unconformity on the Arabian Plate. This unconformity may be a break up unconformity which formed as a result of a possible phase of ocean floor spreading around the northern margin of the Arabian Plate with the opening of a southern Neo-Tethys Ocean. In the Late Tithonian time a narrow ocean (Southern Neo Tethys) may have opened along the Northern and eastern margins of the Arabian Plate (jassim and Goff, 2006). Early Cretaceous time. Basic volcanism occurred in Tithonian-Cenomanian time all around the northern margin of Arabian Plate from the Levant through the suture zone of SE Turkey, NE Iraq, SW Iran and Oman. In Iraq, evaporate deposition in Gotnia Basin ceased in Mid Tithonian time, probably associated with the opening of the southern Neo-Tethys (jassim and Goff, 2006). The Gotnia Basin was succeeded in Late Tithonian time by the Balabo-Gara Basin. During later Cretaceous times, the ophiolites emplaced onto the Arabian plate an episode of collision along the northern and eastern margins of the plate.

In Oligocene time, A NW-SE trending basin this basin is the Mesopotamian Basin, the Carbonate shelf bordered the both sides of this basin. (Aqravi et al., 2010). In late Mid Miocene

time uplifted and rapid subsidence began into new foreland basin in the NE Iraq and SW Iran and continuing into the Late Miocene. Strong compression occurred in latest Late Miocene, this compression propagated into Mid Miocene foreland basin and led to growth of the large Zagros anticline. (Jassim and Goff, 2006). During the Pliocene, a change in plate motion occurred along the collision zone between the Arabian and Eurasian /Iranian Plates, and Iraq became an area of net erosion with the development of Tigris and Euphrates river system.

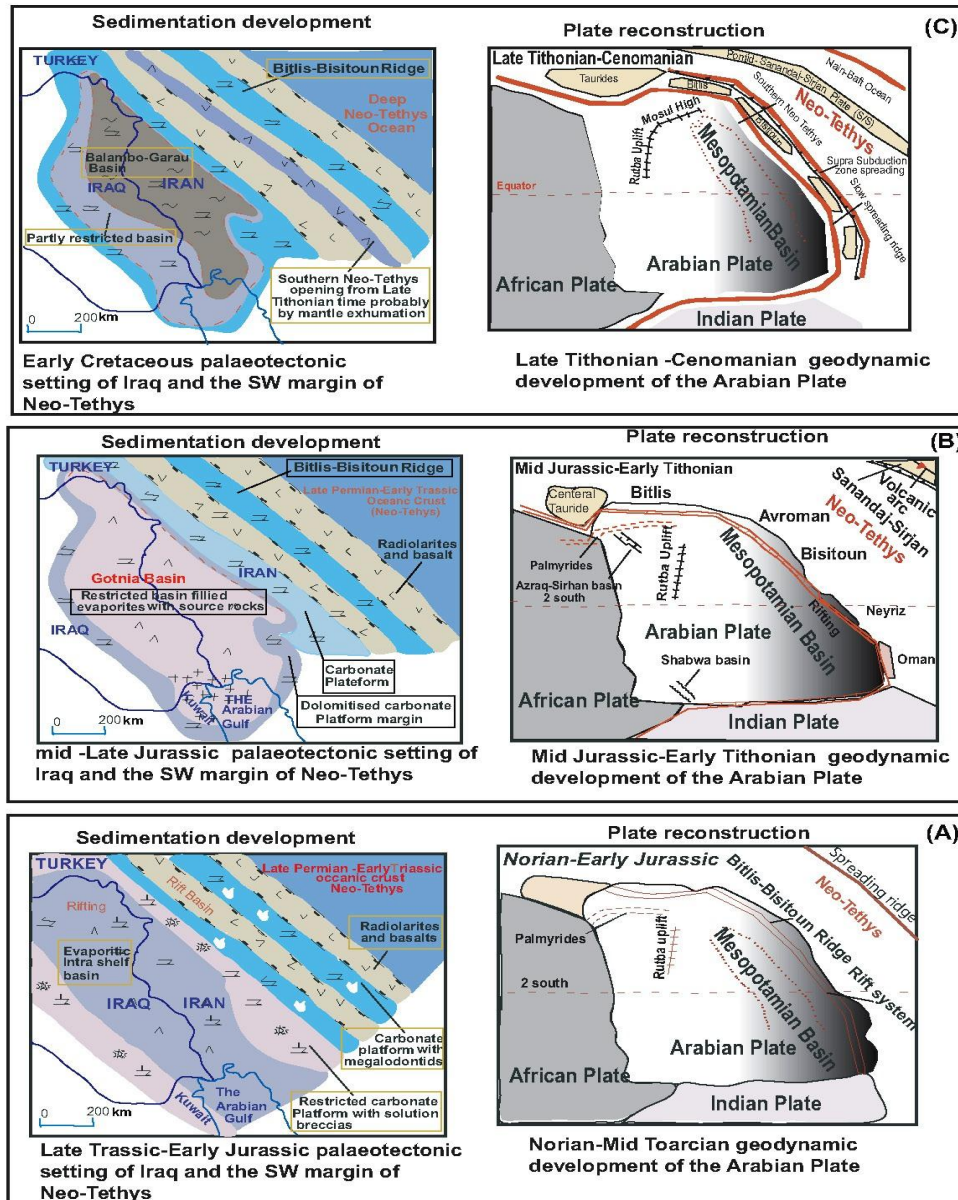


Fig 1.7 Geological evolution of Iraq during the Late Triassic-Early Jurassic (a) Mid-Late Jurassic (b) and Early Cretaceous (c) (modified after Aqrabi et al 2010; Jassim and Goff, 2006).

1.6 Paleogeography during Jurassic- Lower Cretaceous

Beydoun (1988), Alsharhan and Nairn (1997), and Christian (1997), Sharland et al. (2001) have described the lithostratigraphic of the Arabian Plate. Most of the previous lithostratigraphic studies have presented paleofacies, interpreted environments. The lower Paleozoic depositional pattern in the Middle East is relatively simple and has a high degree of correspond with sedimentational history of the northern margin of Gondwana from Maghreb to Iran (Al sharhan and Nairn, 1986). During the Mesozoic, deposition over the Arabian Platform remained relatively simple, and the ramp and platform model of carbonate deposition developed by Murriss (1981) has proven a very fruitful means of considering intracratonic sedimentary sequences (Al sharhan and Nairn,1986,1988,1990). During the Jurassic, the Middle East was, for most part, covered by shallow –shelf sea that showed periodic fluctuation in level. Although the transgressions and regression were relatively small in terms of absolute sea level change they induced major changes in sediment logical environments. In Early Jurassic A progressive of sea level rise began during the Sinemurian, the middle early Jurassic, as a shallow sea speared over the eastern and north eastern parts of carton. The northern and eastern margin of the Arabian Platform the formation of clastic and evaporate resulting from remaining of the Mardin Paleohigh in southeastern of Turkey positive feature and constituted be barrier separating the sallow open sea of northern margin of Arabian from the region to the east (Alsharhan and Nairn (1997). In Northeastern of Iraq and Western of Iran, deep water accumulated in an intershelf basin. Over the northern Arabian Plate in Jordan, Iraq, Syria and Southeastern Turkey, conditions were much the same as further south. During the Early Jurassic, Toarcian, a widespread marine transgression covered the Arabian shelf. The depositional environment was arid and varied from non-deposition and erosion in southern Arabia to a clastic platform in the west. A shallow marine, mostly carbonate, platform developed to the north and east. This time period spanned the deposition of the Mus (Iraq), Marrat (Kuwait, Saudi Arabia, United Arab Emirates), Qamchuqa (Syria) and Nirim (Levant) formations, and their regional equivalents. The eastern Mediteranean opened during this period to create a new passive margin (Al-Husseini, 1997). In Middle Jurassic the transgression of the Early Jurassic continued, again marked by short-lived still stands and/or minor transgressions. By Bathonian major interashelf basin the Lurestan Basin, this had begun to form as early as the late Liassic, developed in Iraq, Kuwait and parts of Iran in the northern Arabian Gulf (Alsharhan and Nairn, 1997). The early Late Jurassic, coinciding in timing with the onset of the southerly drift of Madagascar, as part of eastern Gondwana broke away from Africa and the rest of western Gondwana and an intra-shelf basin developed over most of Arabia this basin was the of the main Jurassic source rocks as well as several important resevoirs. During the Tithonian the Late Jurassic Although the sea level continued to rise, sedimentation rats appear to have more than kept pace with and finally exceeded, the rate of folding, with consequent development of extensive shoal and sabkha environments where extensive evaporates accumulated which correspond to the Arab reservoirs

and Arab Hith and Gotnia Basin (Alsharhan and Nairn ,1997; Al-Husseini, 1997) (subappendix1 Fig 4-7).

1.7 Petroleum Systems in Iraq

A petroleum system as defined is the rock volume within which oil, generated from source rock, migrates to and accumulates in trap (Dow, 1994). Iraq is a major petroleum-producing country in Middle East (Fig.1.11) with current proven reserves of 113 billion barrels of oil (BBO) and 110 trillion cubic feet (TCF) of gas (USGS, 2000; Ahlbrandt et al., 2000; Verma et al., 2004).

Three Total petroleum systems in Iraq (Paleozoic, Jurassic, and Cretaceous/Tertiary (Fig). Most of the petroleum that has been discovered in Iraq is reported to have been sourced from Jurassic rocks and trapped in Cretaceous and Tertiary reservoirs. Qusaiba/Akkas/Abba/Mudawwara system is the Paleozoic system (Ahlbrandt et al., 1997, 2000; Fox and Ahlbrandt, 2002) and it is located mostly in western Iraq represent by Akkas Formation and extends into surrounding portions of eastern Jordan and northern Saudi Arabia represent by Mudawar, Qusaiba Formations respectively. The Jurassic system consists of Middle and Upper Jurassic source rocks the Sargelu, Naokelekan and Gotnia formations and reservoirs of the same age in the Gotnia Basin of Iraq. The Zagros-Mesopotamian Cretaceous –Tertiary System constitutes the single largest petroleum system in the world Petroleum Assessment (Verma et al., 2004). Zubair/Ratawi, Burgan/Nahr Umr and Ahmadi/Rutbah Cretaceous reservoirs formations deltaic, Burgan/NahrUmr and Ahmadi/Rutbah Cretaceous reservoirs formations deltaic Sandstone and Carbonates .Tertiary reservoirs include the Oligocene-Miocene Kirkuk Limestone.

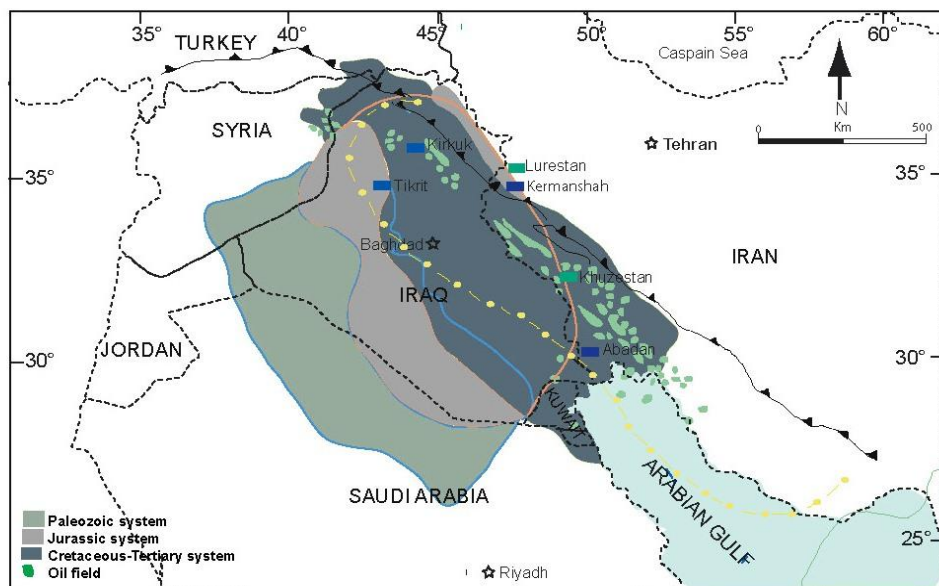


Fig 1.8 Map showing the extent of total petroleum systems in Iraq (modified after Verma et al 2004).

Sources

The most widespread source rocks in Iraq comprise Lower Silurian shale which have provide Paleozoic reservoirs, and the Jurassic –Lower Cretaceous which are the main source of hydrocarbons trapped in Cretaceous and Tertiary reservoirs.(Aqrawi et al, 2010).The Middle Jurassic age Sargelu Formation and upper Jurassic age Neokelekan Formation and the Upper Jurassic /Cretaceous age of Chia Gara Formation is major source rock in the North Iraq In South of Iraq Source Rocks are mostly Tithonian –Lower Cretaceous shale. The Sulaiy Formation is a major source rock in south Iraq, Kuwait and Saudi Arabia (Beydoun1991; Al-Ameri et al, 2009) which is equivalent in age to Chia Gara Formation in the North Iraq.Ratawi Formation equivalent in stratigraphic position to the Garagu Formation of northern and central Iraq (subappendix1 Fig 8 and 9).

Reservoirs

Most of Iraq’s Oil production comes from two reservoirs intervals, the Cenozoic (Kirkuk Group) in the Northern Iraq and the Cretaceous (Zubiar Sandstone and Mishrif Carbonates Formation) in the other parts of the country petroleum systems still either undeveloped or only partially developed. The Mesopotamian Basin in the south and upper most central of Iraq and Zagrose Oregon in the North of Iraq contain most of reservoir oil fields in Iraq (Aqrawi et al, 2010).Cretaceous and Tertiary rocks are the principal reservoirs containing oil derived from Jurassic source rocks. Cretaceous reservoirs account for 76% of the petroleum resources in the southern part of the Mesopotamian Basin with burial 3 Km (Al Gailani, 2003; Verma et al 2004; Pitman, 2004) and the remaining petroleum is production from Tertiary reservoirs in the Zagros fold belt burial depths less than 2Km (Pitman, 2004).The stratigraphic section for the main oil reservoirs in the Cretaceous and Tertiary are carbonates (Beydoun et al.,1992)and the sand stone reservoir of Cretaceous age are present but less common (Pitman et al .,2004).Although a few free gas in Tertiary reservoirs has been encountered along the eastern margin of the fold belt and one (Akkas) produces from Paleozoic reservoir in Western Iraq most fields in Iraq are dominated by oil (Aqrawi et al, 2010) (subappendix1 Fig 8 and 9).

Seals

Regional –scale Cap rocks in Iraq include evaporates of Late Jurassic and Middle Miocene age together with siliciclastics, carbonate seals may provide effective seals at a field scale. Top seal for many large oil reservoirs in Mesopotamian Basin are Cretaceous shale (Alsharhan and Nairn, 1997).For Jurassic source facies the Upper anhydrite (Gotnia Formation) is regional seal (Pitman et al., 2004).The Miocene –age in the fold belt supratidal evaporates and sub-unconformity sealed petroleum traps, but many of the seals have been breached by fracturing and erosion Beydoun et al., 1992) (subappendix1 Fig 8 and 9).

1.7.1 Jurassic Petroleum system in Iraq

The Jurassic petroleum system of Arabia contains the world largest oil field according to the USGS definition. The Jurassic petroleum system in Iraq includes source rock of Sargelu, Naokelkan and Gotnia Formations and reservoirs of the same age (verma et al2004) Fig () and the Jurassic age in Iraq contains very significant source rocks over all southern, northern of Iraq. The Early Jurassic was a time of relative stability as reflected by the deposition of the Alan Anhydrite, Mus Limestone and Adaiyah Anhydrite formations. In the Middle Jurassic, a new basin developed due to Toarcian rifting. It was typified by deposition of black, papery, organic-rich shale of the Sargelu Formation and its equivalents all over the Arabian Plate and most of the Tethys region .This deposition occurred in large, shallow, euxinic, intraplate basins (Hallam 1975; Murriss 1980;Beydoun 1988, 1991). This period of deposition ended at the end of the Bathonian, with the development of a regional unconformity which was associated with widespread erosion.The basin configuration for the end-Bathonian onwards is reflected by the variability in Najmah Formation thicknesses recorded by Dunnington (1959). The Najmah oolites are developed along the western margin of a basin, the center of which is represented by Naokelekan Formation in the Zagros region to the east. The eastern margin to this basin is not known in northern Arabia since it was overthrust during the Late Cretaceous onwards. Large areas of the basin margin were uplifted during the Neocomian around the Khlaisiya High and in the. Southwestern parts of the country. Moreover, Ponikarov et al. (1967) indicated that the Upper Jurassic sediments are absent in the adjacent northeastern parts of Syria. Jurassic rocks consist of four formations, in ascending order (Buday, 1980): the Butmah, Adaiyah, and Mus Formations, and Alan anhydrite. The Butmah is composed of a marine neritic calcareous unit, followed by variegated shale, siltstones, iron-rich sandstones, and a cap of limestone. The Adaiyah Formation, grades into the Mus Formation, which is mainly a thick carbonate platform fades that terminates with the Alan anhydrite. Above, the Middle Jurassic Sargelu Formation consists of basinal black, bituminous, phosphatic marls and argillaceous limestone, dolomites, and shales. Sadooni, 1997 divided the Stratigraphy of Middle–Upper Jurassic sediments in Iraq into three distinctive sequences: First sequence the Bajocian –Bathonian sediments consist of dark, organic-rich, papery shale of the Sargelu Formation. The thickness of the formation is around 115 m in the type locality in the Surdash anticline, Sulaimeniya district, NE Iraq and may have been deposited in a stratified, anoxic sea. On the basin flank to the west, a highstandoolitic shoal of the Muhaiwir Formation was deposited. Aregional unconformity during the Late Bathonian ended this sequence. The second sequence: The Late Bathonian unconformity was followed by basin flooding that led to the deposition of high stand, basin-margin, and shallow water carbonates of the Najmah Formation that on lapped the Sargelu. In the basin center, to the east, the Naokelekan Formation was deposited. The condensed section of Naokelekan consists of around 20 m of bituminous shale (the so-called the Coal Horizon) and bituminous, dolomitic limestone (called Mottled Bed). In Sequence three: The gradual restriction of the basin during the Kimeridgian led to the deposition of the Gotnia evaporates in basin margin settings as a low

stand wedge of gypsum (LSW-G), followed by basin-fill halite (BFH). The Gotnia consists of more than 200 m of bedded and nodular anhydrites with halites in the southwestern parts of Iraq. The formation may be, in general at least, equivalent to the Hith Formation of Saudi Arabia (Al-Sakini 1992; Alsharhan & Kendall 1986). In northeast Iraq, the Gotnia is replaced by the Barsarin Formation. This formation consists of around 17 m of crumbled, brecciated limestones and dolomites with local chert and mixture of shale and marl.

Source Rocks, Reservoir Rocks and Seal Rocks of Jurassic petroleum system in Iraq

Pitman et al. (2004) modeled the maturation of the Jurassic source rocks in Iraq and they considered that the Sargelu and Naokelekan Formations are the most important Jurassic source rock in Iraq and that Cretaceous source rocks had contributed only small amounts of oil to Cretaceous-Tertiary petroleum system. Most Jurassic source rocks in Iraq have already reached or Exceeded peak oil generation and have started to generate significant quantities of gas (Jassim and Al –Gailani, 2006). During the late Mesozoic and early Cenozoic, sedimentation in the area of the present Mesopotamian Basin and Zagros fold belt was controlled by local tectonics, eustatic sea-level changes, and climate variations (Pitman et al., 2004) Sea-level fluctuations in conjunction with slow subsidence led to the formation of large, but shallow intrashelf basins on the passive margin of the Neo-Tethys Ocean and the Arabian Plate from Jurassic to the Late Cretaceous time (Stoneley, 1987; Alsharhan and Nairn, 1997; Murriss, 1980). Under anoxic conditions and high-energy carbonates organic –rich sediments accumulated in the shallow interashelf basins and gave rise to Sargule and Naokelekan Jurassic source rocks (pitman et al., 2004). Most Jurassic reservoirs lie at depths ranging from 1,400 to 3,750m (Alsharhan and Nairn, 1997). The Najmah Formation, equivalent to the Arab Formation of the southern Gulf region ,includes proven reservoir rock intervals .Jassim and Al-Gailani (2006) proposed that 19 structures in Iraq contain hydrocarbons in this formation .Reservoir facies include oolitic –peloidal grain stones and packstones .Thick Gotnia Formation anhydrites represent a potential regional seal for Jurassic Petroleum system in the SE Iraq .In the SW Iraq, the Gotnia Formation is thinner but may seal the underlying Najmah Formation shelfal facies (Al-Naqib, 1967). To the North of Makhul and East Baghdad ,the Gotnia Formation is replaced by the collapse breccias of the Barsarin Formation which probably do not constitute an effective seal

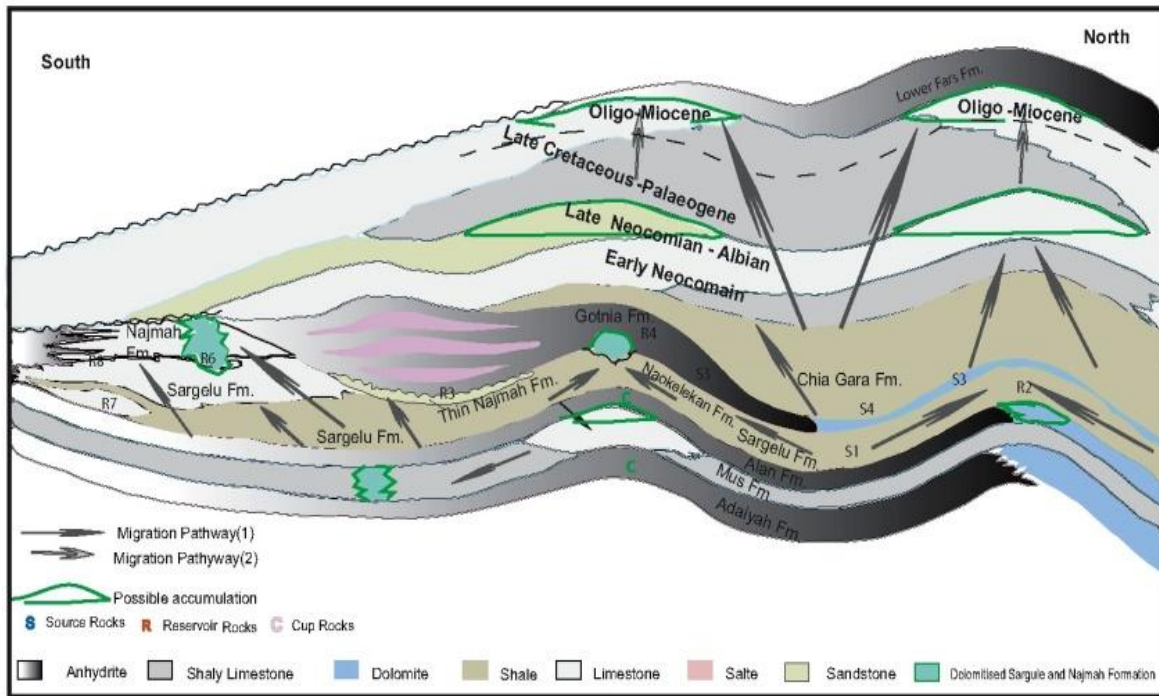


Fig 1. 9: Schematic cross-section through the Jurassic petroleum system in Iraq, showing the spatial distribution of source, reservoir and seal units (modified after Aqrawi et al 2010)

1.7.2 Cretaceous Petroleum System in Iraq

The most important petroleum system in Iraq is the Cretaceous. Although the Tithonian (upper most Jurassic) to lower Cretaceous source rocks charged Cretaceous reservoirs throughout central and southern Iraq and in the Northern and NE Iraq underlying Jurassic source rocks may also have charged Cretaceous reservoir where the Upper Jurassic evaporate seal is ineffective (pitman et al., 2004; Goff, 2005). Ibrahim (1983) studied the maturation of Lower Cretaceous source Rocks in SE Iraq. Throughout southern Iraq, Albian source rocks are less mature than the deeper Tithonian units. Upper Cretaceous intervals are immature throughout Kuwait (Abdullah and Kinghorn, 1996).

Source rock intervals consist of organic –rich shale deposited in the center of the Balambo-Gara Basin. Cretaceous source rocks in Iraq are mainly represents in Chia Gara, Balambo and Sulaiy formations. IN the Southern Iraq Sulaiy Formation is proven oil source rock (Al-Ameri and Al

Obaidi (2004)).Balambo Formation in the Northern Iraq contains a mixture of marine and terrestrial Kerogen including plant, pollen and spore debris (Al-Haba and Abdullah (1989).

Cretaceous reservoir rocks are abundant, especially in the S Iraq .However, four reservoir units contain most of the oil of the region ,the Yamama ,Zubair ,Naher Umer and Mishrif .Other formations are locally important and include the Sulaiy ,Ratawi, Shuaiba ,Mauddud,Rumaila, Khasib-Tanuma-SAdi,Hartha and Tayarat .In N Iraq the Qamchuqa Formation is a reservoir in the Oil bearing structures of the Kirkuk Embayment and in the Mosul High .The Shiranish, Hartha and Kometan Formation are important fractured carbonate reservoirs in N Iraq. The main reservoir in cretaceous petroleum system in Iraq is the Zubair Formation sand stone which is main pay zone in the southern Iraq and may have minor reservoir potential in NW central Iraq. Shale unites within the Zubiar Formation are internal seals in Southern and Central Iraq. IN the Northern Iraq the only sealing facies are marly units at the Lower Qamchuqa Formation which is the Garagu Formation and in the southern Iraq Shaiba is unconformably overlain by NahrUmer Formation channel sandstones and thus lacks a seal (Aqrawi et al., 2010).

1.8 Petroleum system North Iraq

The Zagros Organic Belt in Iraq and Iran is one of the most prolific petroliferous areas and the Zagros basin (Iraq) constitutes a rich petroleum province. Continental collision between Iranian and Arabian plates resulted in the formation of the Zagros fold–thrust belt and its associated foreland basin. During convergence, pre-existing faults in the basement were reactivated and the sedimentary cover was shortened above two different types of basal decollement (viscous/frictional). This led to heterogeneous deformation which segmented not only the Zagros fold–thrust belt but also its foreland basin into different compartments resulting in variation in facies ((Bahroudi and Koyi, 2004). The Zagros Foreland Basin, as an integral part of the ZFTB, is a specific type of the foreland system, which is a site of favorable conditions of Hydrocarbon generation, migration and accumulation, thus the ZFTB is one of the richest oil and gas provinces in the world.

Northern Iraq is a part of the Zagros Folded Belt and is lies in the Northern part of this Belt. In Northern Iraq because of differences in areal distribution of sources, carrier-reservoirs, and cap rocks associated with the different basins, and because of the different times at which primary migration and accumulation occurred, the differently originating oils are now found to occupy different and to some extent mutually exclusive parts of the region. Most of the known oil accumulations of Northern Iraq probably originated by upward migration from earlier, deeper accumulations which were initially housed in stratigraphic or long-established structural traps, and which are now largely depleted. (Dunnington, 2005). Dunnington studied stratigraphic development in the north of Iraq .He pointed out that the Precambrian basement is not exposed anywhere in Northern Iraq, and deep boring has not yet penetrated the base of the Triassic, and Paleozoic rocks crop out in the extreme north of the region close to the Turkish frontier,

Cambrian succession includes bedded salt in its lower parts and this including important salt components, may underlie much of the normally folded zone of the Zagros. Despite the great thickness of post-Cambrian sediments in the Northern of Iraq argues against the presence of any thick salt series at depth. The Triassic basin and its sediments are occupied all Northern Iraq and extended far to Turkey and Syria and Persia. The Liassic basin was more localized than that of the Triassic.

Middle Jurassic in the North of Iraq are markedly bituminous both in the mountain zone and in the thick sedimentation belt, because of the euxinic depositional conditions source potentialities are high. The conditions of the Middle Jurassic were largely repeated in the Upper Jurassic time, with a thin terminal anhydrite unit. Tithonian sediments are regarded as very important potential source rocks, without any apparent outlet to adjacent potential reservoir and the highest-quality source rocks are of late Tithonian-earliest Cretaceous age which shows a similar pattern of TOC variation through the Garau Formation in Iran that led to suggesting similarities between the Iraq and Iranian (Lurestan) source rock systems. At the end of Berriasian time important tectonic movements occurred which could manifested in: tabular elevation of the area lying northwest and west of Mosul and tilting and uplift of a block embracing the Najmah, Qalian and Atshan area. Stratigraphic relationships for Early Cretaceous were rather complex, high tabular feature was raised during the Jurassic-Cretaceous transition period which made and this large uplift was not overlapped until late Barremian – Aptian time. The Upper Cretaceous transgression starts at some time during the upper Campanian, and inaugurated an episode of thick and varied sedimentation. In the Northern Iraq, it is difficult to separate the Jurassic Petroleum system from that in Cretaceous source rock intervals in Cretaceous Petroleum system occur over a similar geographical area to those in Jurassic, and the Oils generated by the two system are very similar in composition (Goof, 2005). They are probably mixed in areas where the Gotnia Formation anhydrite seal is absent or breached by faulting. The importance of uppermost Jurassic – Lower Cretaceous source rocks in charging Cretaceous and Cenozoic reservoirs in northern Iraq were discussed by Dunnington (1958). The prospectively of the Jurassic reservoirs in N Iraq is limited because of the frequent absence of the Jurassic evaporate cap rock. Bordenave and Burwood (1990) and Bordenave and Hue (1995) identified three source rocks system in Iran: the Gara, Kazhdumi and Gurpi Formation, which are equivalent to Balambo, Chia Gara, Naher Umer and Shiranish Formations in Iraq. The most important source rocks are the Shale-Dominated Chia Gara Formation and the Basel parts of the overlying Balambo Formation.

Oil fields of North Iraq are part of the Zagros Fold Belt in a regional extent and mainly within folded zone of elongated area between the thrust zone in the triple junction boundary with Iran and Turkey and the Mesopotamian Foredeep basin, with Khleisya Uplift toward southwestern part of North Iraq. The narrow interior fold belt for Zagros belt plunges SW along the 'mountain-front flexure' into a folded foothills belt, which is the setting for the major Oilfield of Iran and Iraq in the Dezful and Kirkuk embayment (W.J.Koop and R. Stoneley, 1982)

1.9 Objectives

This study focuses on Jurassic-Lower Cretaceous Petroleum system North Iraq for several reasons

1-Northern Iraq lies within the northern part of the Zagros Folded Belt which was strongly influenced by the reactivation of old tectonic fabrics in its basement that can be recognized in the deposition and deformation of the Phanerozoic cover in the Zagros Basin (mountains plus foreland) all these with the repeated reactivation of basement fault make this area supergiant and giant of Oil and Gas fields.

2- The organic matter-rich sediments of the Jurassic Formations in all Iraq and in Middle East in general are an attractive research topic due to the high TOC contents in a thick sedimentary column deposited within a relatively short time interval

3- The importance of Jurassic –Lower Cretaceous Petroleum system in Iraq and especially in the North of Iraq, because of high quality of (source, reservoir and seal rocks) in this system.

4- There are many further questions about the Jurassic-Lower Cretaceous Formations in the North Iraq

Therefore, the aims of this study are to couple data

1-Evaluate the variations in source rock properties (source, thermal maturity (TOC, and Rock-Eval pyrolysis maturation) and hydrocarbon potential of organic matter) to determine the source rock capability and Kerogen type, characterization and amount of generated oil for the Jurassic – Lower Cretaceous Formations in the Northern Iraq.

2- Study the biomarkers distribution for the Lower Jurassic-Upper Cretaceous Formation in the North of Iraq and for the solid bitumen and crude oils in the Miocene reservoirs Formations in the North of Iraq to reach the aims in point 3

3- Comparison between the source rocks and the residual bitumen and crude oils in the Miocene reservoirs to show the relationship between them in order to know the origin of the residual bitumen and crude oils.

Chapter 2

Geology, Palaeofacies maps, well logs, organic geochemistry of the Lower Jurassic-Upper Cretaceous Source rocks NE Iraq.

2.1 Stratigraphic and Geological setting

This study focuses on the northern part of Iraq. The Mesozoic and Cenozoic age Zagros Basin can be divided depending on the presence of salt deposits into two main sub-basins, the Southeastern Zagros Basin (Zagros Hormuz Salt Basin) and the Northwestern Zagros Basin (Bahroudi and Koyi, 2004). The present study area is located in the Northwestern Zagros Basin. In Iraq the Folded Zone has been divided into the High Folded Zone with outcropping Mesozoic rocks and the Low Folded /Foothill Zone in which mainly Cenozoic rocks are exposed (Aqrawi et al., 2010). The Low Folded Zone/Foothill Zone comprises the Mousal-Butmah Subzone and Kirkuk-Hamrin Subzone, which is divided into the Kirkuk-Chemchemal Zone, and Makhul-Hamrin Subzone, which is the deepest part of the northwestern segment of the Zagros folded- thrust belt where the present study is located (Omer and Koyi, 2012). The Mesopotamian Basin, which lies at the east of the stable Shelf (Jassim and Goff 2006; Aqrawi et al., 2010) is an elongated basin running from Syria south-eastwards to the Persian Gulf and it is bordered on the south-west by the Arabian Massif, on the north by the mountains of Anatolia, and on the east by the foothills of Zagros Folded thrust belt.

Rock samples were collected from the Ajeel oil field from two wells (Aj-8, Aj-12). This oil field is one of many fields, which are structurally oriented NW-SE within the northern part. It is adjacent to the low folded zone of the Zagros Fold Belt and located in the low folded zone of the Zagros Fold Belt with transition towards the northern part of the Mesopotamian Foredeep Basin and geographically within the Salahuddin Governorates to the east of the Tigris river between the cities of Tikrit and Beiji. It lies about 30km to the northeast of Tikrit city, North Iraq, and to the southwest of the Hamrin oil field, which lies 80 km from Kirkuk city and parallel to it. The average elevation of the field area is 150-170 m above Mean Sea Level. The structure of the field is an asymmetrical, double-plunging anticline trending NW-SE with a closure of 150 m in height and 10 km long on top of the Gotnia Formation lying within the flat plains of northern Iraq. A number of minor faults dissect the structure. It contains major oil and gas accumulations and a number of minor accumulations mainly of gas. The reservoir structure consists of the main (southern) dome and North West dome. The main reservoir units are the Jeribe and Euphrates formations, and the main source units are Jurassic age Sargelu and Najmah Formations and lower Cretaceous Chia Gara Formation.

Ajeel 8: this well is located on the SW flank of the structure and on the crest maxima of the cretaceous, and of 163 m above sea level.

Location: Elevation: 163 m RTKB. The U.T.M coordinates are as following:

N: 386, 000 E: 389, 050 or N: 34, 87632 ° E: 43, 78598722

Ajeel 12: this well is located on the SW of the structure, and it lies 2650 m SE of Ajeel-8 well.

Location: Elevation: 157 m RTKB. The U.T.M coordinates are as following:

N: 3858 116.5

E: 390, 817 or N: 34, 7241 °

E: 43, 99416966

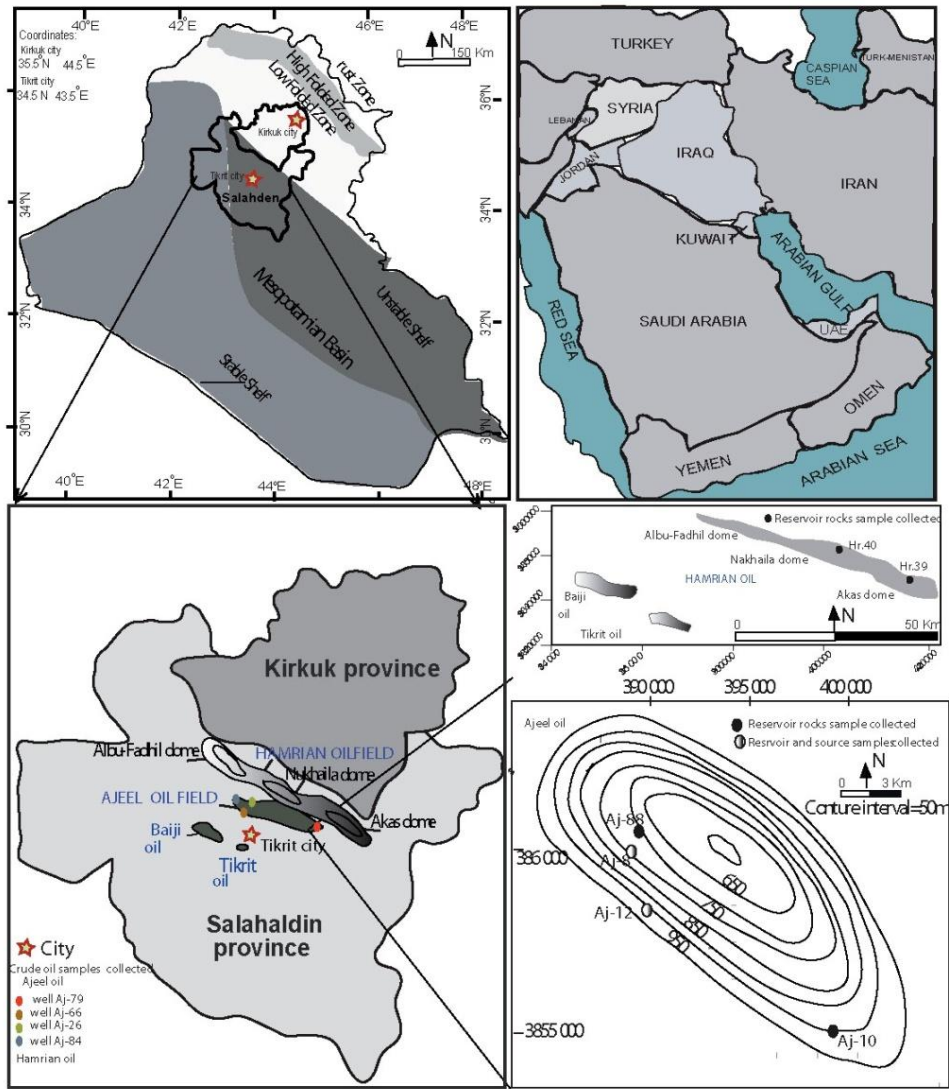


Fig 2.1: (a) a simplified map showing Iraq site with the Arabian plate (b) Regional tectonic setting of Iraq (modified from Jassim and Goff, 2006) and show two province boundaries where samples studied were collect. (c) Location map showing oil fields and wells where the crude oil samples are collect.(d) structure contour map for Ajeel oil field and location map for Hamrin oil field showing the wells where the source and reservoir samples where collect.

Within the early Jurassic sequence, the facies variation is more marked, with the presence of thick evaporate intervals (Alan and Adaiyah Formations) (Burrty, 2015).

The Mus Formation was described by Dunnington in 1953 in well Butmah-2 (Bellen et al; 1959) in the Foothill Zone of Northern Iraq and is on average 40 m thick. It reaches 56 m in its type section, which is in well Butmah-2 (Dunnington et al., 1959). The Mus Formation consists of limestone, dolomitic peloidal limestone with marly limestone, shale and rare anhydrites and is interpreted as a subtidal low-to moderate energy shelf deposit. The Mus Formation overlies the Alan Formation and the contact between them is generally sharp. The contact with underlying Adaiyah is conformable. The Mus Formation has a similar distribution to the underlying Adaiyah Anhydrite Formation in the Foothill and Mesopotamian zones. In NE Iraq, in the high folded zone, the Mus Formation replaced by the Sehkanian Formation which consists of 44 m of highly fossiliferous, organic peloidal, limestone (Dunnington et al., 1959; Kaddouri,1986). The Mus Formation in Iran is equivalent to the lower part of the Marrat Formation (Bellen et al., 1959) and some limestone members of Surmeh Formation (James and Wynd, 1965).

The Alan Formation, which is the uppermost part of the Liassic Sequence in the western parts of the unstable shelf and on the stable Shelf in Iraq is 59 m thick at its type locality at well Alan-1 and comprises bedded anhydrites with secondary pseudo-oolitic limestone (Dunnington, 1953a; Buday, 1980; Jassim et al., 2006). Halite is observed in some localities (Alsharhan and Nairn, 2003). The Formation was deposited in a sabkha environment (Buday, 1980; Jassim et al., 2006) and it is marked as the lowest regional seal.

The Middle Jurassic age Sargelu Formation occurs throughout most of Iraq and it was first described by Wetzel in 1948 (Bellen et al; 1959) from the Surdash anticline of high Folded Zone of NE Iraq. In the Rutba Subzone the Sargelu Formation passes into the Muhaiwir Formation (Dunnington et al .,1959; Jassim and Buday;2006). The Sargelu Formation has variable thickness and at its type locality in the Surdash anticline it is about 115 m thick (Wetzel, 1948; Budy, 1980; Balaky, 2004; Jassim and Buday 2006b, Dunnington et al., 1959). The thickness of the Formation in the North thrust and simply folded zone has a range from 20 m in the northwestern Iraq to 125 m in Northeastern Iraq near Halabja. The thickness of the Sargelu Formation ranges from 100- 400 m in the southern of Mesopotamian Basin. The thickness of the Sargelu Formation in the Iran (Lurestan, Khuzestan) area is 152–213 m and in Kuwait it has a range between 75–83m, in Burgan and Umm Gudair, respectively (James and Wynd, 1965; Jassim and Buday). The lithological composition of the formation is consistent. In spite of the thickness changes, the facies for Sargelu Formation is uniform and it is composed of thin-bedded, black, bituminous limestone, dolomitic limestone, and black papery organic rich shale with chert (Wetzel, 1948; Buday, 1980; Balaky, 2004; Jassim and Buday, 2006b). In Kurdistan, Balaky (2004) recognized four lithofacies types in the Sargelu Formation which are: Dolomite Bositra Limestone, Cherty Limestone and Argillaceous Limestone. The depositional environment of the Sargelu Formation is restricted marine to euxinic. During the Middle Jurassic period the deposition was the same as was

present during the Early Jurassic. The Sargelu Formation was deposited in a marine basin and represents a deeper ramp (Balaky, 2004), and the organic-rich sediments of the Sargelu Formation indicate euxinic (anoxic) conditions (Sadooni, 1997) in his division of the Middle-Upper Jurassic sediment in Iraq (subappendix2 Fig1), he classified the Sargelu Formation into **Sequence S1**: The Bajocian-Bathonian sediments which consist of dark, organic-rich, papery shale. The Formations which underlie the Sargelu Formation are either Sehkaniyan or the Lower Jurassic Anhydrite Alan Formations. They are overlaid by the bituminous limestone and shale of the Upper Jurassic Najmah or Naokelekan Formation. In surrounding countries, the Sargelu Formation is comparable in age to some stratigraphic units, which are the Dhurma Formation of Saudi Arabia; the uppermost part of the Dolaa Group in northeastern and in central Syria; the upper parts of the Cudi Group of southeastern Turkey. In the southwestern part of Iran the Sargelu Formation is equivalent in age to the Lower part of the Surmah Formation (James and Wynd, 1965; Altinli, 1966; Dubertret, 1966; Buday, 1980; Jassim and Buday, 2006b).

In Iraq, the Late Jurassic succession, which includes the **Najmah and Naokelekan Formation**, represents an important source of hydrocarbon produced in the Zagros basin and Fold belts (Othman 1990, Ahmed 2007, Al-Ameri and Zumberge 2012), besides the main Jurassic source units. A different pattern is observed in the Mid-Late Jurassic carbonate sequences, where the shelf deposits of the Najmah Formation, observed around Mousal, pass into the dolomite-rich Naokelekan and Barsarian Formations in Kirkuk and Sulimaniya regions (Burrty, 2015). **The Late Bathonian Najmah Formation** was described for the first time in an unpublished report by Dunnington (1958). The type locality of the Formation is in the Najmah-29 well with a total thickness of around 340m. The Najmah Formation has a fairly complicated stratigraphy due to widespread erosion that both predated and followed its deposition. Sadooni (1997) in his previously mentioned division categorized the Najmah and Naokelekan Formation as **Sequence S2**. Following post-Toarcian rifting in Iraq, basin margin oolitic-peloidal shoals and low relief sponge-algal buildups were deposited in the Najmah Formation. In the basin centre, a condensed section of black shale was laid down (Naokelekan Formation), which consists of around 20 m of bituminous shales (the so-called the coal Horizon) and bituminous, dolomitic limestone (called Mottled Bed). In its type locality the Najmah Formation is composed from the base to the top of: 1- fine-grade, dense, recrystallized limestone; 2-oolitic and pseudo-oolitic limestone with macrofossil fragments; 3-coarse grained dolomite with bulky crystals of dolomite and 4- feathery textured limestone and thin anhydrite. A thin division of limestone and black shale is found in the lower part in some localities (Dunnington, 1953c; Al-Omari and Sadik, 1977; Buday, 1980; Al-Sayyab et al., 1982; Jassim and Buday, 2006b), and according to Dunnington (1959) the formation consists of fine-grained limestone with oolitic and pseudo-oolitic limestone with dolomites and thin anhydrites. The Najmah deposition started with the flooding of the Sargelu Basin that led to the development of a highstand and for the most part the formation was deposited under neritic conditions and restricted lagoonal facies appears in other parts (Buday, 1980). In the type section and surrounding area the contact of the formation is both unconformable with underlain Sargelu Formation and overlain Gotnia Formation. It is possible that the Najmah Formation may also inter finger with the Gotnia Formation, and in the south of Iraq the Najmah Formation is overlain by the Gotnia formation. The Formation extends into Saudi Arabia and Kuwait

(Arab and Jubaila formations; Powers et al., 1966) but the formation does not continue towards the W and N into Syria and S Turkey. In SW Iran, Najmah age is equivalent to the lower and middle part of the Surmah Formation. Upper Jurassic formations are absent in the Iraq/Syria and Iraq/Turkey border areas. The varying thickness of the Najmah Formation during Callovian-Oxfordian time passes laterally into the **Naokelekan Formation** to the SE, and there was an area of non-deposition over the present-day Mousal High (Burrty, 2015). In the Late Jurassic, a foreland Basin developed at the margin of the craton, accommodating the deposition of Naokelekan and Barsarin Formations in the Barsarin area (Murriss 1980; Numan 2000), which are equivalent in age to the Najmah and Gotnia formations. The Naokelekan Formation at its type locality in Naokelekan village comprises three units from the base to the top of: 1- a thin-bedded, extremely bituminous dolomite and limestone with intercalated black shale; 2- a thin bedded, blueish, hard, fossiliferous dolomitic limestone and 3- a laminated argillaceous bituminous limestone alternating with shaly limestone (Wetzel and Morton, 1950). Naokelekan Formation was deposited in lagoonal and shallow open marine environments (Salae, 2001). Balaky (2008) divided the formation into two lithofacies associations: subtidal and open marine. In the Kurdistan regions of NE Iraq, the Naokelekan Formation consists of thin-to medium-bedded, black, bituminous limestones, and dolomitic limestone, intercalated with thin, black, calcareous shale in lower and upper parts (Balaky, 2014).

The Tithonian Gotnia Formation is recorded in northern and southern Iraq and in adjacent parts of Kuwait. It passes to the N and NE into the carbonates and breccias of the Barsarin Formation (Aqrabi, 2010). The type locality of the Gotnia Formation is well Awasil-5 in central Iraq (Dunnington et al., 1959). Here the formation is 193 m thick and comprises anhydrite with subordinate beds of brown calcareous shale, thin black bituminous shale, and recrystallized oolitic limestone (Bellen et al., 1959, Dunnington et al., 1959; Al-Omari and Sadik, 1977; Buday, 1980; Al-Sayyab et al., 1982; Jassim and Buday, 2006 b). There are two main deep centers located mostly within the Mesopotamian Zone. The southern depocentre extends into Kuwait (620 m). The northern deep centre is near Tikirit (466 m) and (261 m) in N Iraq for the Barsarin and Gotnia Formation in well Jabal Kand-1 (Jassim and Goff, 2006). The Gotnia Formation may have been deposited in a hypersaline lagoon environment (Alsharhan and Naim, 2003) and separates a structurally elevated subbasin that was partially isolated from the Gotnia Basin of southern Iraq, which is restricted and starved of clastic sediments. The underlying Najmah or Naokalekan Formation and overlying Chia Gara Formations were both mostly deposited in deep-water euxinic environments (Aqrabi, 2010). **Sequence S3:** is the location of the Gotnia Formation in Saddoni's (1997) division. Gradual restriction of the basin during the Kimmeridgian led to the deposition of Gotnia evaporites in basin margin settings as a lowstand wedge of gypsum (LSW-G), followed by basin-fill halite (BFH). In the southwestern parts of Iraq, the Gotnia Formation consists of more than 200 m of bedded anhydrite with halites. The formation may be, in general at least, equivalent to the Hith Formation of Saudi Arabia. The Gotnia Formation was deposited in a similar setting to that of the Hartlepool Anhydrite Formation of the Upper Permian Zechstein in the northeast England (Tucker, 1991). The Gotnia Formation in Kuwait and the Gulf region the Gotnia Formation has been assigned a Kimmeridgian to Early Tithonian age (Al-Sharhan and Kendall, 1986). In the type locality the contacts

of the formation and in other subsurface sections usually appear conformable. The upper contact with the Makhul Formation is erosional. In the Gulf area and E Saudi Arabia, the Gotnia Formation passes partly into the Hith Formation and partly into units A, B and C of the Arab Formation (Powers et al., 1966). The **Barsarin Formation** was defined by Wetzel in 1950 from the type area in Balambo-Tanjero Zone near Rowandus in NE Iraq. It is 17 m thick at its type locality at Barsarin (Dunnington et al., 1959) and comprises limestone and dolomitic limestone. Argillaceous breccias may have formed by dissolution of anhydrite beds and contorted beds. In the high Zagros Zone of Lurestan (Iran) similar (breccia) facies extends (Setudehnia, 1978).

The Middle Tithonian-Berriasian Chia Gara Formation is considered one of the formations in a sedimentary subcycle, which extended from the Jurassic to early Cretaceous. The Chia Gara Formation was defined by Wetzel in 1950 (Bellen et al., 1959) in the Chia Gara anticline of the high Folded Zone of N Iraq, south of Amadiya town in the strongly folded zone of north Iraq. The thickness of the formation at the type locality area reaches 232 m (Bellen et al, 1959) and the formation consists of thin bedded limestone and marl, interbedded with shale prevailing in the upper part of the Formation. The Chia Gara Formation can be considered a part of the tectonostratigraphic megasequence AP8 and is deposited during both TST and HST stages of the systems tract (Sharland et al., 2001). It is deposited on top of the Gotnia and/or Barsarin Formations. The first appearance of brown to dark shale or argillaceous limestone above the stromatolitic limestone beds is defined as the Chia Gara Formation (Mohialdeen, 2007, 2008) with conformable contact (Budy, 1980). It is uncomfortably overlain by the Lower Sarmord Formation (Mohialdeen et al., 2013) and conformably with the Garagu Formation in N Iraq (Jassim and Gogg, 2006). The depositional setting of the Chia Gara Formation is deep outer shelf to carbonate slope environments (Mohialdeen, 2008) (subappendix2 Fig2). In some parts of northern Iraq, the Chia Gara Formation is gradationally overlain by the unfossiliferous Karimia Mudstone Formation (Dunnington et al., 1959; Jassim and Buday, 2006). It is generally restricted to the Unstable Shelf which gradually passes into the Makhul Formation SW of the Butmah-Chemchemal Subzone in the Foothill Zone and is absent west of the Tigris River. The Chia Gara passes into the Makhul Formation to the E of the Tikrit-Amara palaeoridge. In Southwest Iran the Chia Gara Formation is equivalent in age to the Gara Formation. In the south of Iraq, the Sulaiy Formation is comparable in age to the Chia Gara Formation, which is a major source rock in southern Iraq and continues into Saudi Arabia (Beydoun, 1991). In Kuwait the Makhul Formation is equivalent in age to the Sulaiy Formation and also considered a major source rock. Fig 2.2 shows the division of the Middle-Upper Jurassic sediment in Iraq (Sadooni, 1997).

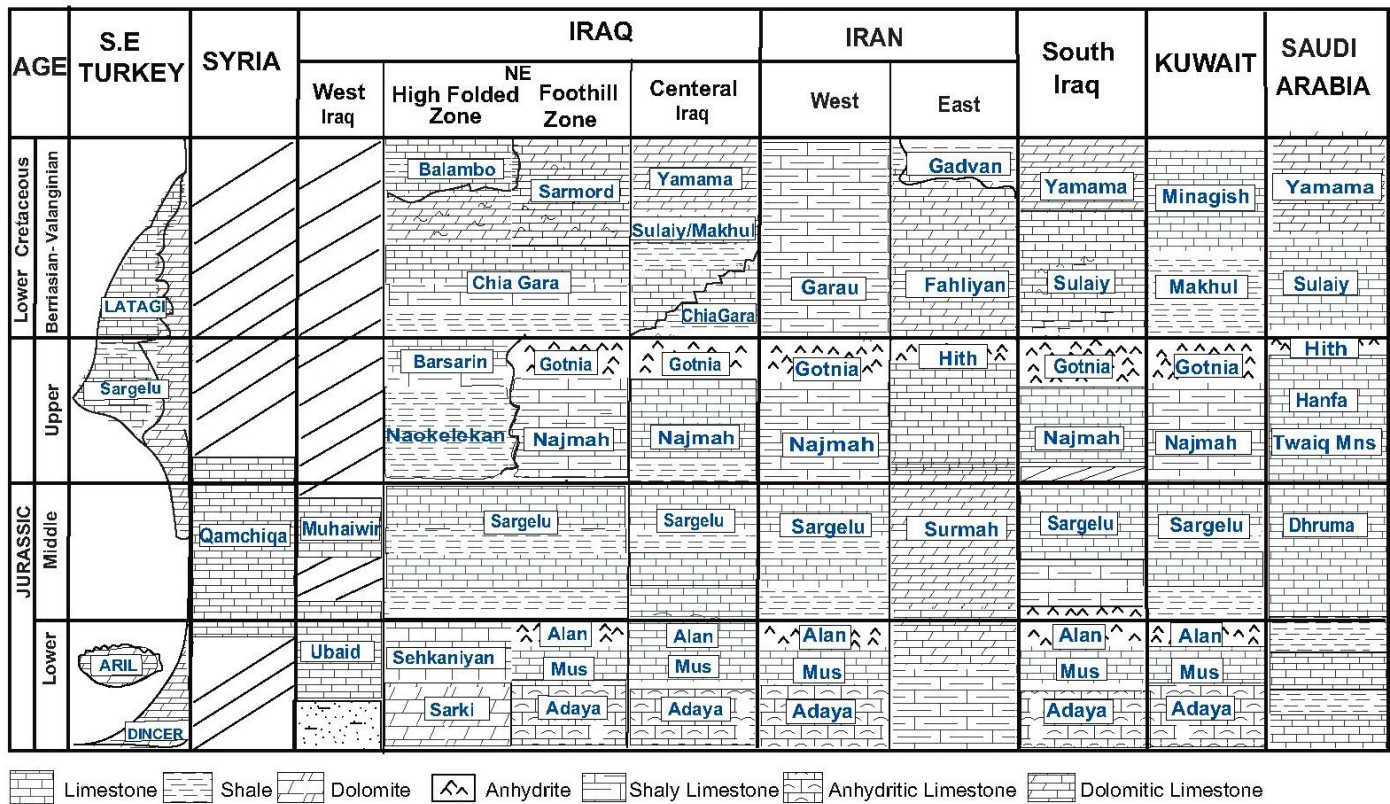


Fig. 2.2. Lithostratigraphic correlation chart of Jurassic-Early Cretaceous strata in Iraq and surrounding countries

(combine: from Bellen et al., 1959; James and Wynd, 1965; Al-Omary and Sadiq, 1977; Al-Sayyab et al., 1982; Murriss, 1980; Beydoun, 1991; Bordenave, 1993, Alsharhan and Nairan, 1997, 2003; Alsharhan and Magara, 1994; Alsharhan and Kendall, 1986; Sadooni, 1997; Jassim and Goff, 2006; Aqrabi et al., 2010.)

The Valanginian-Aptian age Lower Sarmord Formation was defined by Wetzel (1950) in the Surdash anticline of the High Folded Zone in the Sulaimaniya area of NE Iraq and is divided into the Lower, Middle and Upper Sarmord Formation by Chatton and Hard (1960). In NE Iraq, the Sarmord type section represents the Lower Sarmord only. The type locality comprises 455 m of homogeneous brown, blueish Marls, with beds of argillaceous Limestone. The Sarmord Formation was deposited in a deep inner shelf to outer shelf environment, and to the SW it passes laterally into the Qamchuqa Formation. The lower contact of Sarmord Formation is uncomfortably with the Chia Gara Formation, while the upper contact with the Albian Mauddud (upper Qamchuqa) Formation is conformable. In the

south of Iraq, the carbonate-dominated Yamama Formation, equivalent in age to Sarmond Formation, overlies the upper Jurassic-Lowermost Cretaceous Sulaiy Formation. Fig (2,3) showing the Lithostratigraphic correlation chart of the Jurassic-most early Cretaceous Formations in Iraq and the surrounding countries.

The Middle Jurassic Sargelu Formation and the Upper Jurassic Naokelekan Formations yielded the bulk of the oil that charged reservoir rocks in the Mesopotamian Basin and the Zagros fold belt (Beydoun et al., 1992; Sadooni, 1997; Al Shididi et al., 1995), although compared to Jurassic source rocks only small amounts of oil contributed to the total petroleum system from organic-rich rocks of the Cretaceous age (Pitman, 2004).

2.2 Paleogeography during the Early Jurassic - Lowermost Cretaceous in the Middle East

Early Jurassic is the time of deposition of the Mus and Alan Formations in Iraq, Marrat Formation in (Kuwait, Saudi Arabia, and United Arab Emirates), and Qamchuqa Formation in Syria and their regional equivalents. During this time the eastern Mediterranean opened to create a new passive margin. **In Kurdistan north of Iraq**, the Liassic rocks comprise an upper dolomitic limestone unit, about 182.9 m thick, and a lower limestone-shale-anhydrite sequence which is extensively slump bedded (Dunnington, 2005).

Early Jurassic transgression continued into the **Middle Jurassic**, marked by short-lived still stands and/or minor transgression and regression. Middle Jurassic time represents a phase of general sea level rise (Haq et al., 1988) and with it the westward transgression of marine environments for the Arabian Craton. The conditions of deposition were much the same over the northern Arabian Plate in Jordan, Iraq, Syria and southeastern Turkey as further south. The Arabian Plate had passive margins to the Neo-Tethys to the northeast and north, and the sediments were deposited in an open-marine environment, and these formations were deposited as Izhara (Qatar, United Arab Emirates) and Dhurma (Saudi Arabia) formations and their regional equivalents. In the northwest of the Arabian Plate, a narrow marine shelf existed and was covered with shallow-water carbonates and with deeper-water facies further offshore. In Lebanon the Kesrouane Formation was deposited in middle-outer shelf depositional environments. In Iran, low-energy oxygen-deprived facies were deposited in the subsiding Mesopotamian Depression (James and Wynd 1965), and anoxic conditions that prevailed in the depression led to the deposition of the Sargelu Formation in the SW of Iran and the Surmeh Formation in (Khuzestan) Iran. In Iraq the Sargelu Formation was deposited in shallow water carbonate facies. In Northern Iraq rocks of this time interval are markedly bituminous both in the mountain zone and in the thick sedimentation belt, and the presumed semi-euxinic depositional conditions made the source potentialities highly rated.

The sedimentation in north Iraq in this time is oolitic limestone and shallow-water limestone, masses of radiolarian sediments and in some wells a discontinuous bedded-anhydrite, which is not developed in Kurdistan (Dunnington, 2005).

Late Jurassic Callovian to Oxfordian is the time of deposition of the carbonates of Upper Dhume and Tuwaiq Mountains Limestone of Saudi Arabia, the Upper Araej of the Gulf (and equivalents in Lebanon), Hanifa and Naokelekan Formations of the Gulf, Syria and Iraq (Ziegler, 2001). In this time interval carbonate sediments indicate that shallow-marine environments were widespread, although lowstand in sea level prevailed during most of this time (Haq et al., 1988). Four intrashelf basins have been identified in the southern Arabian Gulf (Rub Al Khali and Ras al Khaima basins), central Arabian (Arabian Basin) and at the head of the Arabian Gulf (the Gotnia Basin). The intrashelf basins on the Arabian Plate were developed by differential intraplate subsidence. **In Northern Iraq, the Late Jurassic time** had the same conditions as the Middle Jurassic, euxinic shale and limestone deposited in an euxinic environment, where the thickest sedimentation is found in the Tigris area and in the massive-bedded anhydrite with very thick oolitic and chemical limestone culminated gathered. In the southwestern part of the region, where the youngest sediments are seen, the Upper Jurassic sediments are not exposed. In northern Iraq bituminous shale of the Naokelekan Formation, which was deposited when the foreland basin developed at the margin of craton (Balaky, 2014), was quarried for many decades by local communities as fuel supply (Dunnington, 1959). These organic-rich bituminous and bituminous limestone of the Naokelekan and Sargelu Formations is the richest source rock in the world (Sadooni 1997).

In the Uppermost Late Jurassic time: Kimmeridgian to Tithonian, the Arab and Hith (Saudi Arabia, Qatar, United Arab Emirates) and Gotnia (Iraq, Kuwait) Formations, and their regional equivalents were deposited. This time corresponded to an overall progressive rise in sea level and the deposition of evaporites was widespread, with a correspondingly widespread deposition of shallow-marine carbonates. Along the southern coast of Oman, a new passive margin developed following continental rifting and sea-floor spreading between the Afro-Arabian and Indian plates. Sadooni (1997) suggested that the reactivation of basement faults during the Late Jurassic was responsible for a widespread erosional limit and he reported wide area distribution of the Najmah Formation into Iraq, markedly further than the general Cretaceous erosional limit.

The Very Late Jurassic-basal Upper Cretaceous Transition: Tithonian-Berriasian in north of Iraq. Sediments of this time are regarded as very important potential source rocks, without any apparent outlet to adjacent potential reservoir (Dunnington, 1959). In Kurdistan the sediments comprise about 91.5-182.9 m of radiolarian shale and thin-bedded limestone with abundant ammonites (Spath, 1950).

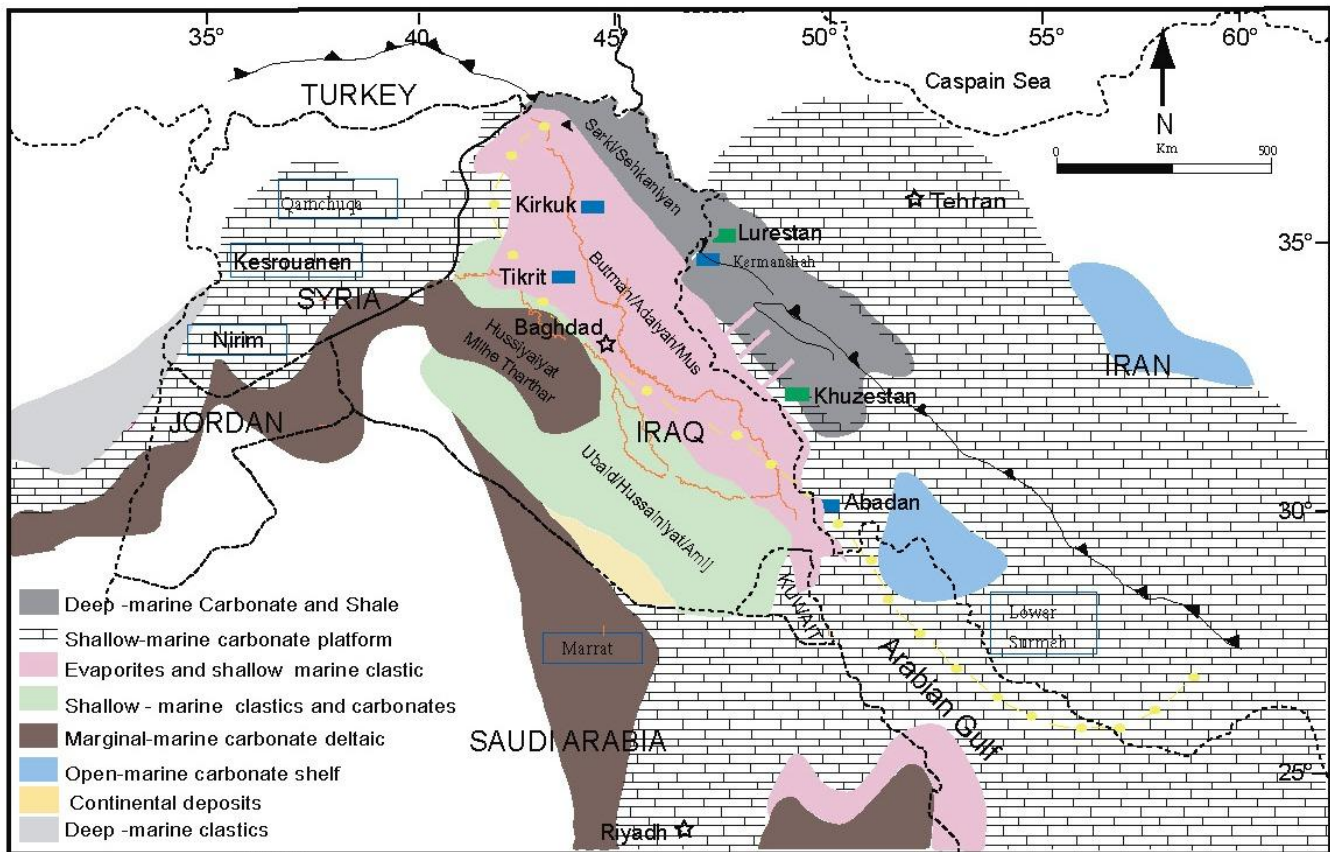


Fig. 2.3. Palaeofacies map of the Early Jurassic showing Formations deposited in Iraq and in surrounding countries. Figure combined from: Dunnington et al., (1959); Murriss (1980); Koop and Stoneley (1982); Bordenave (1993); Ziegler, (2001); Jassim and Golf, (2006).

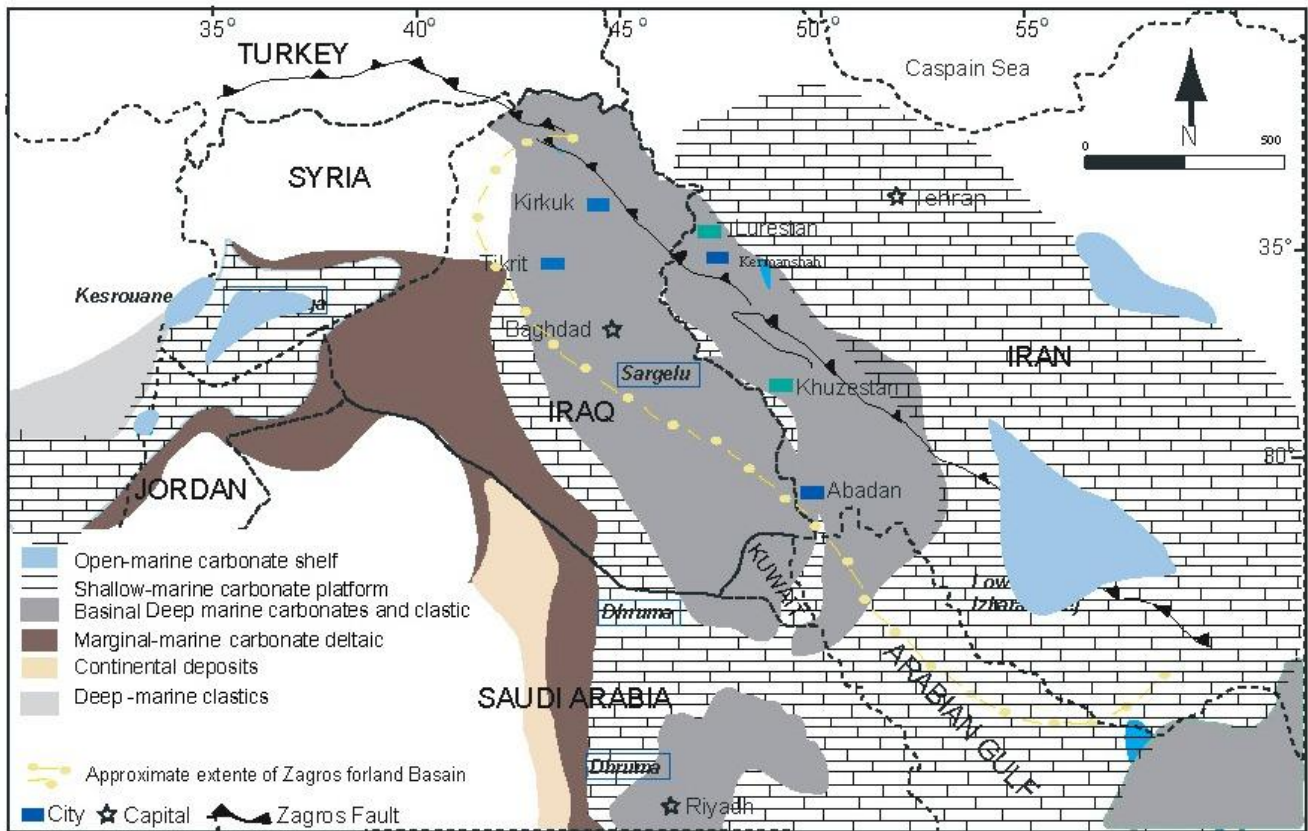


Fig. 2.4. Palaeofacies map of the Middle Jurassic showing Formations deposited in Iraq and in the surrounding countries. Figure combined from: Dunnington et al., (1959); Murris (1980); Koop and Stoneley (1982); Bordenave (1993); Bordenave and Huc, (1995); Ziegler, (2001); Pitman et al., (2004); Dunnington, (2005); Jassim and Golf, (2006); Bordenave and Hegre, (2010).

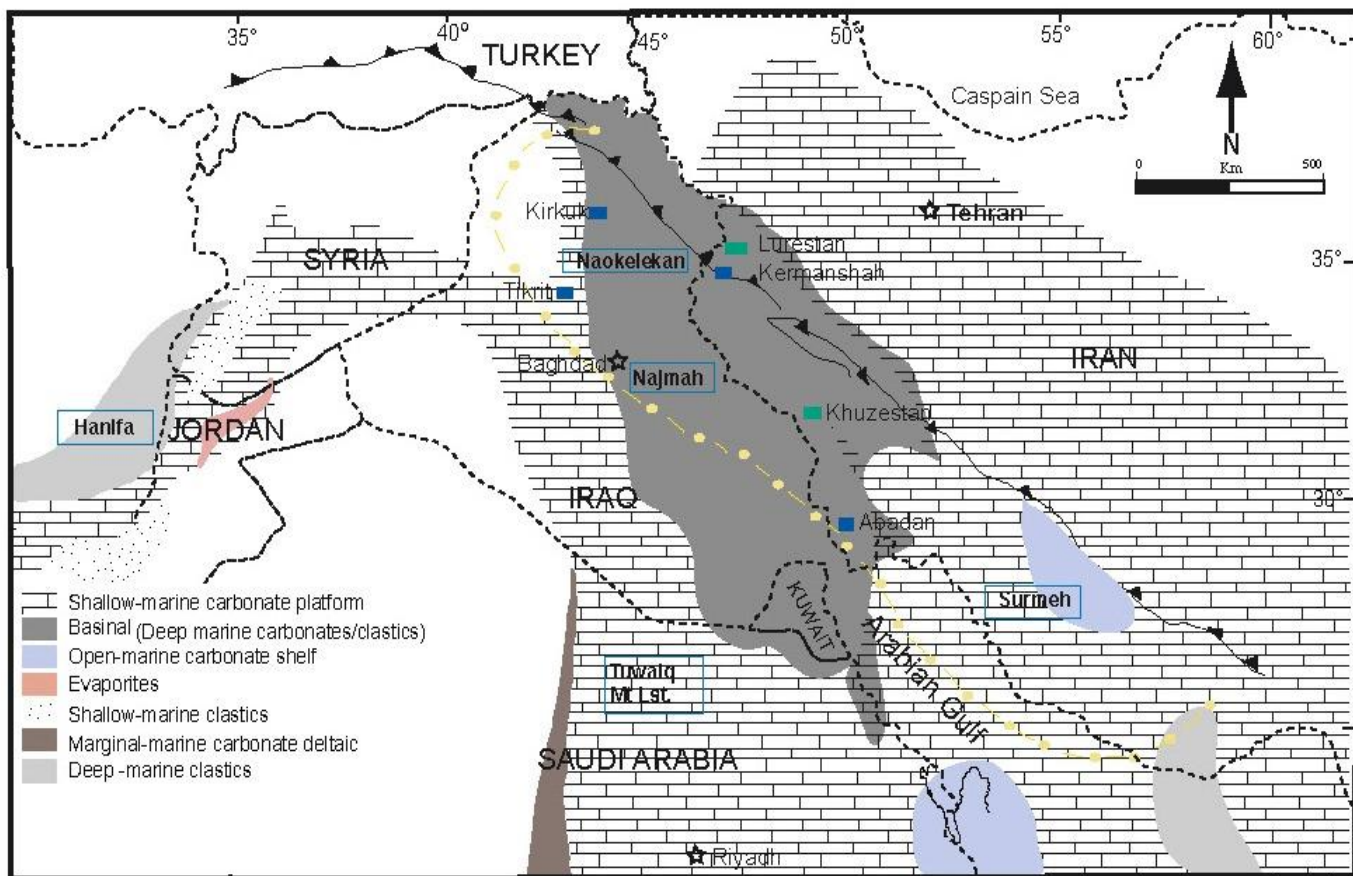


Fig. 2.5. Palaeofacies map of the Middle-Late Jurassic showing Formations deposited in Iraq and in the surrounding countries. Figure combined from: Dunnington et al., (1959); Murriss (1980); Koop and Stoneley (1982); Bordenave (1993); Sadooni, (1997); Ziegler, (2001); Dunnington, (2005); Jassim and Golf, (2006).

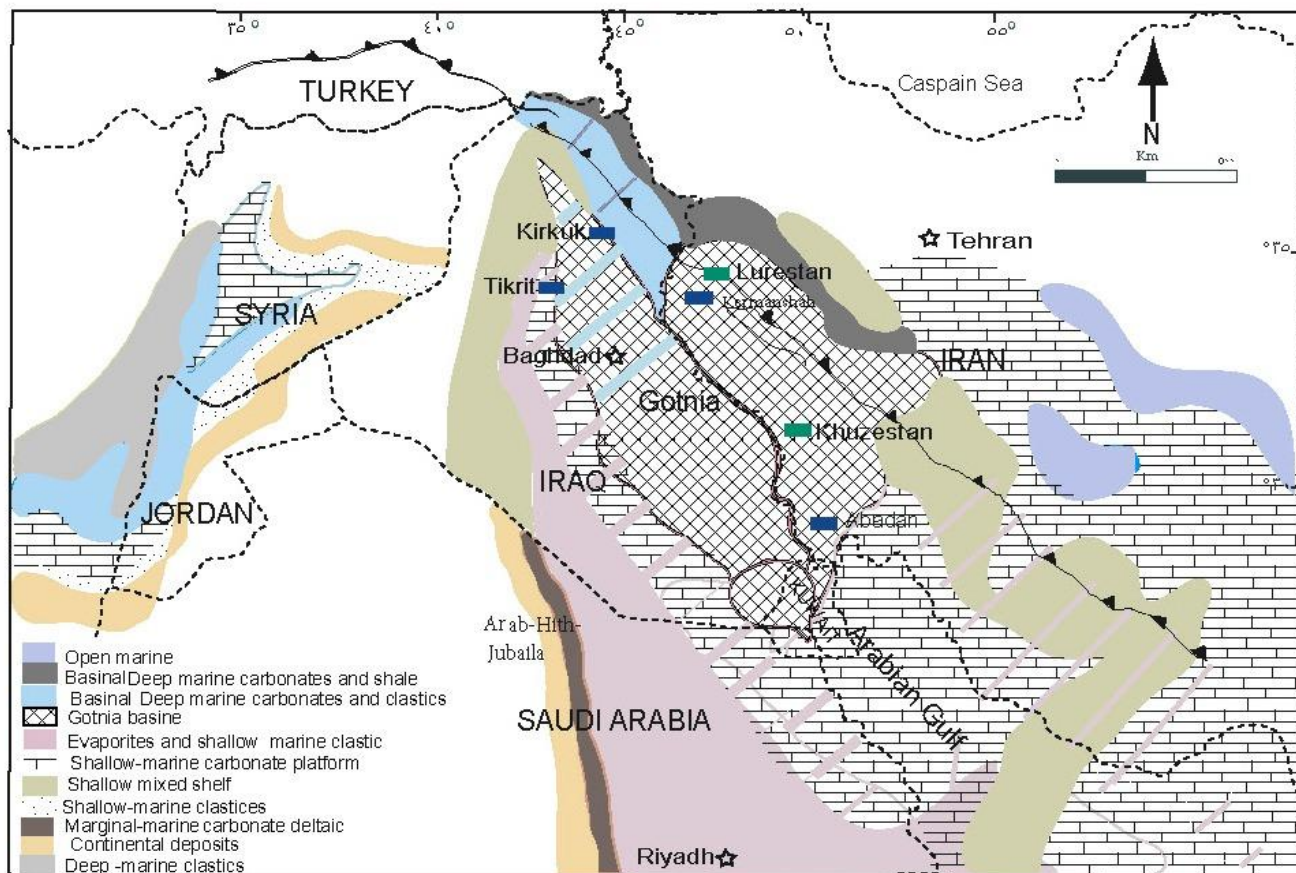


Fig. 2.6. Palaeofacies map of the Late Jurassic showing Formations deposited in Iraq and in the surrounding countries. Figure combined from: Dunnington et al., (1959); Murriss (1980); Koop and Stoneley (1982); Bordenave (1993); Al-Husseini, (1997); Ziegler, (2001); Dunnington, H. V., (2005); Jassim and Golf, (2006).

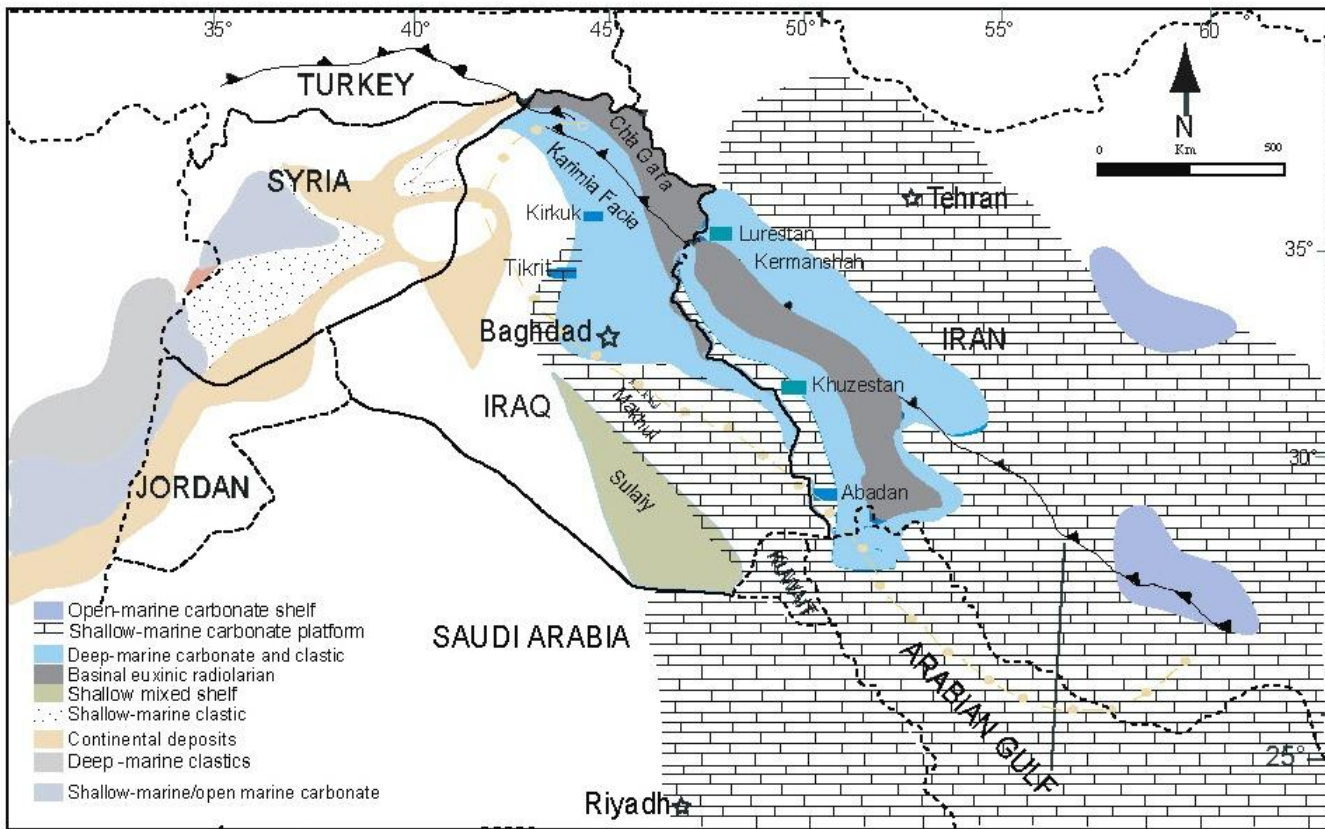


Fig. 2.7 Palaeofacies map of the basal Early Cretaceous showing Formations deposited in Iraq and in the surrounding countries. Figure combined from: (Dunnington et al., 1959); Murriss (1980); Koop and Stoneley (1982); Bordenave, (1993); Bordenave and Huc, (1995); Ziegler, (2001); Dunnington, H. V., (2005); Jassim and Golf, (2006); Bordenave and Hegre (2010).

In Early Cretaceous: Berriasian to Valanginian. In this time the Yamama, Minagish, Habshan, and Rayda Formations and their regional equivalents were deposited. During this time most parts of Arabian Plate were affected by a late Valanginian unconformity, with the exception of Oman where relatively continuous sedimentation took place. The sediments were deposited on an open platform and within intrashelf basin of the Arabian Plate which was surrounded to the north, east, and south by passive margins of the Neo-Tethys. The shallow-water carbonates Yamama, Minagish, and Habshan Formations

covered the eastern shelf platform of the Arabian Plate, with the exception of the areas of the former Gotnia Province and the residual Arabian

Basin, where argillaceous limestone of the Sulaiy/Makhul formation were deposited. **In the north of Iraq** stratigraphic relationships in this time were rather complex, and the interdivision between formation is common and the thin deposition in the northwest is due in part to absence of sediments of Valanginian and Hauterivian over the high tabular feature which was raised during the Jurassic-Cretaceous transition time.

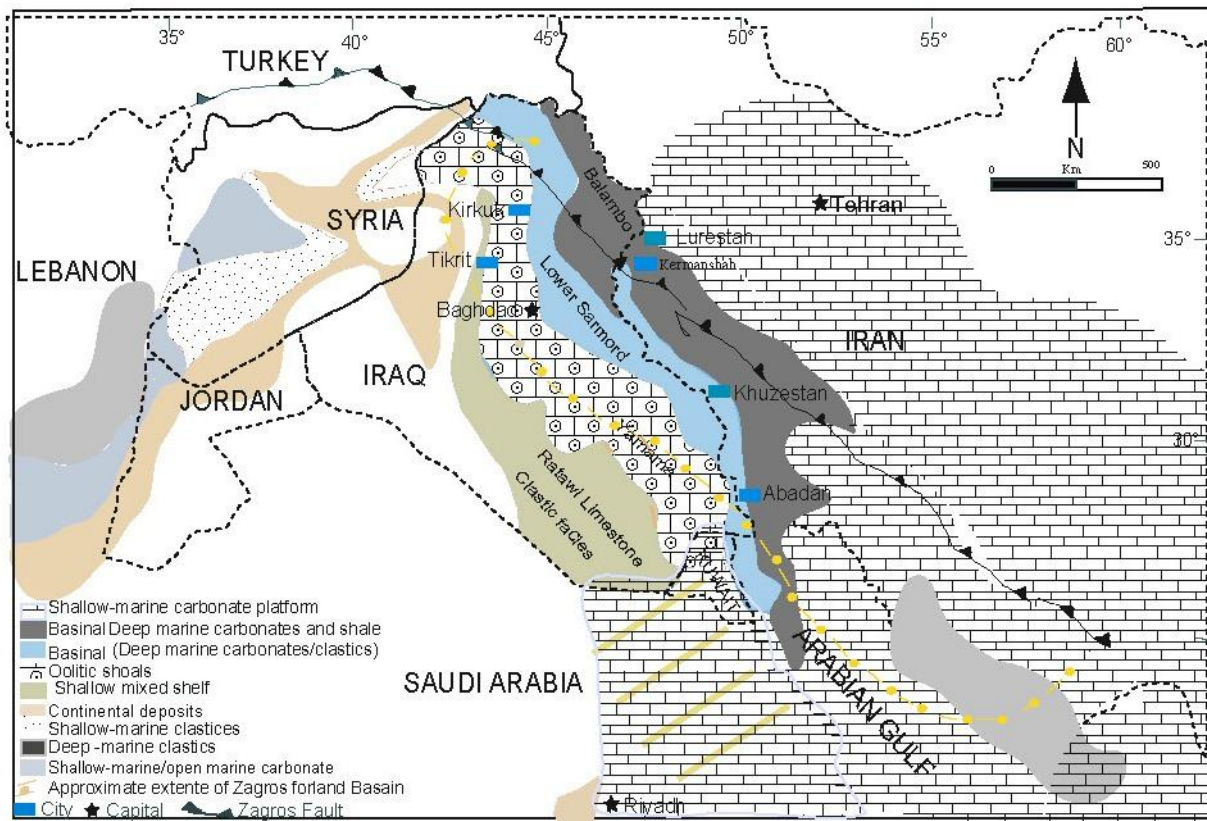


Fig. 2.8. Palynofacies map of the Early Cretaceous showing deposition of the Formations in Iraq and in the surrounding countries. Figure combined from: Dunnington et al., (1959); Murriss (1980); Koop and Stoneley (1982); Bordenave (1993); Bordenave and Huc (1995); Ziegler, (2001); Dunnington, H. V., (2005); Jassim and Golf, (2006).

2.3 Material and Methods

A total of 195 core and cutting samples were taken from two well sites (Aj-8 and Aj-12) in the Ajeel Oil field (Mesopotamian Basin). Samples were crushed, powdered and dried in an oven at 40°C for about 48 h afterwards.

2.3.1 Organic geochemical Analysis

Cutting and Core preparation

The cutting and core, contaminated by either oil or water-mud, was cleaned to avoid the influences of the geochemical analysis, and contaminants and back-fall were removed.

Total organic Carbon analysis

Total carbon content (TC) was carried out on 195 samples by using a Vario EL-III Elemental Analyzer (Elementary analyze system, Hanau, Germany) and using (3 mg) of crushed and ground rock. Elemental concentrations of Carbon (C), Nitrogen (N), and Sulfur (S) were measured in duplicate for 195 samples from the Mus, Alan, Sargelu, Najmah, Gotnia, Chia Gara, and Lower Sarmond Formations in Aj-12 and Aj-8. The carbon was determined as a total because the instrument cannot separate organic from inorganic carbon. The total inorganic carbon (TIC) was determined as well by a Vario EL-III coupled with a TIC module Soli TIC in which the carbonates were dissolved with 10% hydrochloric acid (HCl) and the released CO₂ was detected with the Elemental Analyzer. Then Total Organic Carbon (TOC) was calculated by subtracting the TIC from TC. For calibration (2% TC) was used as standard sample during the analysis and run between ten sample-intervals.

Rock- Eval parameters

A basic problem in petroleum exploration is how to assess the petroleum-generative potentials of prospective source rocks. Rock-Eval pyrolysis of whole rock is used to rapidly evaluate the petroleum-generative potential and thermal maturity of rocks (Peters, 1986) and provides information on the quantity, type and thermal maturity of the associated organic matter (OM) (Espitalie et al, 1977). Rock-Eval provides information on the thermal maturity stage of the kerogen and indicates the presence of migrated bitumen or impregnation (Espitalie et al, 1977; Peters, 1986; Bordenave et al .,1993; Schwark, L. et al.,2009). Pyrolysis is defined as the heating of OM in absence of Oxygen, to yield organic compounds. In Rock-Eval pyrolysis, pulverized samples are gradually heated under an inert atmosphere. This heating distills the free organic compounds (bitumen), then cracks pyrolysis products from the insoluble OM (kerogen), (Peters, 1986). Rock-Eval pyrolysis provides four important parameters: (from S1 peak) the amount of total free hydrocarbons which represents the milligrams of hydrocarbons that can be thermally distilled from one gram of the rock; (from S2 peak) pyrolysate represents milligrams of hydrocarbons generated by degradation of kerogen in one gram of rock upon heating during pyrolysis or the amount of remaining hydrocarbon, and (from S3 peak) the amount of carbon dioxide (CO₂) released during temperature programming up to 390 C, which is analyzed by thermal conductivity detection

(TCD). In the United States a number of researchers prefer the use of P1, P2, and P3 instead of S1, S2 and S3 (Peters, 1986). The fourth parameter is the temperature for generating a maximum amount of hydrocarbon (Tmax) (Peters, 1986; Tissot and Welte, 1984). The crushed samples weighing up to (80-100 mg) depending on their TOC value were heated at 300 C° for 3-4 min in an inert atmosphere (Helium, 50 ml/min). During this period, the free hydrocarbons were thermally desorbed from the sample. This was followed by programmed pyrolysis at 25°C/min to 550 C°, both in a helium atmosphere. Allowing time to cool the oven, each analysis requires about 20 min (Peters, 1986). This methods has been described in detail (Horsfield et al., 1983). The free hydrocarbons were quantified using a Flame Ionization Detector (FID) and recorded as the S1 peak in units of mg HC/g rock. The amount of hydrocarbons generated from kerogen was again measured using a FID and reported as the peak S2 in units of mg HC/g rock. Because Rock-Eval pyrolysis is rapid (20 min) and requires only small samples (100 mg) it is commonly used at the well site to screen large numbers of core and cutting samples for further study (Peters et al., 1983). The Rock-Eval II plus TOC (Delsi, Inc.) determines TOC by summing the carbon in the pyrolysis with that obtained by oxidizing the residual OM at 600 °C

2.3.2 Analysis of the soluble organic matter

Extraction

The type of organic matter and its maturity as well as its depositional environment mainly controls the composition of the SOM of source rock. The general trend of variations of SOM ratios with increasing thermal evolution is well known in the hydrocarbon generation curves with depth, as established for different basin.

A total of 58 core and cutting samples were taken from two well sites (Aj-8 and Aj-12) in the Ajeel Oil field (Mesopotamian Basin). Bitumen extracts were obtained from solvent extraction using an ASE@ 200 (Accelerated Solvent Extraction; Dionex). Powdered samples were extracted with dichloromethane (DCM) at a temperature of 75°C and a pressure of 50 bar, the static extraction phase was set to 20 minutes. The total bitumen extracted was treated with acid-activated copper to remove elemental sulfur, which could interfere with GC-MS analysis. Copper was normally employed in an Erlenmeyer flask, and a small amount of concentrated (25%) hydrochloric acid was added and heated. When the copper reached its boiling point and the typical bright color appeared, the acid was decanted and the copper was rinsed with distilled water until pH neutral. Then, to remove water, copper was rinsed with Acetone (seven times at least), and finally with DCM super clean (seven times). Each extract dissolved in DCM was then filtered over a cotton wool-plugged Pasteur pipette to remove the copper and was subsequently evaporated to dryness by a Büch Syncore evaporation system.

Gas Chromatography (GC)

The analysis of saturate, aromatic and polar components of petroleum is commonly used in petroleum geochemistry (Murphy; 1969, Peters et al., 2005). The separation of these components into individual fraction is required because compounds of interest, such as steranes, hopanes, phenanthrenes, and

aromatic steranes, are often present in trace quantities compared to the bulk of the sample and must be enriched before they can be accurately analyzed (Peters et al., 2005). A standard column was prepared by taking a glass column (10 cm*0.72 cm, a Pasteur pipette) plugged with a small amount of cotton wool and few centimeters of alumina, then the pipette filled with silica gel (Silica Gel 60, 230 – 400 mesh size). A silica gel was activated for 2 h at 130 C (Bastow et al., 2007). The extracts were separated into a saturated, aromatic and a polar hydrocarbon fraction on liquid column chromatography. The saturated fractions were eluted with 3.5 ml *n*-hexane, aromatic hydrocarbons with 3ml *n*-hexane/DCM (7:3, v/v) and polar hydrocarbons with 3 ml DCM/MeOH (1:1 v/v). Before separated into different fractions all dry extracts were dissolved in a few amounts of *n*-hexane.

Gas- Chromatography-Mass Spectrometry (GC-MS)

The fractions were analyzed using gas chromatograph-mass spectrometry (GC-MS). The GC-MS analysis was performed on an Agilent 7890 Series gas chromatograph (GC) instrument equipped with a split/splitless injector. The column was a fused silica capillary (ZB-1HT for aliphatic and ZB-5HT for aromatic) of 30m length and 0.25 mm internal diameter with 0.25 µm film thickness; Phenomenex. The GC oven temperature was started with an initial temperature of 70°C (3 min hold) and ramped to 140°C at 10 C min, then to 340°C at 3 C min and held for 13 min at 340°C. Helium was used as a carrier gas with a pressure controlled flow rate flow of 1 ml/ min. The Agilent 5975B inert mass spectrometer was operated in SCAN 50-750 and in electron ionization (EI) at (70 eV).

2.4 Relation between rock properties and wireline logs

Source rocks are commonly shale and limestone that contain significant amounts of organic matter (Tissot and Welte, 1984). This organic matter may be derived from aquatic organisms and bacteria (Limbach, 1975) and it is commonly called kerogenous, or from land plants. Many studies have been made by using conventional wireline logs to evaluate source rocks potential, firstly by identifying organic rich zones (MANN *ET AL.*, 1985; PASSEY *ET AL.*, 1990).

Introduction

The feasibility of interpreting organic matter from wireline measurements uses geophysical methods to derive lithological information and petrophysical properties, such as clay content, porosity, or rock density, which differ considerably from one rock to another according to the mineral components found therein. The source rock intervals generally show higher radioactivity (Gamma ray), lower density, higher sonic transit time, higher porosity and higher resistivity than other sedimentary layers. These phenomena can be used to identify source rocks on wireline logs. The approach presented here to establish a quantity correlation between well logs (gamma-ray, density, neutron, and sonic in short interval) and total organic carbon, and display log responses in source rocks are based on comparing log-derived TOC values with measured TOC values from cores or cutting samples.

This part focuses intensively on well Aj-12, because the covering of available log data (Gamma ray, density, neutron) was good from the Mus, Alan, Sargelu, Najmah, Gotnia, Chia Gara, and Lower Sarmond Formations in this well.

2.4.1 Principles of well log data interpretation

- **Gamma Ray log** is a lithology log, sensitive to the natural radioactivity of rock formations as the sum of three radioactive elements (U, K, Th), which are predominantly associated with small grains such as silt or clay (Serra, 1984). Natural Gamma-Ray logs application has been primarily for lithological identification, and the evolution of depositional environment (Lucia, 1999), and for the determination of organic matter content (Schlumberger, 1987).

- **Porosity logs.** The three common porosity logs (density, sonic and neutron logs) are sensitive to rock porosity. Formation density logs basically measure the electron density which is directly related to the true bulk density that is a function of the composition of rock matrix material. Density log is used to estimate the amount of pore space in rock and determine lithology and changes of clay mineralogy, and detect gas-bearing zones (Asquith and Krygowski, 2004). Sonic Logs: The interval transit time, DT, is the reciprocal of the velocity of the compression wave and a function of formation lithology, porosity, and the types and distribution modes of fluids (water, gas, oil, kerogen, etc.) present in the pore space. Furthermore, the sonic log can be used to determine source rock qualitatively; as the interval time is affected by water, organic matter, and mineral content. Neutron logs measure the hydrogen content in a formation. In clean, shale free formation, where the porosity is filled with water or oil, the neutron log measures liquid filled porosity.

Geophysical Well-Log Responses to TOC content

Total organic carbon (TOC) content present in potential source rocks significantly affects the response of various well logs, and it is an important parameter in the evaluation of kerogen (Alyssa and Susan, 2013). Sediments can be regarded as consisting of heavy and light fractions. The heavy fraction is the mineral matter, and the light fraction is the formation fluids, for source rocks, the contained organic matter is also part of the light fraction. For well Aj-12, cross plots of TOC vs. DT, bulk density and Neutron porosity show linear relationships).

Results and Discussion

- Gamma-ray log

Organic-rich rocks can be relatively highly radioactive, that is, they can have a higher gamma-ray reading than ordinary shale and limestone (Schmoker, 1981). The natural radioactivity is usually due to Uranium, Thorium and Potassium enrichment. This is particularly true in marine environments, whereas lacustrine source rocks (i.e., continental deposits) appear to have no excessive gamma ray activity, mainly because of the scarcity or absence of U ions in freshwater environments. The correlation of gamma-ray reading with organic content indicates that the higher radioactivity levels are related to the

presence of organic matter (Nederlof, 1990). The study of gamma ray vs. TOC content of the (Alan, Sargelu, Najmah, Gotnia, Chia Gara, and Lower Sarmond) Formations in Aj-12 are shown in Fig. 2.11

- Density log

The density log can be used to determine the organic carbon content. Since the density log measured bulk density of a formation which consists of the matrix density and fluid density, in shale with a similar degree of compaction and similar matrix and fluid density, water saturation should be equal. Solid organic matter has a similar density to that of water and thus less than that of the surrounding rock matrix (Nederlof, 1990). When the density read in the source rock is lower than the density reading in normal shale, this would be a function of the amount of organic matter which is present. Fig 2.11 displays the density value vs. TOC value in the Alan, Sargelu, Najmah, Gotnia, Chia Gara, Lower Sarmond Formations in well Aj-12 and it is apparent that density decreases when TOC amount increases.

- Neutron log

The Neutron log porosity responses are higher in source rocks than in non-source rocks. As shown in Fig. (2.11), a neutron log shows a direct relationship with TOC wt. %.

- Sonic log

TOC content tends to increase the apparent interval transit time. In this study there is poor data for DT log reading. The DT values for the Najmah and Sargelu Formations are shown in Fig. (2.10). The relationship between TOC and acoustic log responses for these formations in well Aj-12 increases with higher DT values.

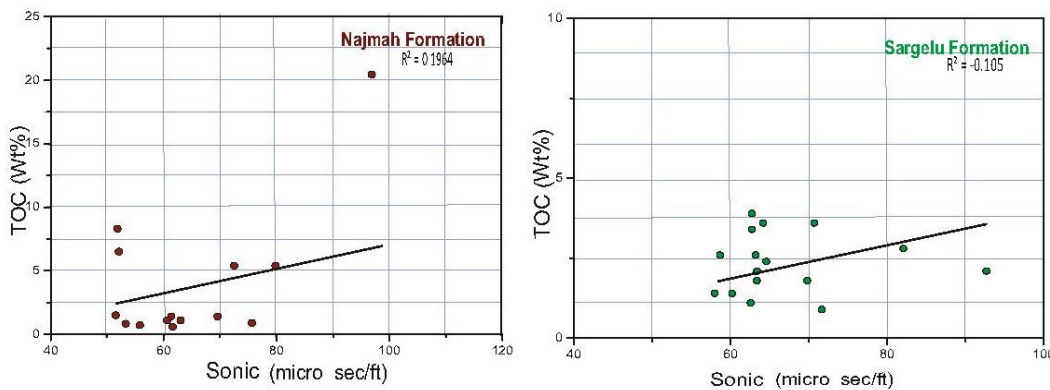


Fig. 2.9 Plot of sonic travel time vs. measured TOC for the Najmah and Sargelu Formations studied show positive relation between them.

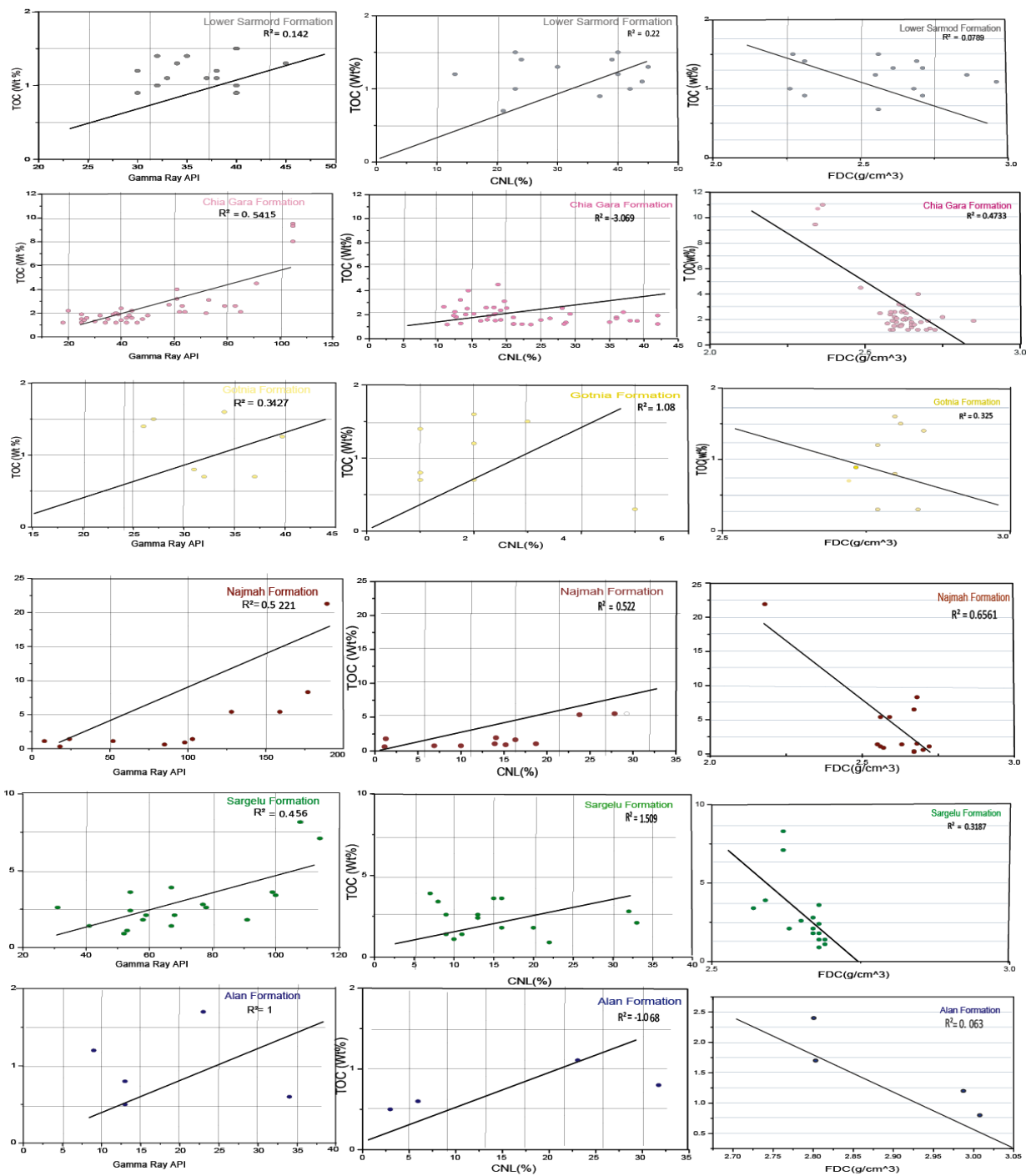


Fig. 2.10 Cross-plots of the measured TOC(wt%) vs. digitized values from well logs (Gamma ray API, CNL%, FDC g/cm³) for the Formations studied show the positive relation between the TOC wt% and digitized values from the Gamma ray and CNL logs and inverse relation determined logging values from density log.

2.4.2 Method of computing TOC from Wireline Logs

TOC can be measured on core accurately or can also be estimated on the logs with different methods. The Schmoker (1983) method of TOC calculation with well log data is one of the most popular methods. In this study the total Organic Carbon (TOC) was calculated in well Aj-12 utilizing the Schmoker and Herster equation (1983) and the results compared with TOC values from core and cutting samples as follows:

$$\text{TOC (wt \%)} = (154.497/\text{pb}) - 57.261$$

Where TOC: is the Total Organic Carbon per weight (wt %) and

pb: is the bulk formation density as measured by density logs.

TOC calculated with the Schmoker method showed a trend for cross plot of TOC values calculated from rocks (core and cutting) with TOC values calculated from logs (Fig. 2.12).

Furthermore, the bulk density (pb) used to calculate sediment porosities in well Aj-12 were based on the standard density-porosity relation:

$$Q = (\rho_m - \rho_b) / (\rho_m - \rho_f) \quad (\text{Serra, 1984})$$

Where water densities (ρ_f) were assumed to be constant and equal 1 g/cm, and grain/matrix densities (ρ_m) different depending in the lithology of layers.

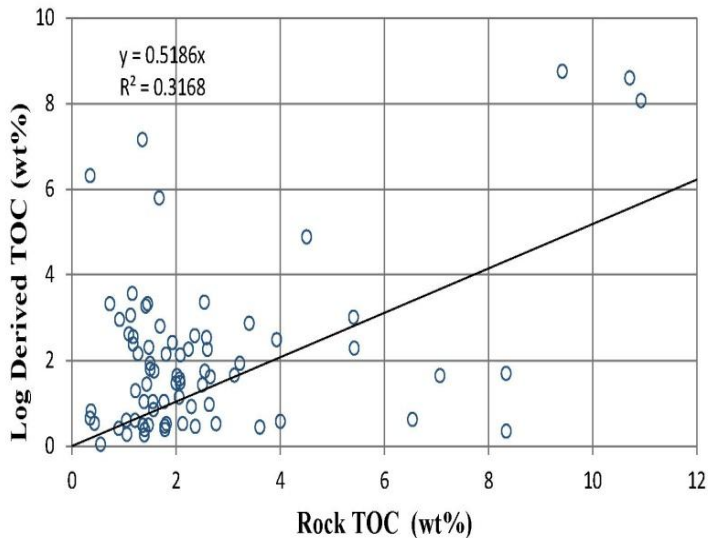


Fig. 2.11 Cross plot for well Aj-12 comparing core TOC versus Log-Derived TOC (wt %) (Schmoker method).

2.5 Distribution and composition of organic matter

The aims of this section were to evaluate (Jurassic-Lower Cretaceous) source rocks in North Iraq by studying their organic matter richness, its origin, and to delineate the general thermal maturation trend occurring during their deposition depending on Total Organic Carbon content (TOC), and Rock-Eval parameters.

Introduction

Petroleum source rocks are sedimentary rocks, and they are organic matter-rich rocks that could generate a significant amount of petroleum (potential source rocks) or have already generated (effective or active source rocks) (Tissot and Welte, 1984). The quantity of organic matter is usually expressed as total organic carbon (TOC) and the capacity of source rock to generate petroleum depends on the quantity of (TOC), its quality, and the thermal maturity of organic matter (Hunt, 1996). With the Kerogen type, these factors control the organic matter quantity available for hydrocarbon generation, the quality of the source rock and its remaining potential.

2.5.1 Total Organic Carbon (TOC) content

Total Organic Carbon content (TOC) in sediment is an indicator of the total amount of organic matter presents in the sediment (Ronov, 1958) and is usually expressed as a weight percentage of the total rock. TOC content, which describes the quantity, but not quality of the organic carbon in rocks and source rocks, can be described in terms of their TOC content. Total organic carbon includes the combination of soluble (bitumen) and insoluble (kerogen) and represents the amount of organic matter in rock sample (Tissot and Welte, 1984; Peters and Cassa, 1994, subappendix 2 Fig3). To qualify as effective carbonate and shale source rocks, they must have a minimum 0.3% and 0.5% of TOC values respectively, and these minimum TOC values apply only to immature and low mature source rocks. This is not the case, however, with increasing maturity in the advanced stages of maturity where the TOC content decreases due to hydrocarbon generation and expulsion. Peters and Cassa (1994) point out that TOC is not always a good indicator of source rock potential because measurements may include carbon that has little or no generating potential.

The most important factor controlling the generation of oil and gas is the hydrogen content of the organic matter (OM). The quantity of petroleum generated and expelled increases as the atomic hydrogen to carbon (H/C) ratio of the OM decreases (Hunt, 1995).

The TOC content and Rock-Eval parameters are used to study the generation potential (quantity) of an immature source rock of the kerogen type and the products generated (quality) and thermal maturity of a mature source rock (Peters and Cassa, 1994).

Kerogen Type

Sedimentary rocks commonly contain minerals and organic matter with the pore space occupied by water, bitumen oil, and/or gas. Kerogen is the particulate fraction of organic matter remaining after extraction of pulverized rock with organic solvents (Peter and Cassa, 1994), and it is a mixture of macerals and reconstituted degradation products of organic matter. Kerogen is organic matter disseminated in sediments and made up of high-molecular-weight compounds (Whelan and Thompson-Rizer, 1993). It is insoluble in organic solvents and its different types reflect largely the composition of the original biological matter deposited. As different types of OM have different hydrocarbon potentials, a distinction between various types of sedimentary organic matter (OM) is essential for proper source appraisal. The main contributors to kerogen in sediments are the remains of bacteria, phytoplankton, zooplankton and higher plants (Tissot and Welt, 1984, Killops and Killops, 1993).

The following are the four main Kerogen types:

Type I This type of Kerogen consists of algal material derived from closed basins, lagoons and lakes, shallow-water environments where the anoxic conditions (Tissot and Welte, 1984; Killops and Killops, 1993) prevail. It initially has a high oil potential and high H/C ratio around 1.5 and low O/C ratio less than 0.1 with high Hydrogen Index HI (600 mg/g TOC).

Type II This type of kerogen is the most commonly occurring kerogen in proven source rocks. It has a relatively high H/C ratio (1.2-1.5) and low O/C ratio with high HI (300-600 mg/g TOC), and it consists of saprogenic organic matter deposited in anoxic marine environments, dominated by mixed autochthonous phytoplankton and zooplankton organic matter deposited in reducing conditions (Tissot and Welte, 1984; Killops and Killops, 1993). This type of kerogen "alginite-type" has produced oil and gas, although it has lower oil potential than type I.

Type III This "vitrinite-type" consists of humic, coaly material derived from continental higher plants. For the low H/C ratio (<1) and high O/C ratio (up to 0.3) with low HI (50-200 mg/g TOC) for type III kerogen yields less hydrocarbons than type I and II during pyrolysis or burial maturation and is usually gas prone, especially for methane, if buried deeply enough (Tissot and Welte, 1984; Killops and Killops, 1993).

The transitional composition of kerogen is called Type II/III. This describes a transitional composition between type II and type III that represents a mixture of marine and terrigenous organic matter deposition in a paralic marine setting and has intermediate H/C ratio and HI value (Tissot and Welte, 1984; Killops and Killops, 1993).

Type IV This kerogen has a high atomic O/C ratio and a low atomic H/C ratio and it is derived from older sediment that was severely oxidized on land and then transported to its deposition site or from thermally combusted deposits, or biologically oxidized organic material before burial (Tissot and Welte, 1984; Killops and Killops, 1993).

One other kerogen type is recognized and can be added to the other types. It is type IIS Kerogen, which contains high organic sulfur (8-14 wt. % S or atomic S/C more or equal to 0.04) but is otherwise similar to type II kerogen in composition (Orr, 1986).

Maturity

Maturity is the degree of thermal alteration of organic matter due to heating (Peters and Cassa, 1994). There are three different maturity phases for organic matter: the first is immature, which may be affected by biological diagenesis processes and has not been obviously affected by temperature. Mature, which has been converted to petroleum due thermal processes and is (or was) within an oil window. Postmature, which is hydrogen reduced due to the influence of high temperatures and is in the gas window (Peters and Cassa, 1994). The maturity of organic matter in petroleum source rocks is characterized by the temperature index T_{max} , which is the maximum hydrocarbon generation obtained from Rock-Eval pyrolysis data, its values rising in response to increasing maturity of organic matter (TISSOT & WELTE, 1984).

The type of organic matter in petroleum source rocks can also be characterized by Rock Eval data. For type I kerogen the range of variation of T_{max} is in a narrower window than for type II and type III kerogens due to increasing structural complexity (Espitalie et al, 1985; subappendix2 Fig 4), and for this reason T_{max} cannot be used as a maturation parameter in type I kerogen (range of variation 435°C - 450°C) but is a good maturation index in type II (range 420°C - 460°C) and type III kerogen (range 400°C -550°C).

Result and discussion

Total organic carbon content (TOC) and type of organic matter

Total organic carbon (TOC) content and Rock-Eval pyrolysis data were a basic and important factor in characterizing the organic content, hydrocarbon potential of the organic matter and its thermal maturity level. For samples studied in the Ajeel oil field (well Aj-12) the TOC values were as follows: for the Mus and Alan Formations the TOC % range between 0.5 and 2.4% with an average of 1.2% ; the Sargelu Formation had TOC% value ranging from 0.9 to 8.3% with an average of 2.9%. TOC% values for the Najmah Formation range from 0.3 to 21.9%, with high values in the upper part from this Formation which show very dark color in studied samples collected from this part and lower TOC values in the lower part from this Formation which show light color in studied samples from this part, that could be indicate color of samples could be refer to the TOC values (Fig 2.13). Samples studied from the Gotnia Formation has TOC values of 0.3-2.7%, with a 1.1% average; TOC values in the Chia Gara Formation ranged from 1.2 to 10.9% with a 2.5% average, while the Lower Sarmond Formation had TOC values between 0.3 and 1.5% with an average of 1.1%. In well Aj-8 the TOC values generally show a higher reading compared with Aj-12 due to the location of the well, which is nearer to the basin centre. The Mus Formation did not appear in the stratigraphic section in this well, the Alan Formation had TOC values between 2.2 and 3.6% with an average of 2.7%; for the samples from the Sargelu

Formation, the TOC values vary from 1.4 to 13.6% with a 3.1% average, as with the Aj-12 well. The highest TOC value contents in this well were present in the Naokelekan Formation, which is equivalent to the Najmah Formation ranging up to 19.2% with an average of 11.1%. The TOC value range for the Gotnia Formation is 1.2-6.6% with an average of 3.3% and for the from the Chia Gara Formation range from 1.3 to 17.3% with a 5.2% average, the TOC% for the Lower Sarmond Formation is range from 0.9-2.5% with a 1.4% average value. The highest TOC contents occurred predominantly in the lower part from the Chia Gara Formation and Najmah Formation and the upper part from the Sargelu Formation in the studied stratigraphic column in both wells (Aj-12 and Aj-8).



Fig. 2.12 Pictures for core samples studied collected from Najmah Formation show color changing with TOC values change (dark color refer to high TOC values, while the light color refer to low TOC values). The figure also show high TOC values in the upper part from this Formation and low values from TOC in the lower part from this Formation. (field work).

According to the classification of Peters (1986, subappendix2 Tab 1), the Formations in general can be considered as having “very good” to “good” TOC quality. In contrast, some samples from Anhydrite Formations (Gotnia and Alan) in the studied wells had a lower TOC content (0.3-0.6%). Relatively higher TOC contents may have resulted from better depositional conditions, which could have been more prone to the preservation/accumulation of relatively higher amounts of organic matter.

For distinguish the Kerogen type different plots are used, the hydrogen index (HI) calculate values versus the Oxygen index (OI) calculate values and the total organic carbone (TOC wt%) versus S₂(mg HC/g rock) from Rock-Eval pyrolysis for the samples studied are used and plotted in the diagram and plotted in (Peters, 1986) diagram the samples studied have Kerogen type II and Type III with mixture of type II and III kerogen (Fig 2.14,15). The samples from the Chia Gara Formation show kerogen from type II and the samples studied from the well Aj-8 show high ratio from Type II kerogen. The samples studied from the Lower Sarmond Formation in the both wells (Aj-12 and Aj-8) show type III kerogen.

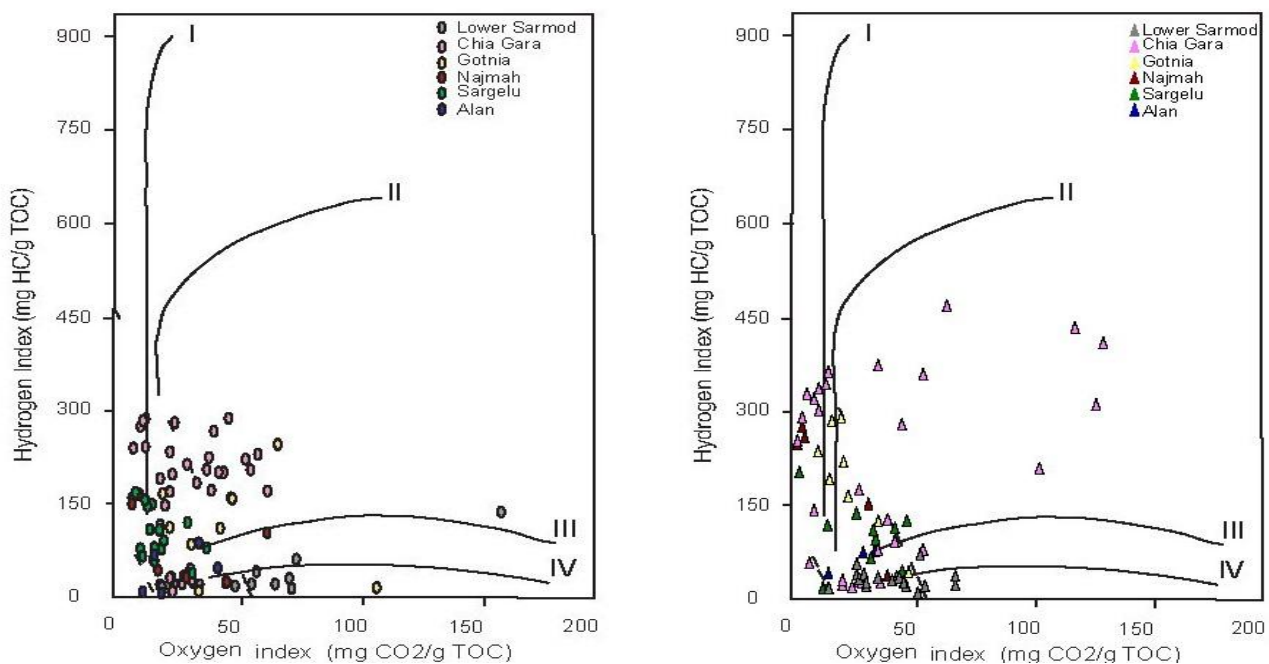


Fig. 2.13 Cross- Plot of S₂ and TOC for samples inform Ajeel oil field (left (circles) well Aj-12 and the right (triangles) well Aj-8. The Type lines are from Peters (1986).

Other diagram which is commonly used to study the kerogen type depending on the HI values versus T_{max} values from Rock-Eval pyrolysis is also used for the Formations studied and plotted in a (Peters and Gassa, 1994 diagram) the plots show that the Kerogen type II and III with mixture type II and III is the type for the kerogen for the samples studied and they are in oil zone (Fig 2.15).

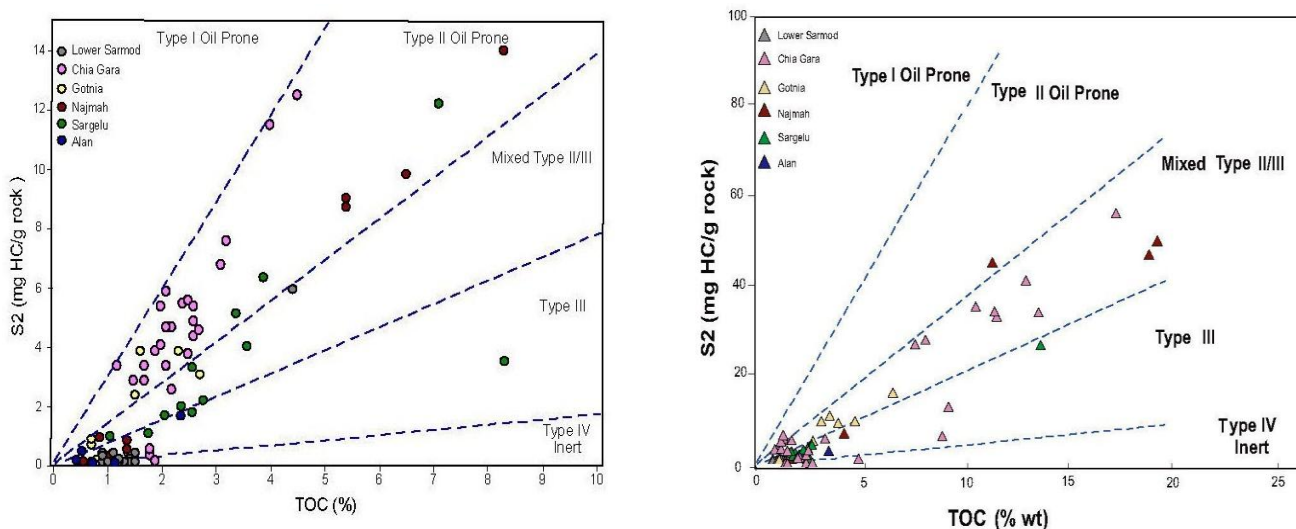


Fig. 2.14 Cross- Plot of S2 and TOC for samples inform Ajeel oil field (left (circles) well Aj-12 and the right (triangles) well Aj-8. The Type lines are from Peters (1986).

Thermal maturity

The thermal maturity of dispersed organic matter, which describes the impact of heat and time during the burial of sediments and is a character of the organic matter conversion to hydrocarbon generation from oil or gas (thermal exposure converts kerogen into petroleum). For this reason, when assessing hydrocarbon generation one has to be aware of the effect of maturation on the organic matter. Thermal maturity refers to the extent of temperature-time driven reactions that convert sedimentary organic matter (source rock) to oil, wet gas, and finally to dry gas. Several data types and parameters have been used to evaluate the level of organic maturity. The evaluation of thermal maturity of organic matter in the study source rocks was carried out using pyrolysis **T_{max}**, which represents the temperature at the point where the S2 peak is at its maximum (Espitalie et al., 1977) and in general reflects the effect of thermal maturity, which may also be influenced by kerogen type (Tissot and Welte, 1984; Peters, 1986; Bordenave, 1993; Hunt, 1996) and **Production Index (PI) or transformation ratio**, which is a proportionality between the hydrocarbons that were already generated (S1) from kerogen and a quantity of whole hydrocarbons that can be obtained from kerogen (Tissot and Welte, 1984). It is related to the type and thermal maturity of organic matter; for that reason it is not the same for different types of organic matter (Tissot and Welte, 1984; Peters and Cassa, 1994). It can be mathematically expressed as $[S1/(S1+S2)]$. According to Hunt (1996), a PI value of 0.1 indicates the beginning of a considerable amount of oil generation and 0.4 indicates the termination of oil generation and the initiation of gas

generation. The relation between Tmax and PI can be summarized as follows: (1) immature organic matter has Tmax and PI values below 435°C and 0.10, respectively; (2) mature organic matter has a range of 0.1–>0.4 PI. At the top of the oil window, Tmax and PI reach 450°C and 0.4, respectively; (3) mature organic matter within the wet gas zone has PI values greater than 0.4; and (4) postmature organic matter usually has a high PI value and may reach 1.0 by the end of the dry gas zone (Peters, 1986; Peters and Cassa, 1994) (subappendix2 Tab2). The Tmax maturation range varies with the different types of organic matter (Tissot and Welt, 1984; Espitalie et al., 1978, Peters, 1986; Bordenave, 1993) and for the different types of Kerogen, the range of Tmax variation is narrow for type I Kerogen, wider for type II and much wider for type III kerogen because of the structural complexity of the organic matter (Tissot et al., 1987).

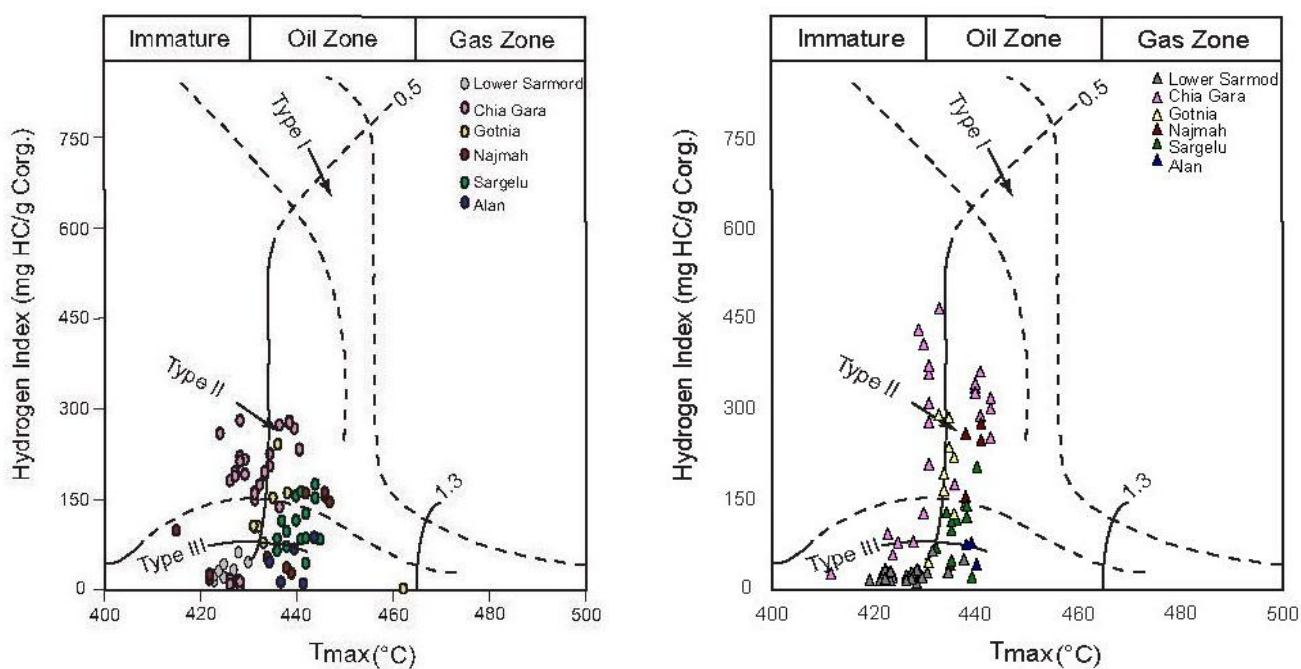


Fig. 2.15 Cross plots for the Tmax vs. HI for the samples studied the left (circles) from Aj-12 and the right (triangles) from Aj-8.

The thermal maturity of organic matter in the analyzed samples is also evaluated based on the Tmax of the S2 peak. According to Peters (1986), Peters and Cassa (1994), and Bacon et al. (2000), in their definition of the maturity level based on Tmax and PI, the studied formations are mature and appear to be within the oil window (Fig. 2.16) results are listed in (Appendix I)

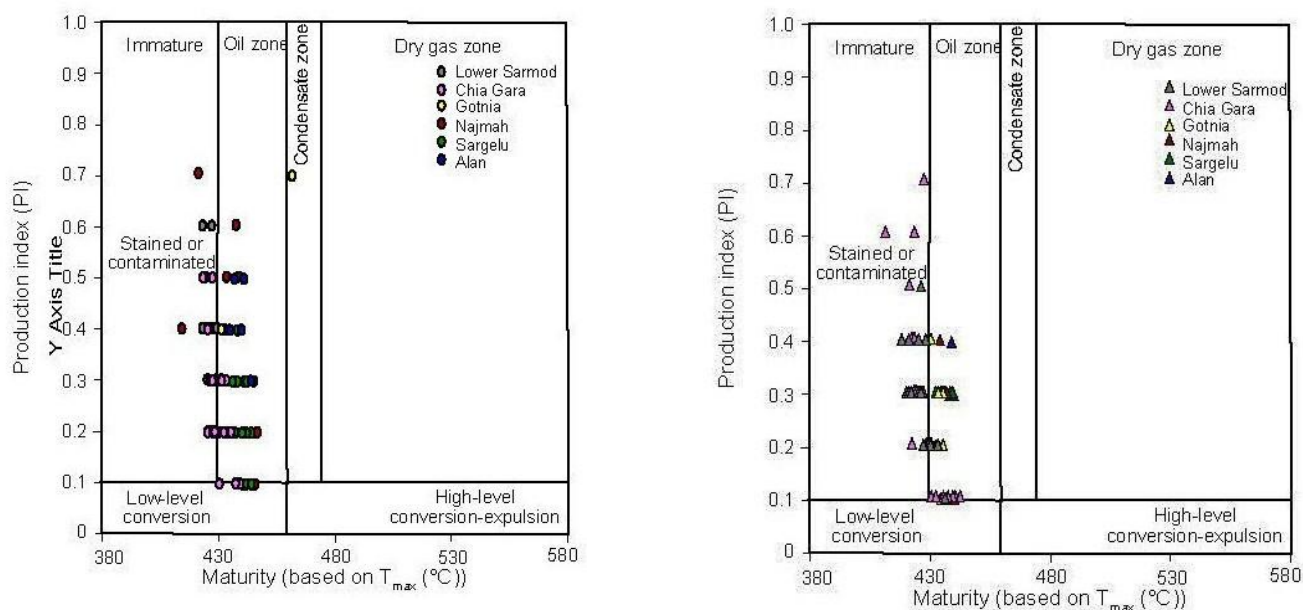


Fig. 2.16. Genetic cross plot maturity based on T_{max} and PI for samples studied the left (circles) inform well Aj-12 and the right (triangles) inform Aj-8 (diagram from Espitalie et al., 1986).

2.5.2 Source rock generative potential

A potential source contains adequate quantities of organic matter to generate petroleum but only becomes an effective source rock when it generates bacterial gas at low temperatures or reaches the proper level of thermal maturity to generate petroleum. An active source rock generates and expels petroleum at the critical moment, most commonly because it is within the oil window (Dow, 1977a). An inactive source rock has stopped generating petroleum, although it still shows petroleum potential (Barker, 1979).

Genetic potential (GP) is a summation of the amount of free hydrocarbon that has already been generated from the kerogen (S1) with the quantity of remaining hydrocarbon which has not yet been converted to hydrocarbon (S2). This can be mathematically expressed as $(S1+S2)$ and is not a hydrocarbon type indicator, although it can be used to evaluate quality of prospective organic matter (Pitman et al., 1987). Table 3 in (subappendix2) show the Genetic Potential values and their comparable source rock evaluations.

For the two wells studied AJ-8 and Aj-12, the GP values were generally good for the Chia Gara and Najmah formations, with an average of 8,6 and 7,9 respectively and moderate for the Sargelu and Gotnia formations, averaging 4,6 and 2,4. The Alan formation had poor genetic potential with a 0.9 average. Source rock genetic potential for the Formation studied are listed in the (Appendix I).

Hydrocarbon generation potential

The kerogen type and which hydrocarbons might be generated were characterized based on organic geochemical properties. In addition, there is a direct correlation between pyrolysis data and hydrocarbon generation potential (e.g. Bordenave et al., 1993; Hunt, 1995). The Rock-Eval parameters enable one to predict the type of hydrocarbon that could be generated (Peters, 1986). Most useful parameters in this matter are shown in Table 2.4. The constituents of different organic matter can be identified by plotting S2 versus TOC (Enk et al., 2006). This graph may also be used to: 1- determine the kerogen type; 2- measure dissolved organic matter by the surface of rock particles; and 3- make corrections to the hydrogen index (Dahl et al., 2004; Erik et al., 2006). Samples with a hydrogen index greater than 300 mg HC /g TOC can generate oil (Bordenave et al., 1993; Hunt, 1995), while the samples with hydrogen index values below 200 mg HC /g TOC can generate gas, if they are subjected to sufficient burial and heating.

The amount and material composition of the kerogen determine petroleum potential and can differ vertically or laterally within a source rock. In the Ajeel field these values meet the accepted standard of source rock with good to excellent hydrocarbon-generative potential (Fig. 2.16). Excellent source potential in Aj-12 well is found in the Chia Gara and Naokelekan Formations. Very good source potential also occurs in parts of the Sargelu Formation. Excellent source potential in the Aj-8 well is found in the Chia Gara and Naokelekan Formations. Very good source potential also occurs in Carbonate layers of the Gotnia Formation . Sulfur content (wt%) for study samples vs. TOC (wt%) in (Aj-12 and Aj-8) are plotted. In general, the Gotnia Formation has high sulfur content with an average of 9.2 and 7.2% in Aj-12 and Aj-8 respectively. For the Lower Sarmond the average of TS% was 0.9% in Aj-12 and 0.8% in Aj-8, Chia Gara Formation has TS % average 1.8% in Aj-12 and 2.5% in Aj-8, the TS(wt%) average in Najmah Formation was 3.3% in Aj-12 and 3.6% in Aj-8, for Sargelu Formation the average was 1.7% in Aj-12 and 1.6% in Aj-8. Alan Formation which concedes seal in both wells has high TS average reach 12.7% in Aj-12 and 5.6% in Aj-8 the results are listed in (Appendix I).

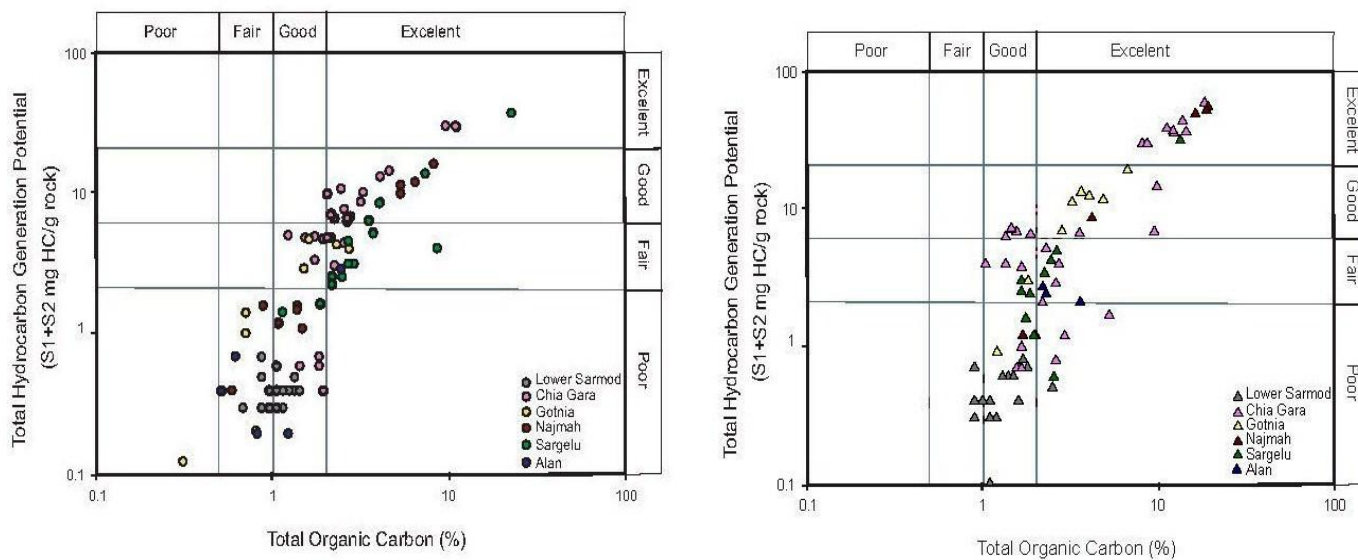


Fig. 2.17. Cross Plot for the TOC(wt%) versus hydrocarbon genetic potential from (S1+S2) for the studied samples (circles) from the well Aj-12 and (triangles) from the well Aj-8.

2.6 Bitumen bulk geochemical parameters

Detailed structural information on kerogen is limited because of its heterogeneous composition and the difficulties associated with the chemical analysis of solid organic matter (Peter and Cassa, 1994). The discovery of insoluble biopolymers in living organisms, sediments, and sedimentary rocks has led to a reappraisal of the structure of kerogen (Rullkötter and Michaelis, 1990). The amount of extractable organic matter (EOM), or total hydrocarbon yield is presented in (appendix I). In well Ajeel-12, the Alan Formation had EOM yields ranging from 112 to 233 with the exception of one sample near the contact with the Sargelu formation, which had high a 1677 ppm value of extraction. The cross plot of TOC wt. percent versus extraction in ppm for the Alan Formation shows poor source rocks. The overlying Sargelu Formation EOM yield ranges from 247 to 3239 ppm and is considered good to excellent source rocks. The Najmah Formation had the highest EOM yield compared with the other formations, ranging from 1974 to 10110 ppm which makes it very good to excellent source rocks. The overlying Gotnia formation could according to the cross plots show high values from extraction in ppm in the Carbonate layers from this Formation which make it excellent source rocks with values from extraction reach to 1900 ppm. The Chia Gara Formation which had an EOM yield range from 73 in the

upper part to 16266 in the lower part of this formation, making it good to excellent source rocks in the lower part from it and poor source rocks in the upper part from it. The Lower Sarmond Formation which is overlying the Chia Gara Formation had an EOM range of 45 to 277 ppm and is considered poor source rocks. The cross plot of TOC wt. versus extraction in ppm for the Formations studied is shown in the (Fig. 2.17) and the result are listed in the (appendix I). In the Ajeel-8 well all the formations plotted very similarly to the Ajeel -12 plot with extraction values in ppm for the Formations studied as follow: the Sargelu Formation had an EOM range from 628 to 3952 ppm for the Najmah Formation is considered very good to excellent source rocks with an EOM range from 11819 to 2590 ppm. The Gotnia Formation in Aj-8 showed high values for extraction with make it excellent source rocks in the carbonates layers and low values in the Anhydritic layers from this Formation with range values from 368 to 6376 ppm. The ChiaGara Formation showed higher values for extraction compared with values in Aj-12 and similar in distribution in raised values in the lower part from this Formation the range for this value lies between 348 and 7746 ppm. The Lower Sarmond Formation had an EOM range from 38 to 251 ppm, and is thus it considered poor source rocks.

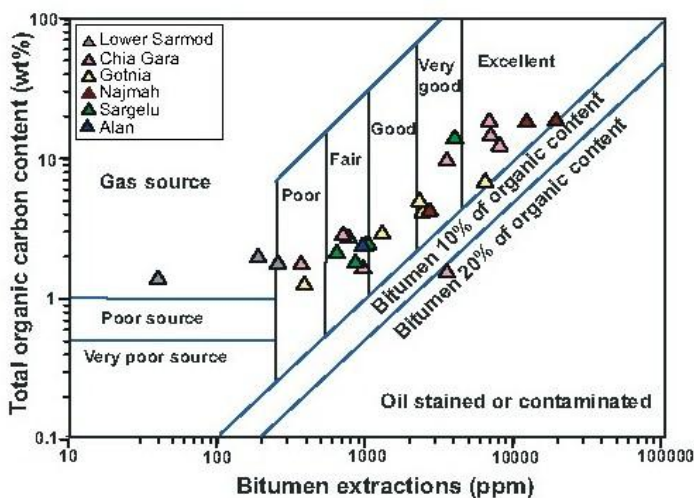
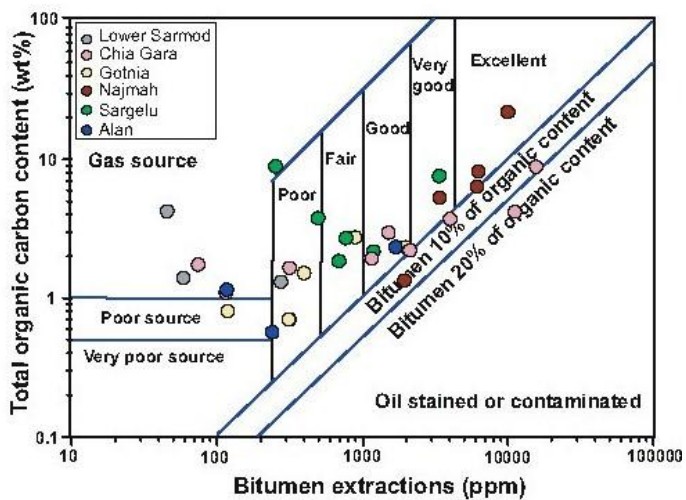


Fig. 2.18. Cross plots of the TOC(wt%) versus extraction in ppm for the Formations studied (circles) inform Aj-12 and (triangles) inform Aj-8.

2.7 Conclusions remarks

Mus and Alan Formations

Basal Mus Fm. (Aalenian) is composed of shallow water carbonates with no source potential (TOC < 0.5%; HI < 50) and passes into the anhydrites of the Alan Fm., which is more anhydrite at the base (40-60% anhydrite, GR < 10 API; TOC < 0.5%) and more argillitic at the top (30-40% anhydrite, GR 20 - 60 API; TOC 0.5-2.5%) and average for genetic potential (0.9, 2.4) in wells Aj-12 and Aj-8 respectively and extraction average 674.6531 ppm in Aj-12 and 954.587 ppm in Aj-8. The high PI (0.3-0.5) and low T_{max} values (437-440°C) argue for impregnation of anhydrites with migrated oil but a minor source potential can be ascribed to the Alan Formation.

Sargelu Formation

The overlying Sargelu Fm. is 80 m in thickness and based on carbonate content, GR (gamma ray in API units), and TOC content can be subdivide into 2 shaling upward cycles. This formation has been listed as potential source rock (Verma et al., 2004, Pitmann et al., 2004, Jassim and Goff, 2006, Aqrawi et al., 2010), which is confirmed in more detail in our study. In Aj-12 the average of TOC is 2.95% (n=17) ranging between 0.9 and 8.35% TOC. At a present day depth of 3510 to 3590m, with a T_{max} of average 442°C and a PI of 0.24 with average 4.6% for Genetic potential and extract average 1090.092 ppm, the Sargelu is in the petroleum generation stage. In Aj-8 the average of TOC is 4.5% ranging between 1.4-13.6% with T_{max} of average 436°C and PI 0.3 and genetic potential average 5.2 with 1613.681 ppm average for extract samples. (Figs.2.32 to 2.38). In their study of the Shorish-1 well, Sachsenhofer et al. (2015) found the TOC average for the Sargelu Formation equal to 2.2% with a T_{max} range of 454-463°C and HI range of 12-59 mg HC/gTOC which shows that the Sargelu Formation has high maturity in this well. Our study with Sachsenhofer et al study shows the Sargelu Formation to be more mature in the north-east of Iraq. This is also improved by Abdula (2014) in his study of the Sargelu Formation in widespread part of the north of Iraq in cutting core samples from 4 wells. He observed that TOC wt. percent content of the Sargelu Formation decreased to the east and northeast, which can be due to the change of lithofacies as a result of environmental condition variations, which means that land derived organic matter contribution increases toward the northeast. The plots for the TOC values content versus extractable organic matter show that the sediment in the Sargelu Formation as very good source rock with good to very good potential for oil generation, especially in the upper part, while plots of samples selected from the lower part from this Formation show fair source rock.

Najmah Formation

The overlying Oxfordian to Kimmeridgian basinal Najmah Fm. or its facies equivalent the shallower Naokelekan Fm. have also been listed as potential source rocks. The thickness comprises only 30 m, which can be subdivided into 3 distinctive units: the basinal carbonate (85-90% carbonate, GR 10-40 API) is followed by a shale unit (carbonate >30%, GR >100 API), which is overlain by an interval of shale/carbonate alternations (carbonate 30-70%, GR 80-100 API). Though a similar tripartite facies

development has been noted by Aqrabi et al. (2010), the organic matter distribution in the Ajeel field is different to their report. A basinal transition bed to the underlying Sargelu contains the highest TOC content of 21.9% (GR >120 API), followed by moderate TOC of 0.4 to 1.4 in the top and basal unit, whereas the central unit has TOC values of 5.4 - 8.34%. The central unit shows T_{max} values of 447°C and a PI of 0.17 - 0.20, arguing for ongoing oil generation, whereas over- and underlying units are impregnated by expelled or migrated oils (T_{max} 447°C, PI of 0.39 - 0.80), genetic potential for this formation in this well had an average of 7.9 and a 5611.334 ppm value average for extraction. Fig. 2.29 shows some of study samples from the Najmah Formation. In Aj-8 the Nakelekan Formation, equivalent to the Najmah Formation with a thickness of only 11 m, and also considered potential source rocks, can be subdivided into 3 distinctive units: basinal similar to Aj-12 containing the highest TOC content of 19% (GR > 125 API) (carbonate > 40%), followed by the central unit which could be divided into two subunits (the lower part bituminous limestone with a high TOC content of 11% while the upper part Limestone has 1.7% TOC content) (carbonate > 80%), and the top unit is composed of bituminous limestone with TOC content of 4.2%). The basinal unit with the lower part of the central unit argues for ongoing oil generation with T_{max} values of 441°C, PI 0.1), while the upper part of the central unit and the top unit are impregnated by expelled or migrated oils (T_{max} 435-438°C, PI of 0.3-0.4) and has a high average of genetic potential reaching 33.5 and the average for extraction in ppm reaching 11031.69. Sachsenhofer et al. (2015) gave TOC (wt%) average 4.6% as a result of analysis of samples from the Nakelekan Formation in the Shorish-1 well in north east Iraq and TOC contents in this Formation may reach up to 47%, T_{max} values (454-463°C), indicating a relatively high maturity which make this Formation with Sargelu Formation very good source rock potential in the Shorish -1 well. In this study the units that the Nakelekan Formation are divided into are similar to Balaky (2014) in his study of the Nakelekan Formation in the north-east of Iraq. Abdula (2014) in his study of this formation observed that TOC values decrease from the west toward the east, the increase in the richness towards the west and northwest parts in the north of Iraq is due to the change of sedimentary facies and distance from the land.

The Gotnia Formation

The Gotnia Fm. in the Ajeel field ranges from a depth of 3444 to 3486 m, with interbedded anhydrite and argillaceous carbonate layers. The anhydrite interval bears no organic matter but the carbonates reach TOC values of up to 2.4% in the transition to the overlying Chia Gara Fm and TOC value 2.7% in depth 3478 m. The TOC average in this well reaches 1.1% with T_{max} ranging (431-436°C) and PI (0.1-0.9) with average 0.4 and HI average 100 mgHC/gTOC. Genetic potential has an average value of 1.5 and the average of extraction in ppm was 642.845. In Aj-8 analyses of the Gotnia Formation indicated a TOC content of 1.2-6.6 wt% with 3.3% average T_{max} ranging from 431 to 439°C with an average of 434.58°C and HI average of 235 mg HC/gTOC and PI of 0.1-0.4 with an 8.5 average for genetic potential and 2527.805 ppm average for extraction. These data indicate that the Gotnia Formation is good source rock and with good to excellent hydrocarbon-generative potential in the particular in the carbonatic not the anhydritic layers. This study considers Gotnia Formation as a good source rock with a petroleum potential in carbonate layers is different to other studies which considered Gotnia Formation

regional seal in all its parts (Figs. 2.18) show pictures for some of samples studied collected from the Gotnia Formation in carbonate layer and in anhydrite layer.

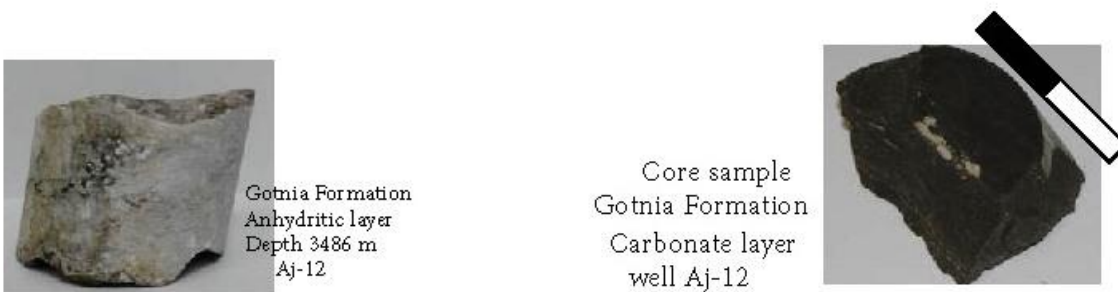


Fig. 2.19. Pictures for core samples studied collected from Gotnia Formation, the (left) from the Anhydritic layer and the (right) from the Carbonate layer (Field work)

The Chia Gara Formation

These strata can be considered to be the main source unit in the region, with a thickness of app. 220 m, an average TOC content of 2.5% (n=50) in well Aj-12 and HI value of 193 mgHC/gTOC (n=40). The Chia Gara Fm. passes from basinal shales into carbonates and then into coarse grained siliciclastic. This indicates that in upsection direction, the quality of source rock potential decreases rapidly due to basin shallowing and an increase in hydrodynamic regime. The lowermost part is mostly organic matter rich with TOC contents around 10% at a T_{max} of 439°C at the beginning of the oil window, confirmed by PI values of 0.12 to 0.15. Genetic potential has an average of 8.6 in well Aj-12 and the extract average 4153.402 ppm. In Aj-8 the Chia Gara Formation has a TOC average of 5.2 (wt%) with TOC content reaching up to 17%. Maturity parameters were , T_{max} reaching 443°C with an average of 431°C PI (0.1-0.7 in the upper part of this Formation), genetic potential reaches an average of 14 and extract average 3145.782 ppm .Together these data indicate that the Formation is highly oil prone. In the Chia Gara Formation in both wells (Aj-12 and Aj-8), the most active source rock could be noticed in the lower part of this formation, one section of around 15 m thickness averaged a TOC of 7% and reached 11% (wt) with T_{max} 440 and PI 0.1 in Aj-12 and an average TOC of 10.6% and T_{max} reaching 443°C with PI 0.1. Mohialdeen et al., 2013 studied the Chia Gara Formation in three wells (Hr-1, Tk-3, Bj-1), finding Chia Gara sediments rich in amorphous organic matter with high TOC values ranging from (1.05-7.42%). The lower part from the Chia Gara Formation show high values from the TOC (wt%) reach to 17.3% in the depth 3172 m in the well Aj-8 (Fig 2.19), while the upper part from this Formation show lower values from the TOC comparing with the lower part from this Formation. Moreover, the (HI, PI, T_{max}) values from the Rock-Eval pyrolysis support that the lower part from this Formation which is around 30 m is the effective source rocks from this Formation.



Fig. 2.20. Pictures for core samples studied collected from the lower depth interval from Chia Gara Formation show the high TOC(wt%) values in this interval which make the lower interval from this Formation is the main source rock from it. (Field work).

Lower Sarmond Formation

The overlying Lower Sarmond Fm. in the Ajeel field becomes progressively carbonate enriched and bears no significant source potential, with TOC values averaging 1.1% at an average T_{max} of 430°C with genetic potential of 0.9 and an extract average of 126.821 ppm in Aj-12. In Aj-8 the TOC average was 1.4% with an average T_{max} value of 427 °C and 157.877 ppm average for extraction. The genetic potential in this well has an average of 0.5, and these parameters show that there is no significant source potential for this formation in this well, as in Aj-12 . The figures (2.20 to 2.25) show the vertical variation for different parameters from (well logs and Rok-Eval analysis, TOC(wt%), extraction in (ppm)) for the Formations studied in the wells (Aj-12 and Aj-8) .

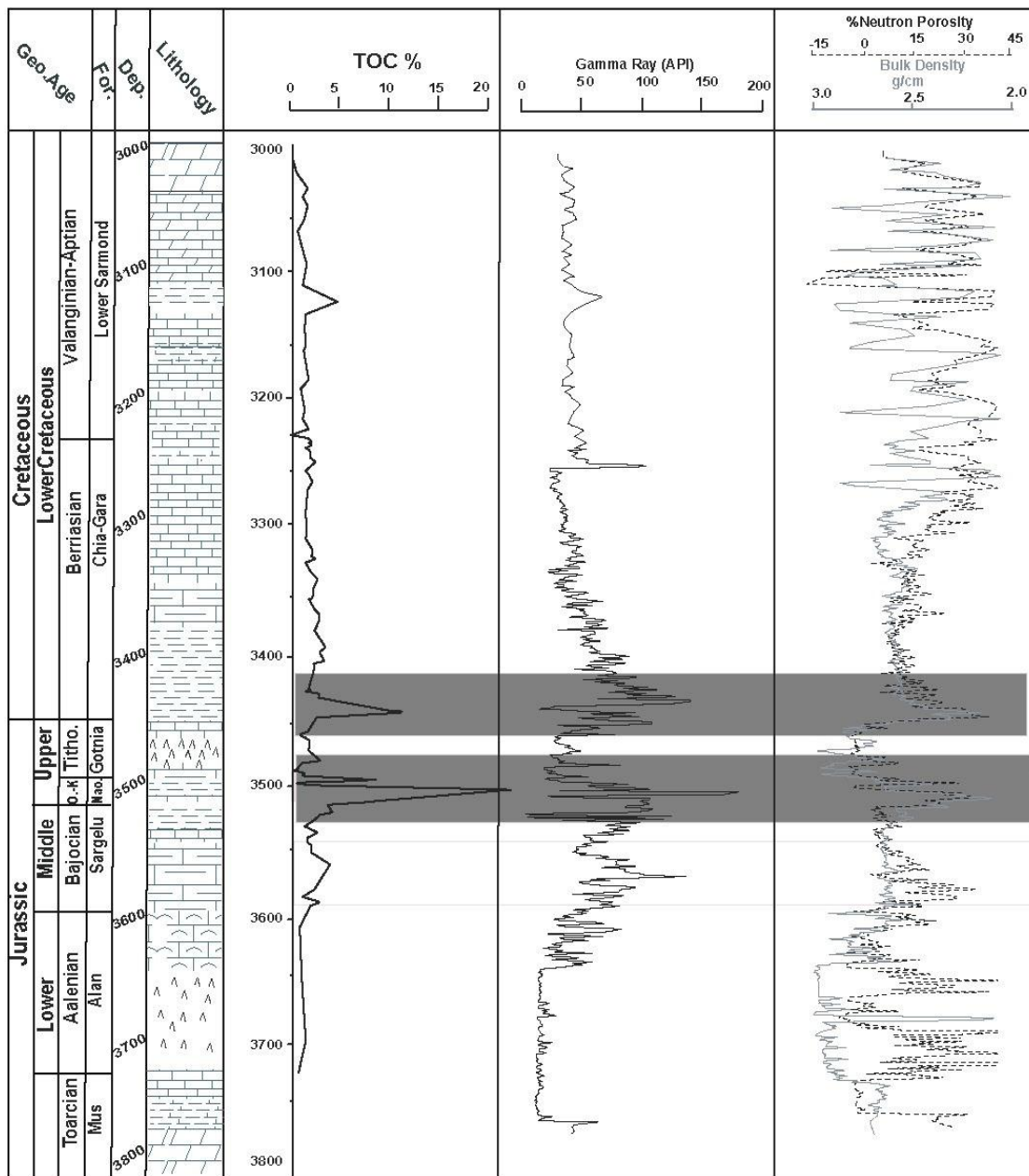


Fig. 2.21 Vertical variation of the TOC(wt%) and logs digitized values with depth for Formations studied. The data inform well Aj-12.

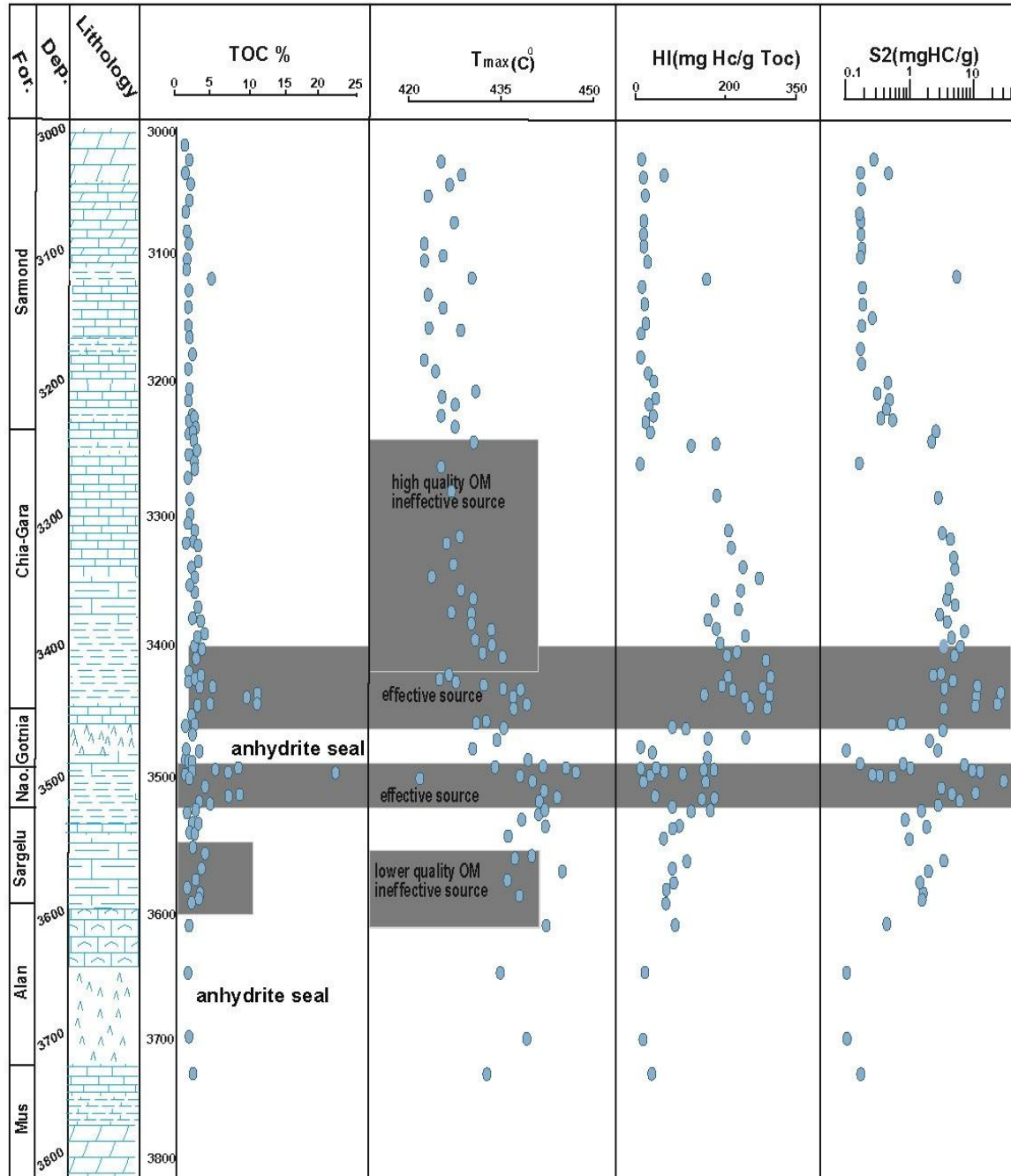


Fig. 2.22 Vertical variation of the TOC(wt%) and Rock-Eval parameters(T_{max} , HI and S_2) values with depth for Formations studied. The data inform well Aj-12 .

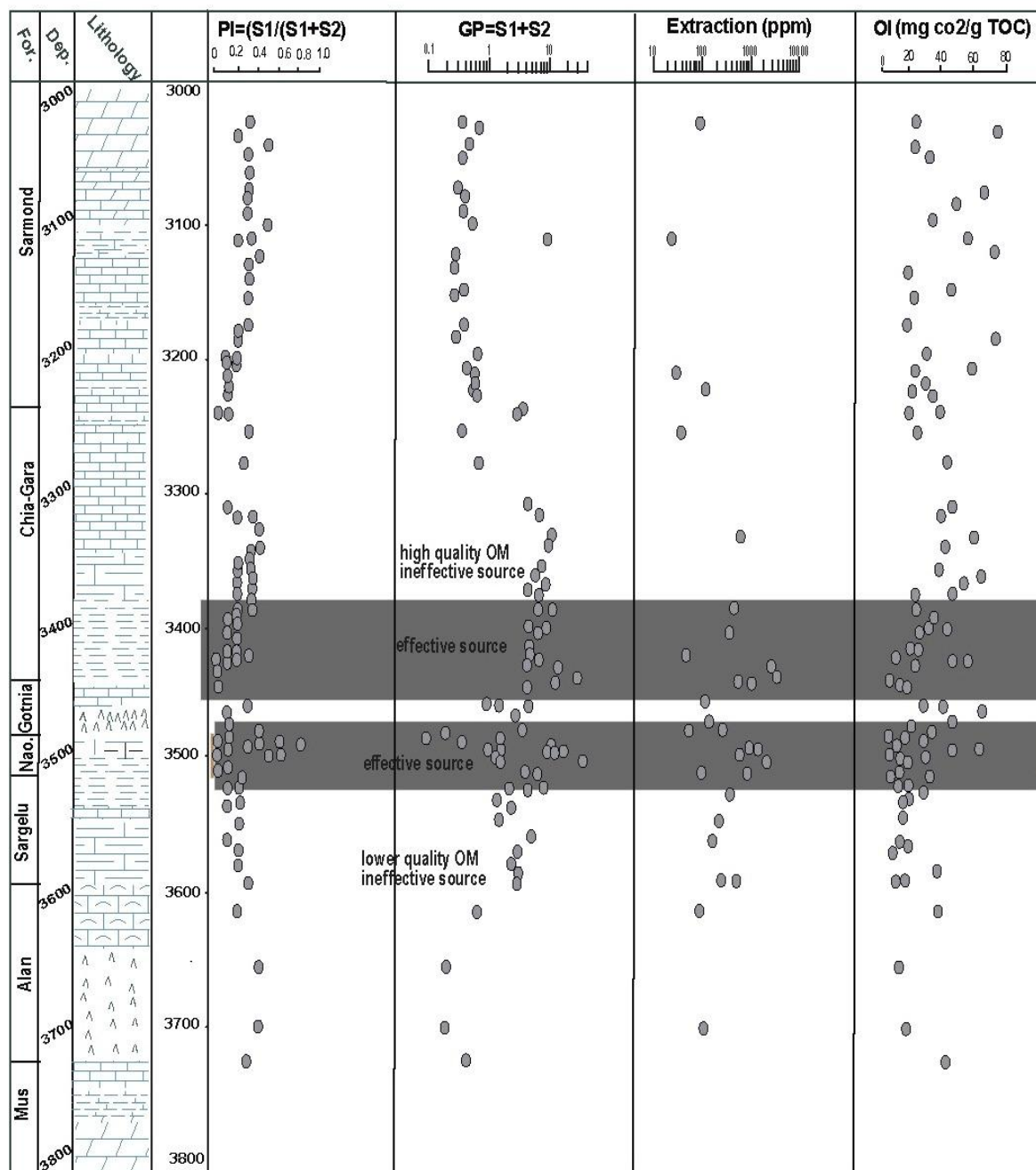


Fig. 2.23 Vertical variation of the Extraction in (ppm) and Rock-Eval parameters with depth data inform well Aj-12 .

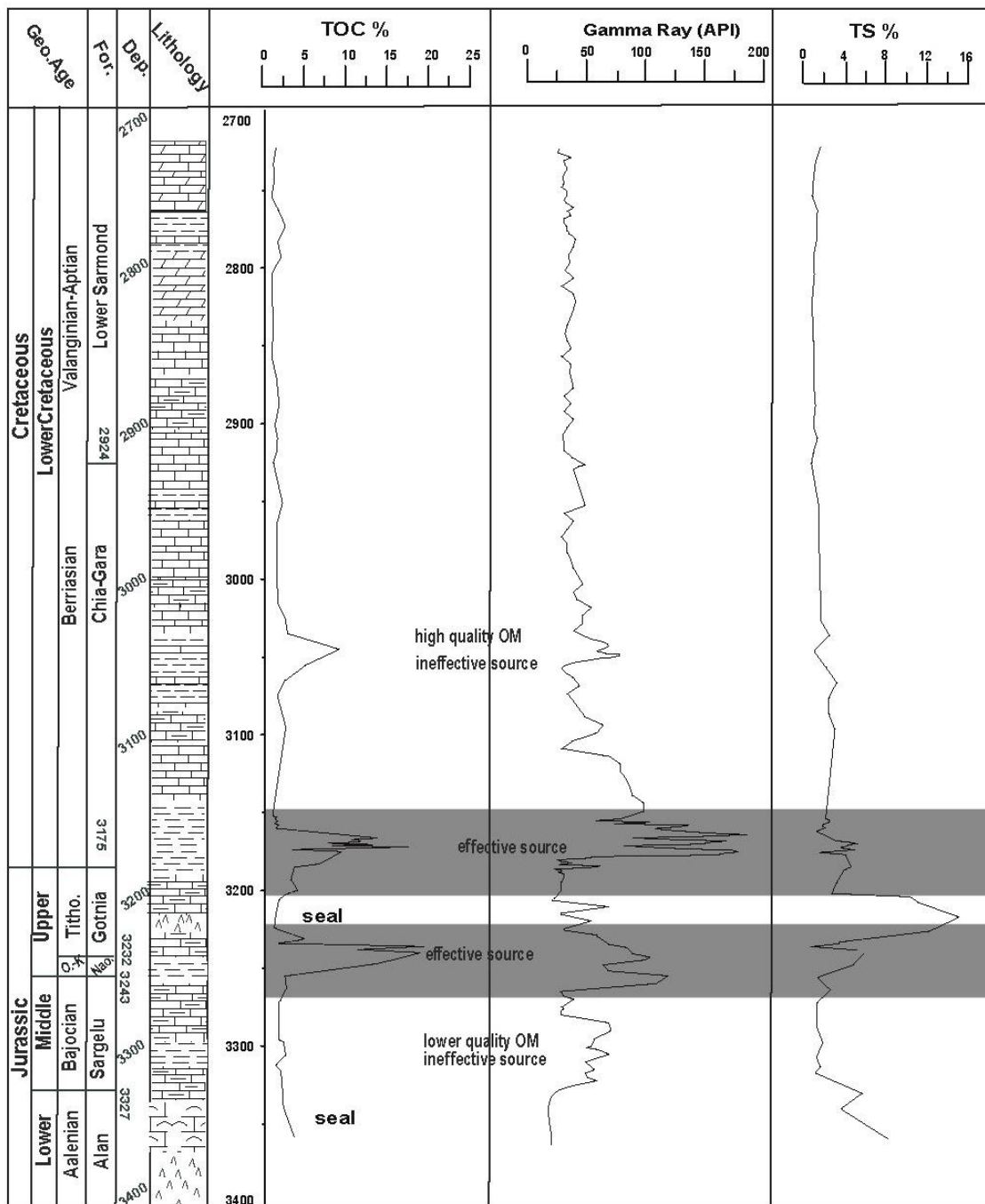


Fig. 2.24 Vertical variation of the TOC(wt%), TS(wt%) and Gamma ray log values with depth for Formations studied. The data form well Aj-8

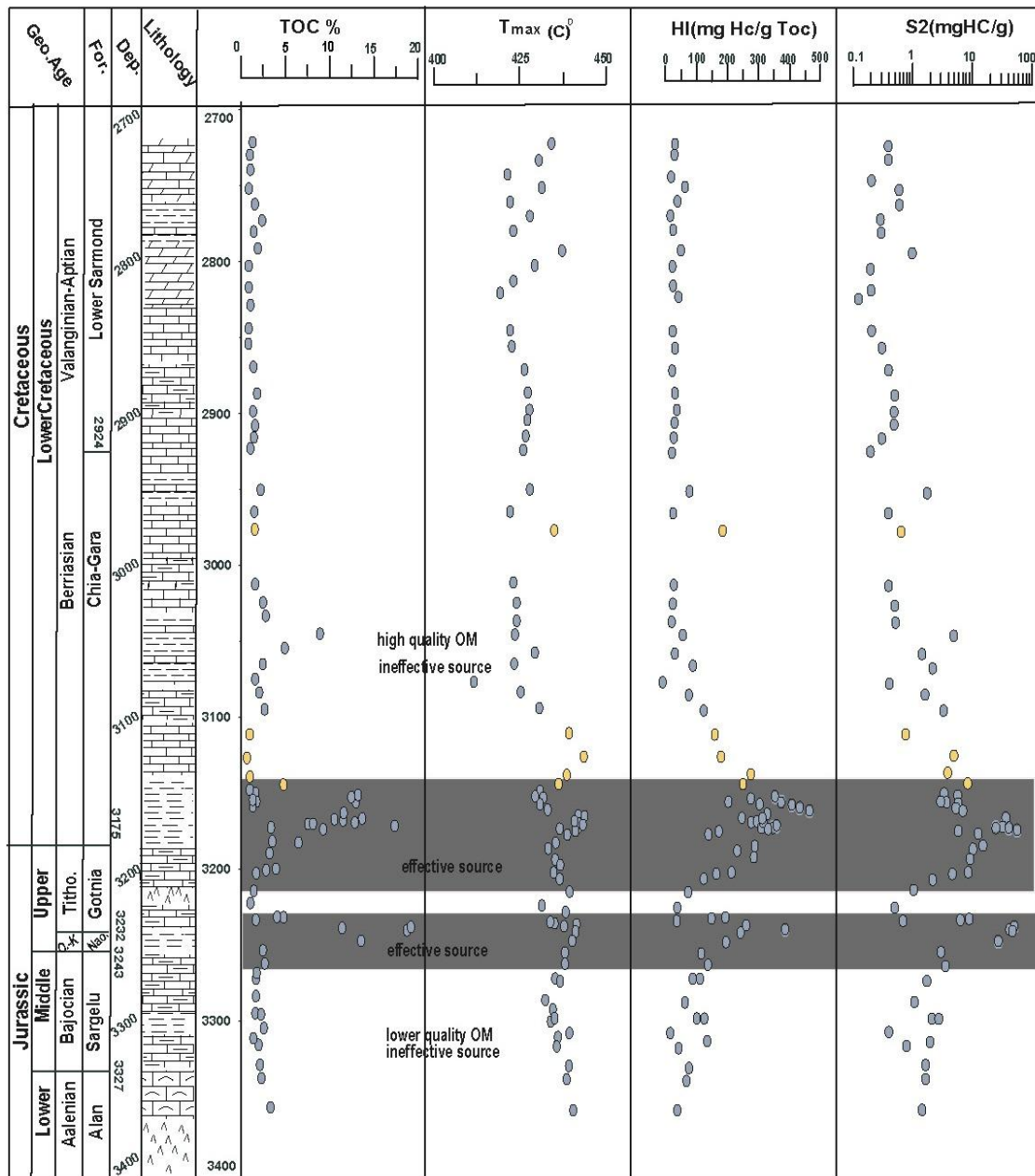


Fig. 2.25 Vertical variation of the TOC(wt%) and Rock-Eval parameters(T_{max} , HI and S_2) values with depth for Formations studied. The data inform well Aj-8 .

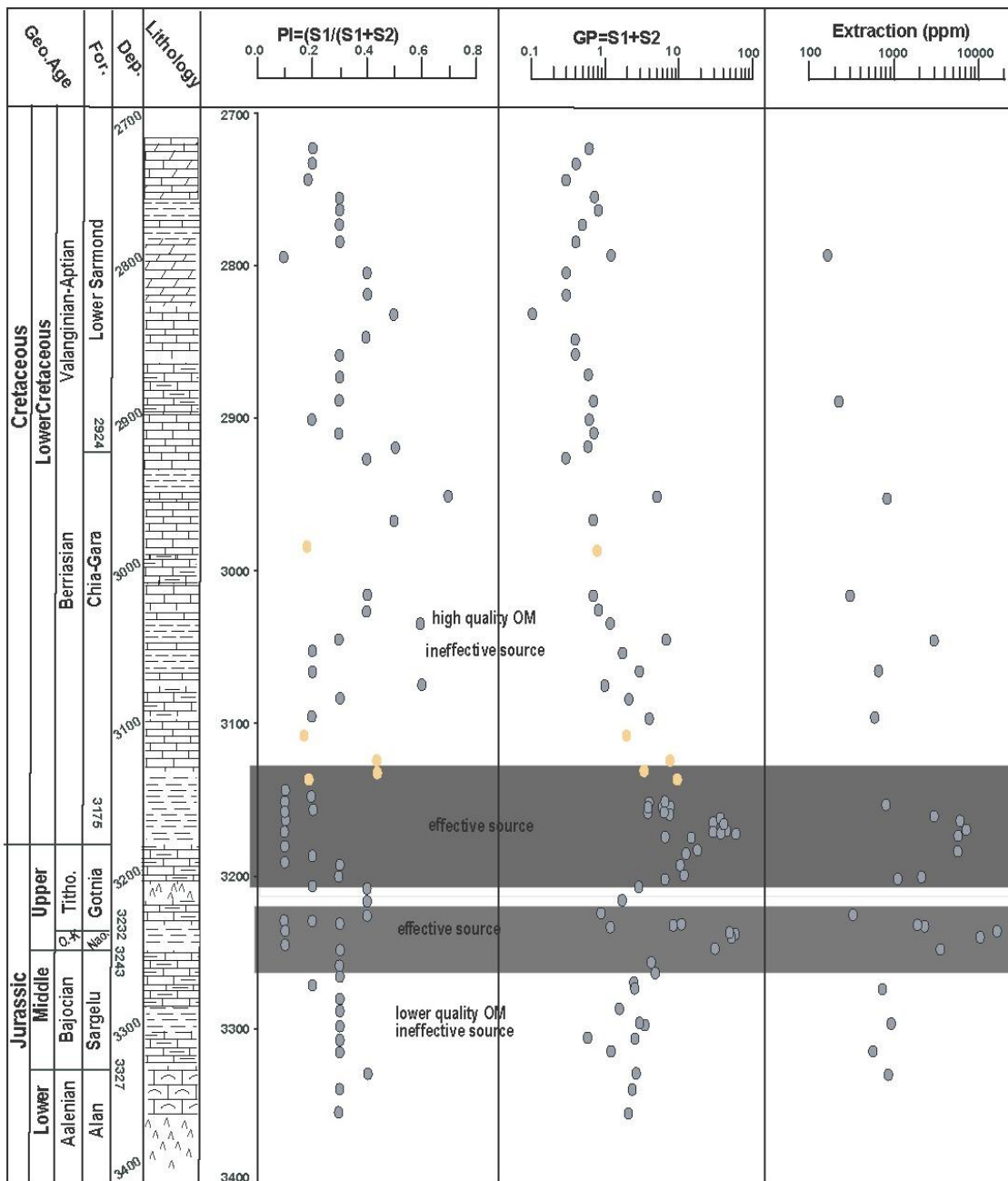


Fig. 2.26 Vertical variation of the Extraction in (ppm) and Rock-Eval parameters with depth data inform well Aj-8

Chapter 3

Biomarkers features of the Lower Jurassic- basal Early Cretaceous source rocks NE Iraq

Introduction

Northern Iraq is host to significant hydrocarbon reserves, making Iraq the sixth largest oil reserve in the world (Verma et al., 2004). Throughout the country, the Middle Jurassic-Lower Cretaceous contains very significant source rocks owing to the high organic carbon, with a high hydrocarbon generation potential. The Middle Jurassic Sargelu Formation and the Upper Jurassic and the Lower Cretaceous Chia Gara Formations are considered to be the most important source rocks in the region, with organic rich rocks of the Triassic, Cretaceous and Cenozoic ages which also have source potential (Al-Ameri et al., 2014; English et al., 2015).

1.2 Stratigraphic and Geological setting

The present study area is located in the Northwestern Zagros Basin in Northeast Iraq which is located in the far north and NE of the Arabian Plate and in the low folded zone of the Zagros Fold Belt with transition toward the northern part of the Mesopotamian Foredeep Basin (Fig.2.1) and within the Salahuddin Governorates east of the Tigris River between the cities of Tikrit and Baiji and to the southwest of the Hamrin oil field which lies 80 km from Kirkuk city and parallel to it. The average elevation of the field area is 150-170 m above mean sea level. The structure of the field is an asymmetrical, double-plunging anticline trending NW-SE

The Middle Jurassic-Lower Cretaceous source rocks are organic rich and have a high hydrocarbon generation potential. Aqrawi and Badics (2015) in their study on the NE Arabian Plate show that a total of about 2,550 billion barrels oil-equivalent of petroleum may have been generated in the Zagros fold belt in the Kurdistan region of Iraq and they considered that the Middle Jurassic Sargelu Formation and the Upper Jurassic Naokelekan Formation are the most important sources in the region (Fig. 2.2a). The Jurassic petroleum system is based on Middle to Upper Jurassic source rocks deposited in the Gotnia Basin (Goff, 2005), and the Cretaceous petroleum system is based on Lower Cretaceous source rocks which is the most important system in Iraq, separated by the anhydritic parts of Gotnia Formation, but in some parts of northern Iraq where the anhydritic sealing Gotnia Formation is replaced by the non-sealing Barsarin Formation, it is difficult to separate the Jurassic and Cretaceous systems (Aqrawi et al., 2010, Aqrawi and Badics, 2015). For this study the biomarkers in source rocks from Lower Jurassic to most base Upper Cretaceous age were studied in two wells (Aj-12 and Aj-8) in completed stratigraphic column in these two wells which contained the formations from the older to the younger as follows: Mus, Alan, Sargelu, Najmah/Naokelekan, Gotnia, Chia Gara and Lower Sarmond Formation. Figure 2.2b shows the lithostratigraphy of one of the wells studied, the Aj-12 well from the Ajeel oil field.

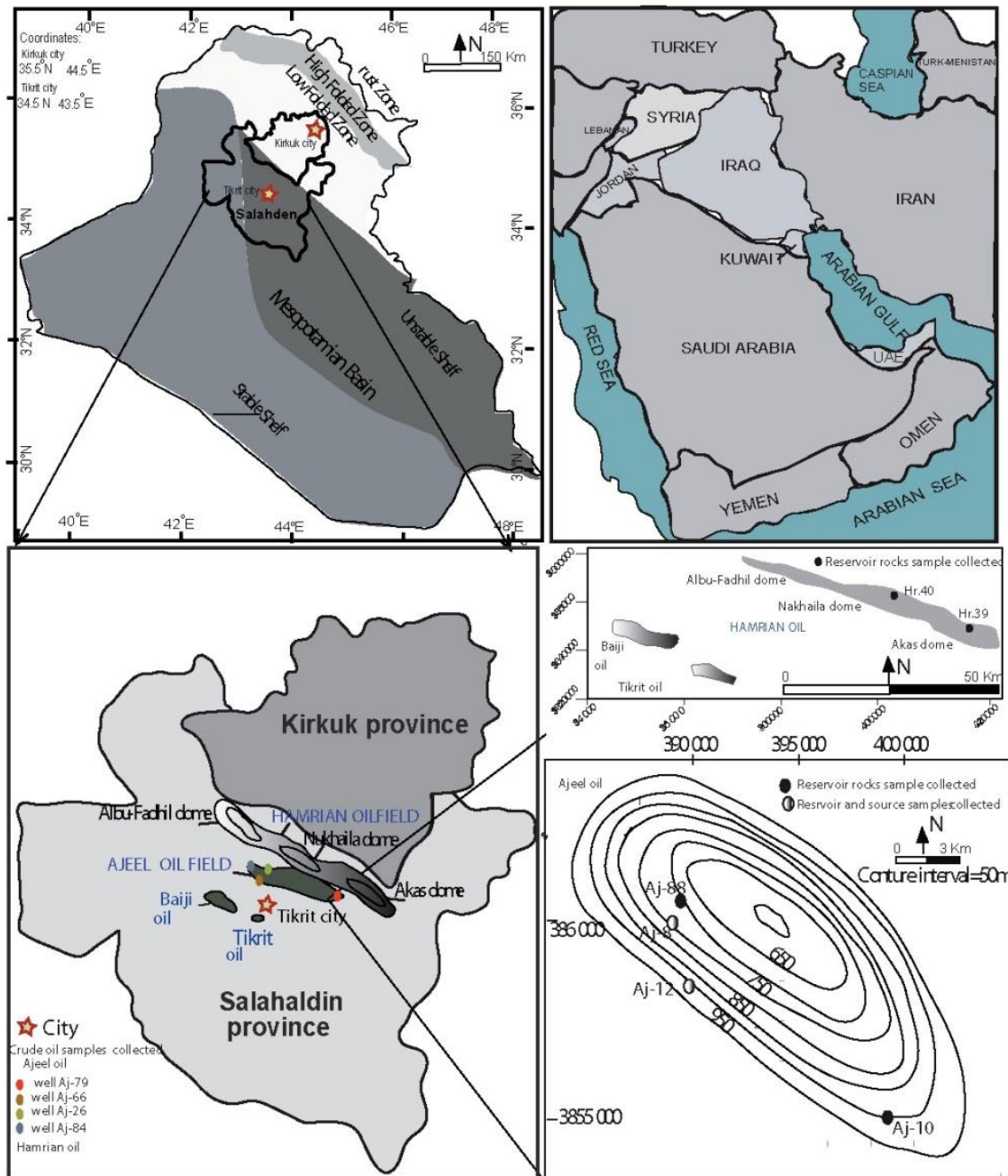


Fig 3.1 (a) a simplified map showing Iraq site with the Arabian plate (b) Regional tectonic setting of Iraq (modified from Jassim and Goff, 2006) and show two province boundaries where samples studied were collect. (c) Location map showing oil fields and wells where the crude oil samples are collect.(d) structure contour map for Ajeel oil field and location map for Hamrian oil field showing the wells where the source and reservoir samples where collect.

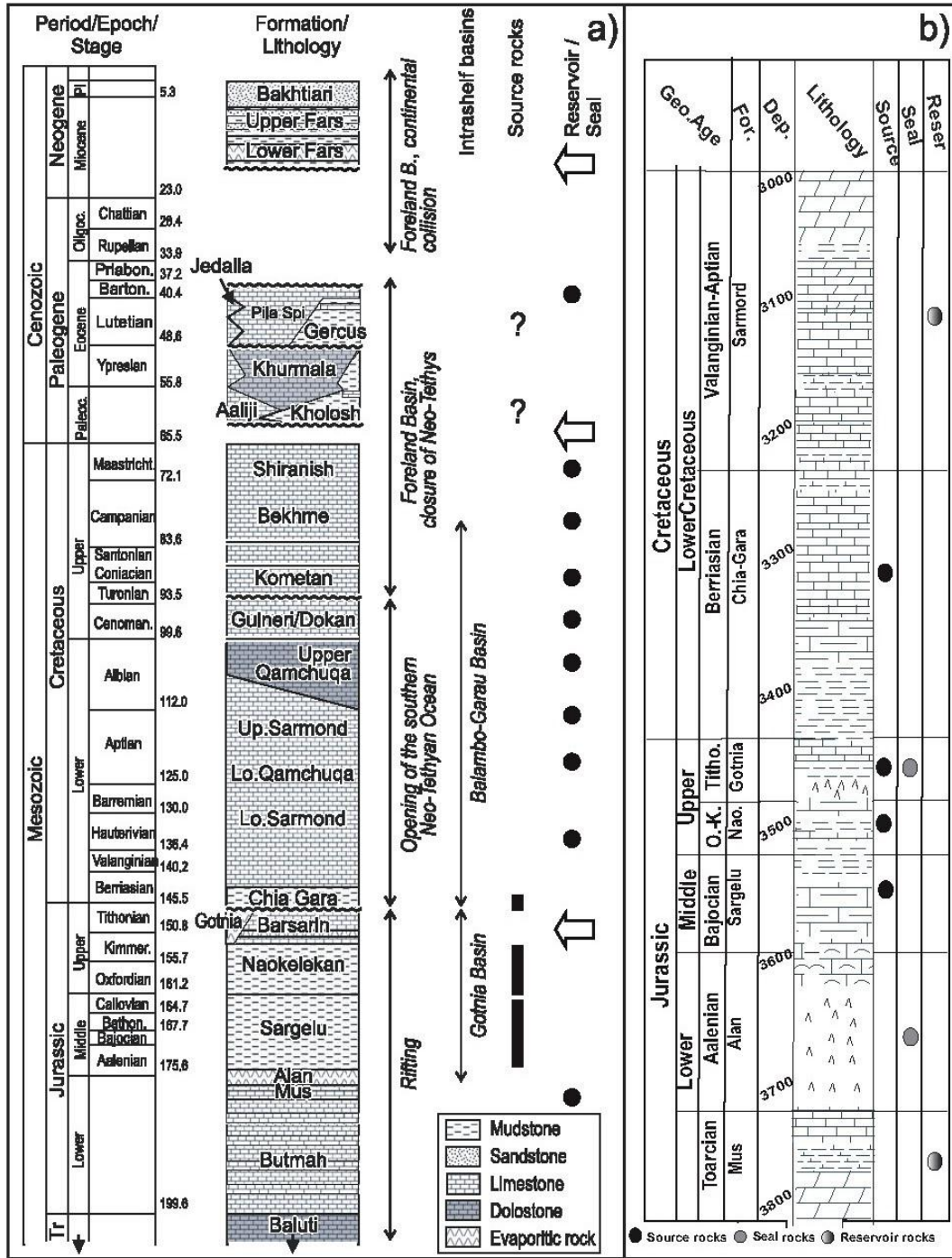


Fig 3.2. (a) Lithostratigraphy of the Low Folded Zone in Iraq (simplified after Aqrabi et al., 2010). (b) Lithostratigraphy of one of the wells studied the well is (Aj-12 well) from Ajeel oil field.

2.2. Molecular Ratio or Biomarkers

Biomarkers are molecules occurring in sediments, which originally derive from living organisms. Therefore, the biomarker carbon skeleton of hydrocarbons or other lipids can be recognized although they may be altered slightly by diagenesis. This makes biomarkers a valuable tool for description correlation and recognition of the depositional environment; this is much the same as geologists use fossils (Tissot and Welte, 1984). Biomarker distributions have been used to describe the input and depositional environment conditions of organic matter preserved in sediments (Walples and Machihara, 1991; Hunt, 1996; Peters et al., 2005). 57 rock samples from well-Aj-12 and Aj-8 were selected for biomarker analyses quantitatively by GC-MC. The biomarker analysis results are listed in Appendix 2.

3. Carbonate-anhydrite sequence facies of a sabkha environment from the Gotnia Formation: A molecular approach

Introduction

In fact, molecular parameters are being used by petroleum geochemists to solve oil-source rock correlations and to assess the maturities of oils and sediments. Organic geochemistry at a molecular level also offers new possibilities through specific pattern recognition to aid the reconstruction of past depositional environments (Didyk et al., 1978; Connan et al., 1986). Sediments deposited under hypersaline conditions, particularly those laid down in the transition zone between marine carbonates and evaporites, are increasingly recognized as a potential source for oil, hence the interest in sabkha sequences both of the carbonates and the anhydrites. Although they are devoid of petroleum potential, the knowledge regarding anhydrites is important for a complete appraisal of the sabkha deposit and their geochemical signatures are useful for studying the environment of deposition conditions and inferring the organic matter input. Relatively little work has been published in the use of molecular parameters in the sabkha environment and the environment of deposition as modern sabkha deposits were very restricted. Palaeosabkha-type sequences have been studied in the Aquitaine Basin (France) and in Guatemala by Connan, and in La Luna and Colombia by Palacas. The aim of this section is to define a facies sequence in a sabkha environment based on biomarker parameters.

Gotnia Formation carbonate-anhydrite sequence facies The Gotnia Formation was deposited in a hypersaline lagoon environment (Alsharhan and Naim, 2003) and separates a structurally elevated sub basin that was partially isolated from the Gotnia Basin of southern Iraq, which is restricted. The underlying Najmah or Naokalekan Formation and overlying Chia Gara Formations were both mostly deposited in deep-water euxinic environments (Aqrawi, 2010). **Sequence S3** shows the location of the Gotnia Formation in Saddoni's (1997) division. The gradual restriction of the basin during the Kimmeridgian led to the deposition of Gotnia evaporates in basin margin settings as a lowstand wedge of gypsum (LSW-G), followed by basin-fill halite (BFH). The Gotnia Sabkha environment of the Gotnia Formation in Iraq is very poorly studied

and all published work on this subject from Iraq has considered the Gotnia Formation in Iraq as seal rocks which separate Jurassic source rocks from Cretaceous source rocks without concentrating on the carbonate parts of this formation and linking Jurassic oils in Miocene reservoirs to the permeable parts of this formation, and furthermore without noticing that carbonate parts from the Gotnia Formation could provide oils to the Miocene reservoirs. This section of the present study will focus on the carbonate-anhydrite facies of a sabkha environment in the Gotnia Formation by using molecular parameters based on Connan et al. (1986), who used such parameters in their study of a sabkha palaeoenvironment in Guatemala. The palaeofacies map of the Late Jurassic in Iraq and in the Middle East Fig. (2-3,4) shows the sabkha environment for the study area where studied samples were collected from the Gotnia Formation and equivalent formations with their lithology respectively.

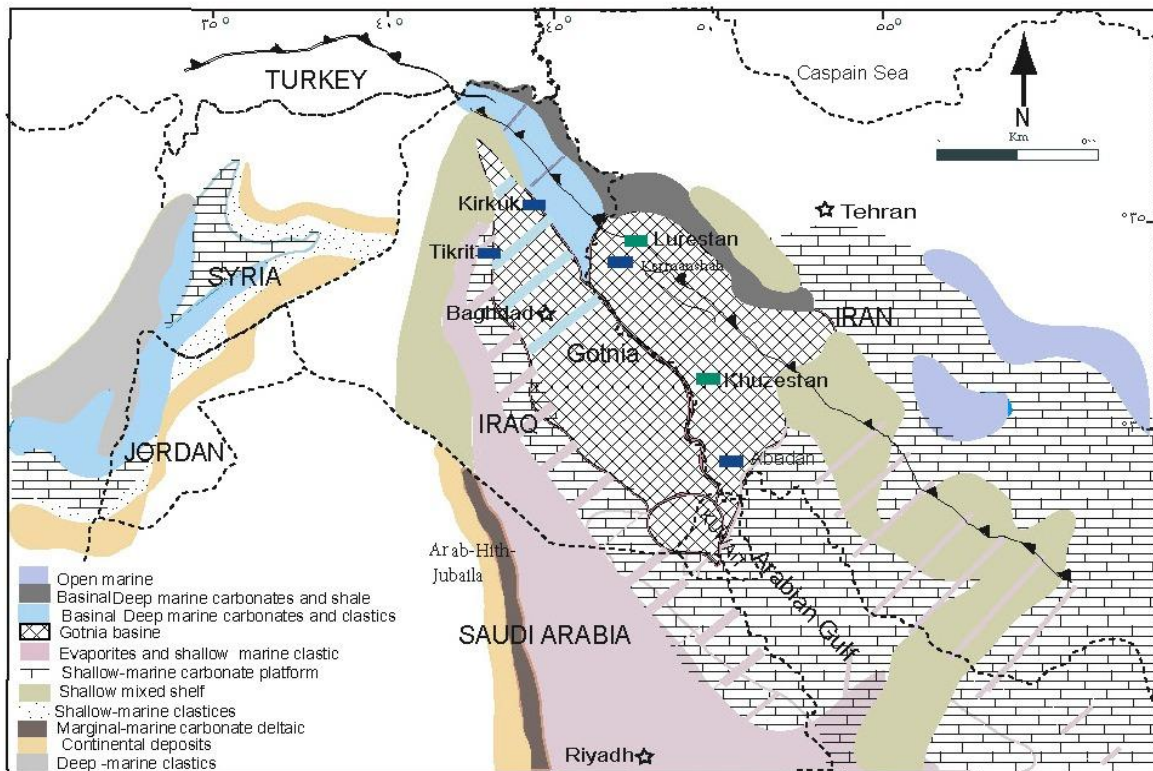


Fig.3.3 Palynofacies map of the Late Jurassic showing deposition of the Formations in Iraq and surrounding countries combined from: (Dunnington et al., 1959); Murriss (1980); Koop and Stoneley(1982); Bordenave (1993); Bordenave and Huc (1995); Ziegler, (2001); Dunnington, H. V., (2005); Jassim and Golf, (2006); Bordenave and Hegre (2010).

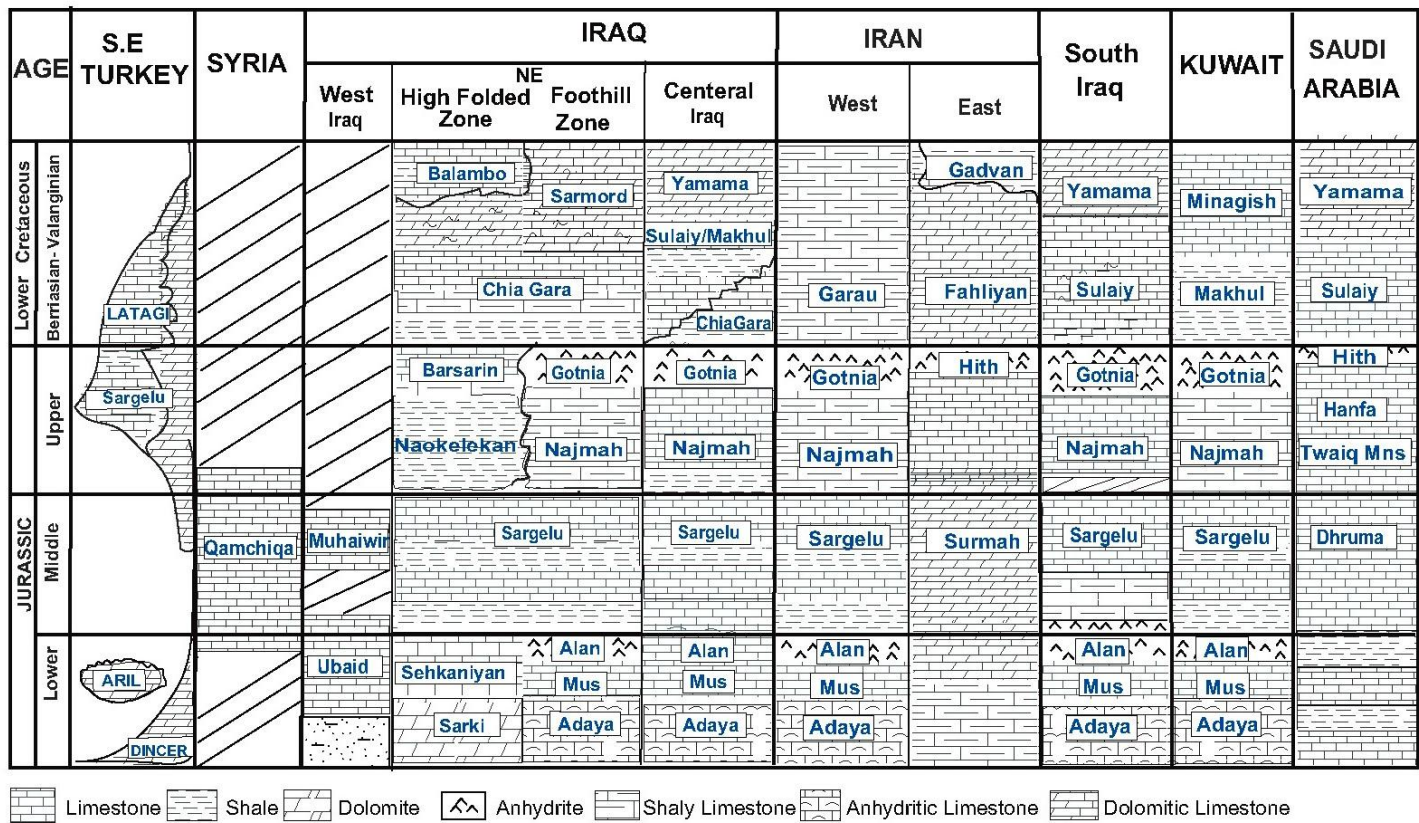


Fig 3.4 Lithostratigraphic correlation chart of Jurassic-Early Cretaceous in Iraq and surrounding countries. Figure combined from Bellen et al., 1959; James and Wynd, 1965; Al-Omary and Sadiq, 1977; Al-Sayyab et al., 1982; Murriss, 1980; Beydoun, 1991; Bordenave, 1993, Alsharhan and Nairan, 1997, 2003; Alsharhan and Magara, 1994; Alsharhan and Kendall, 1986; Sadooni, 1997; Jassim and Goff, 2006; Aqrabi et al., 2010.

Samples analyzed

In order to reach our aim, 11 selected samples (cores and cuttings) from different depths in the Aj-12 and Aj-8 wells from the Gotnia Formation are run in GC-MS to study their biomarkers. These samples are selected from 21 Gotnia Formation samples (wells Aj-12 and Aj-8) analysed with bulk geochemistry which compared the biomarker results.

Bulk geochemical analyzed

Different cross-plots are used to study the bulk geochemical results of 21 rock samples from the Gotnia Formation (lithology description, quantity and quality of organic matter, capacity of source rock to generate petroleum).

The cross-plot of TS (wt%) measured by an element analyzer and TOC (wt%) was calculated and shows differences in lithology for the studied samples in Fig. 2.4 in both studied wells (Aj-12, Aj-8). Total organic carbon (TOC) varies more than 6.59% in the carbonate layer for the samples studied. In anhydrite layers and because of carbonates intermixed with the anhydrites in some parts, TOC ranges from 0.7% to 2.8%. Total sulfur content (wt%) ranges from 0.27 to 1.8, and between 6.6 and more than 20 in the anhydritic layers. The plots show two different patterns for samples: samples with high TS and low TOC values suggest anhydritic rocks, while samples with low TS and high TOC values point to carbonate rocks.

The cross-plot of total organic carbon (TOC wt%) was calculated against bitumen extractions (ppm) for studied samples from the Gotnia Formation. The organic extract, lower than 300 ppm in anhydrites, increased steadily in TOC and reached 6376 ppm in the carbonate layer. Figure 2.4 shows the variation in samples studied plots between poor source rocks (anhydritic layers) and (good-excellent) source rocks in carbonate layers. **The cross-plot of total hydrocarbon generation potential (S1+S2 mg HC/g rock) was measured by Rock-Eval pyrolysis against total organic carbon (TOC wt%).** The S1+S2 varies between 0.1 in anhydrite layers and 18 mg HC/g rock in the carbonate layers. The plots show that samples of carbonate layers from the Gotnia Formation fall into the good-very good hydrocarbon generation potential category, while the samples from anhydritic layers are considered to have fair hydrocarbon generation potential (Fig.2.4), which means that the Gotnia Formation carbonate layers could provide hydrocarbons. Moreover, the cross plots for **S2/S3 mg HC/g rock vs. total organic carbon (TOC wt%)** for the studied samples from well (Aj-8) show the same result.

The cross-plot of total organic carbon (TOC wt%/TS%) ratio calculated against (TOC wt%/ TIC%) ratio shows two different trends with different lithology in the carbonate and anhydritic layers of the Gotnia Formation in both wells studied (Aj-12 and Aj-8). High values for the TOC/TS ratio are found in the carbonate layers, while the anhydritic layers yield low values for this ratio Fig 3.5

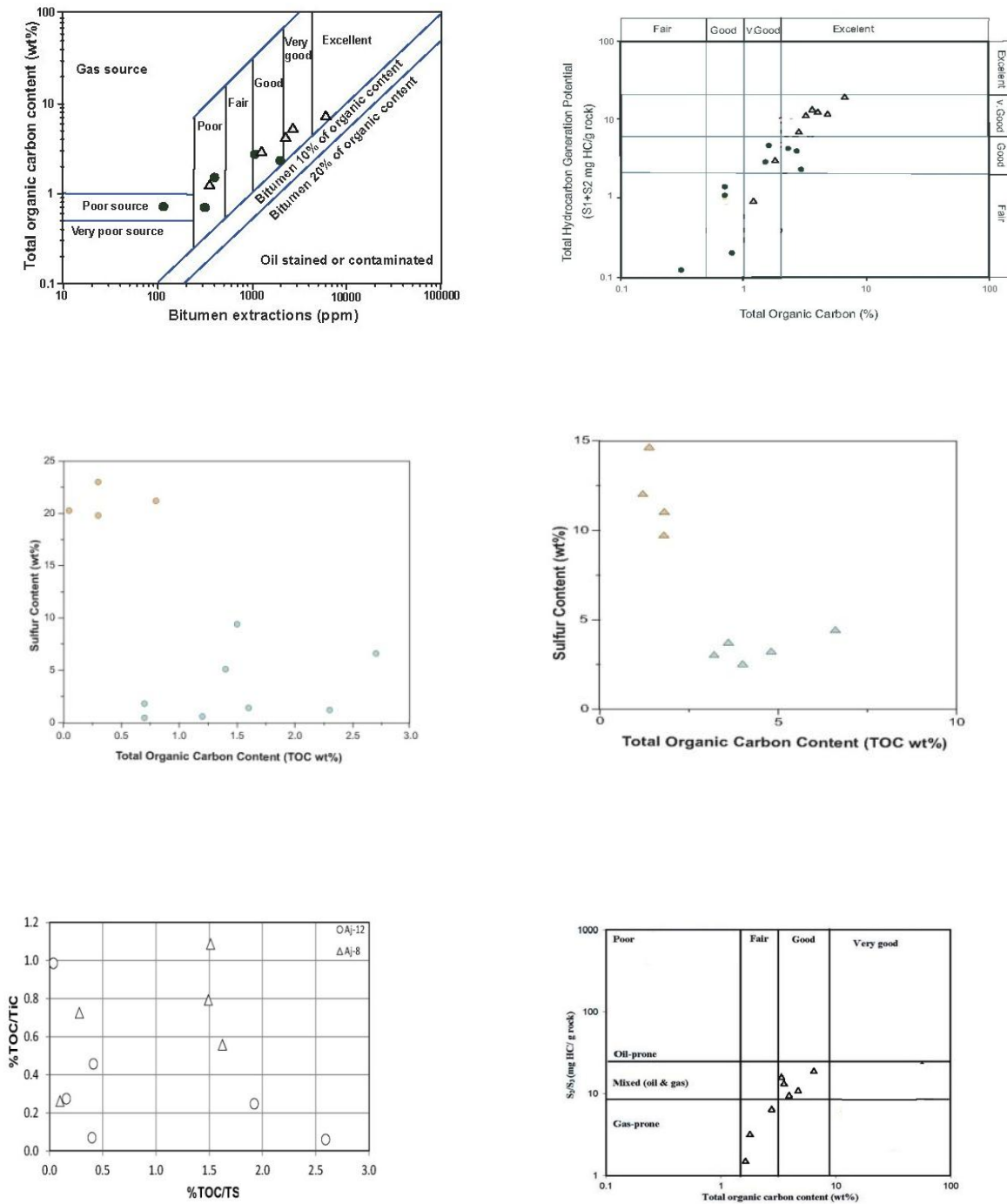
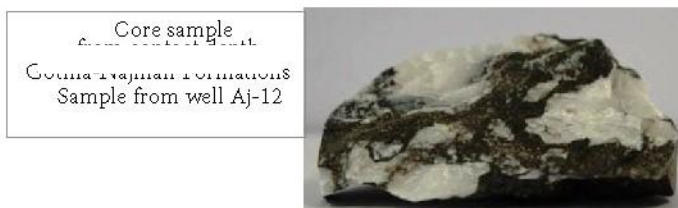


Fig. 3.5. Cross-Plot of (TOC%wt) with different bulk geochemical analysis. Samples studied from Gotnia Formation from the wells (Aj-12 -circles and Aj-8- triangles) versus (a) extractable organic matter (EOM) in ppm. (b) Total hydrocarbon generation potential (S1+S2) Rock-Eval pyrolysis. (c,d) Sulfur (wt %) content elemental analyzed. (f) Rock-Eval pyrolysis (S2/S3, mgHC/ g rock). (e) The ratio of TOC/TS versus the ratio of the TOC/TIC elemental analysis.

4.2 Molecular parameters

Different biomarker parameters were used to study carbonate-anhydrite facies sequence of the Gotnia Formation in the Aj-12 and Aj-8 wells and to compare it with some plots chosen from TIC-elementary analysis and lithological descriptions with the consideration that there is mixing between the carbonate and anhydrite layers in some depths, as shown in Fig. 3.6.

Fig.3.6 photo show mixing between the Carbonate and Anhydrite layers in Gotnia Formation (field work)



The biomarkers used were as follows:

Representative total ion chromatograms of saturated hydrocarbon fractions of n-alkanes from 85 m/z and isoprenoids from Tic for the sample extracts from the Gotnia Formation in wells Aj-12 and Aj-8 in the carbonate and anhydrite layers were studied (Fig.) to show the difference in distribution from these fractions with differences of lithology. The carbonate layers show unimodal distributions for n-alkanes (from 85 m/z) with short-chain n-alkanes which indicate high maturity, while the samples from the anhydrite layers generally show bimodal n-alkane distributions.

Another petacyclic terpane 17 α (H),21 β (H)-29, 30-bisnorhopane, which was identified by Schmid (1984) as C₂₈ pentacyclic terpane (17 α (H),21 β (H)-29, 30-bisnorhopane), was found in all Gotnia samples. The ratio of the **BNH/(BNH+C29 hopane)** versus **Pr/Ph** and **Ts/(Ts+Tm)** ratios is used for the extra source samples from the Gotnia Formation in the two wells studied (Aj-12 and Aj-8) to show the changes in the plots with the facies change. The Figure shows the trend for the plots in all ratios used and also shows the different behaviors of the carbonate and anhydrite layers. The plots also show the reverse direction of the trend in the two wells studied (Aj-12 and Aj-8) which depends on the different locations of the two wells. Well Aj-8 is deeper and located nearer to the basin, while well Aj-12 is located nearer to the margin. **The Ph/Ph ratio** in well Aj-8 ranges from 0.33 to 0.72 and it is relatively high in the carbonate layers, while the range of this ratio in Aj-12 was 0.33 to 0.70 with relatively high values from the anhydrite layers. The **BNH/(BNH+C29 hopane)** ratio in both wells studied (Aj-12 and Aj-8) is comparatively high in the anhydrite layers, ranging from 0.14 to 0.20. **The Ts/(Ts+Tm) ratio** is controlled by variations of facies and depositional environments. According to this, the variability in the calculated values from this ratio is related more to the differences in facies than to differences in maturity. To identify the poor and rich source rocks for the extract studied, two sterane parameters are used (**C29 $\beta\beta$ / ($\beta\beta$ + $\alpha\alpha$)** and **(C21+C22)/all steranes** (Fig.). The plots show the variety of the samples studied between good and poor source rocks. In general, the carbonate layers reveal a trend indicating them to be good source rocks. Dibenzothiophene

(DBT) and phenantrenes (Phen) are present in variable amounts in all extract samples studied from the Gotnia Formation.

The DBT/Phen ratio is high in general with a range of 1.37 to 7.89 in both wells (Aj-12 and Aj-8). Samples studied with one sample from well Aj-12 has a value of 0.82. The samples were collected from a marine environment and under a water column containing H₂S and some portion of this H₂S was integrated in the organic matter, producing **elevated DBT/Phen ratios** in the **high TOC and low TS**.

Pr/Ph. ratio vs. 4/1 DBT: Aromatic sulfur compounds methyl dibenzothiophene (MDBT) 4-MDBT/1-MDBT vs. Pr./Ph. is used to study the behavior of the plots in the carbonate and anhydrite layers. The carbonate samples studied from the well Aj-12 show relatively low values for the 4/1 DBT ratio at around 1.5, while the anhydrite layers yield around 2.5 in terms of this ratio. Furthermore, the plots show the reverse trend when comparing the plots of samples collected from well Aj-8, showing high values for the 4/1 DBT ratio in the carbonate layers, reaching more than 2.5, compared with the anhydrite layers in this well (Fig.).

Pr/Ph. ratio vs. MP-2+MP-3/MP-1+MP-9: Another aromatic sulfur compound is used to study facies in the Gotnia Formation. The methylphenanthrenes (MP-2, MP-3, MP-1, MP-9) vs. Pr./Ph. ratio shows the trend for the sample studied plots, and furthermore shows relatively higher values for the (MP-2+MP-3)/(MP-1+MP-9) ratio in the carbonate compared with the anhydrite layers (Fig.). Moreover, 9- methylphenanthrene which was enriched in organic matter from a marine environment (Budzinski et al., 1995) was found in high concentrations in samples studied with values reaching 3, indicating a marine environment for the samples studied.

C_{23/3} tricyclic/C_{24/4} tetracyclic The terpene distribution patterns (*m/z* 191 mass fragmentograms) show that all samples have a high abundance of tetracyclic terpanes (C_{24/4}) relative to the tricyclic terpanes (C_{23/3}) in the Gotnia Formation which occur with an average of 0.34 for the C₂₃ tricyclic/C₂₄ tetracyclic ratio in both wells (Aj-12 and Aj-8). **The C₂₉/C₃₀ hopanes** ratios are generally high (>1) in oils generated from organic rich carbonates-evaporates, as reported by Connan et al. (1986). **The strong predominance of the regular C₂₇-C₂₉ steranes** is commonly recorded in carbonate source rocks from evaporate sequences (Aquitaine, Iraq, Connan et al., 1983; LaLuna, Colombia, Palacas, 1983, in Connan et al., 1986).

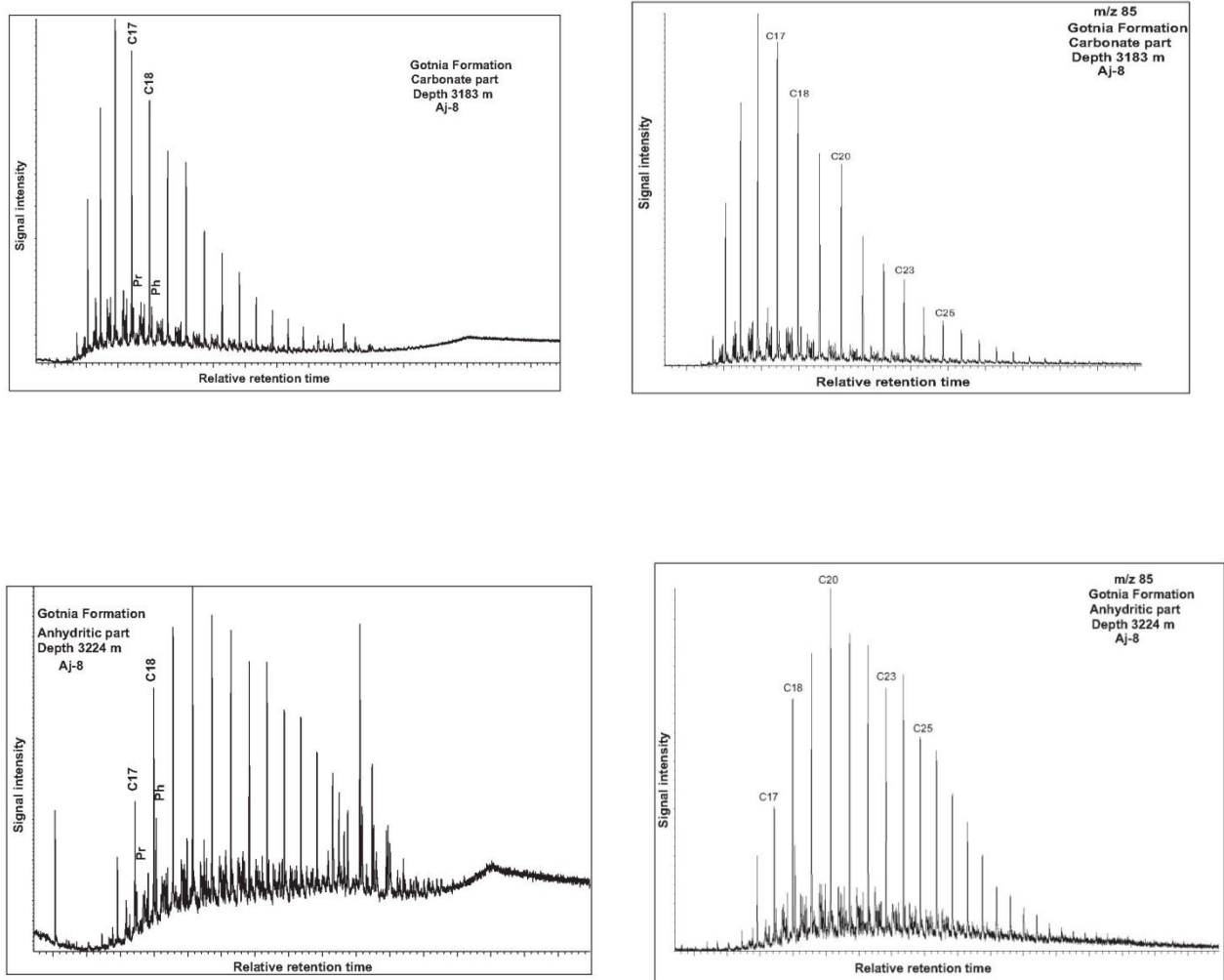
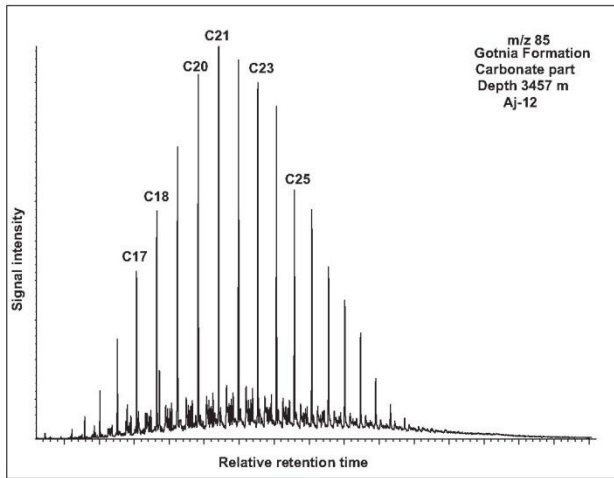


Fig. 3.7. Representative total ion chromatogram of saturated hydrocarbon fractions showing distribution of n-alkanes from 85 m/z and isoprenoids from Tic. The samples extracts from Gotnia Formation in well Aj-8 in Carbonate layer and Anhydrite layer.



small portion
from Anhydrite



Core sample
Gotnia Formation
Carbonate part
well Aj-12
Ajeel oil

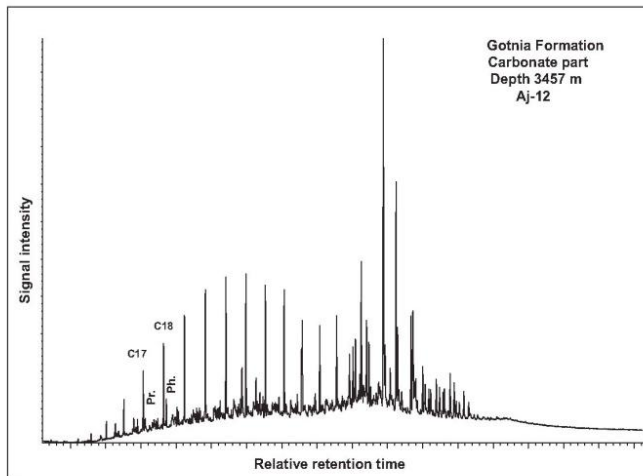
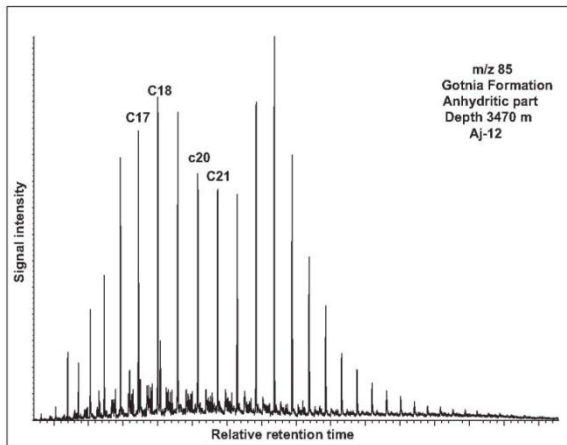


Fig. 3.8. Representative total ion chromatogram of saturated hydrocarbon fractions showing distribution of n-alkanes from 85 m/z and isoprenoids from Tic. The sample extract from Gotnia Formation in well Aj-12 in Carbonate layer with photo show the sample studied.



Core sample
Gotnia Formation
Anhydrite part
well Aj-12

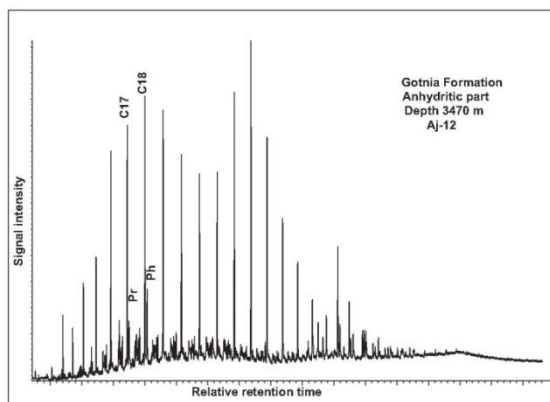


Fig. 3.9. Representative total ion chromatogram of saturated hydrocarbon fractions showing distribution of n-alkanes from 85 m/z and isoprenoids from Tic. The sample extract from Gotnia Formation in well Aj-12 in Anhydrite layer with photo show the sample studied.

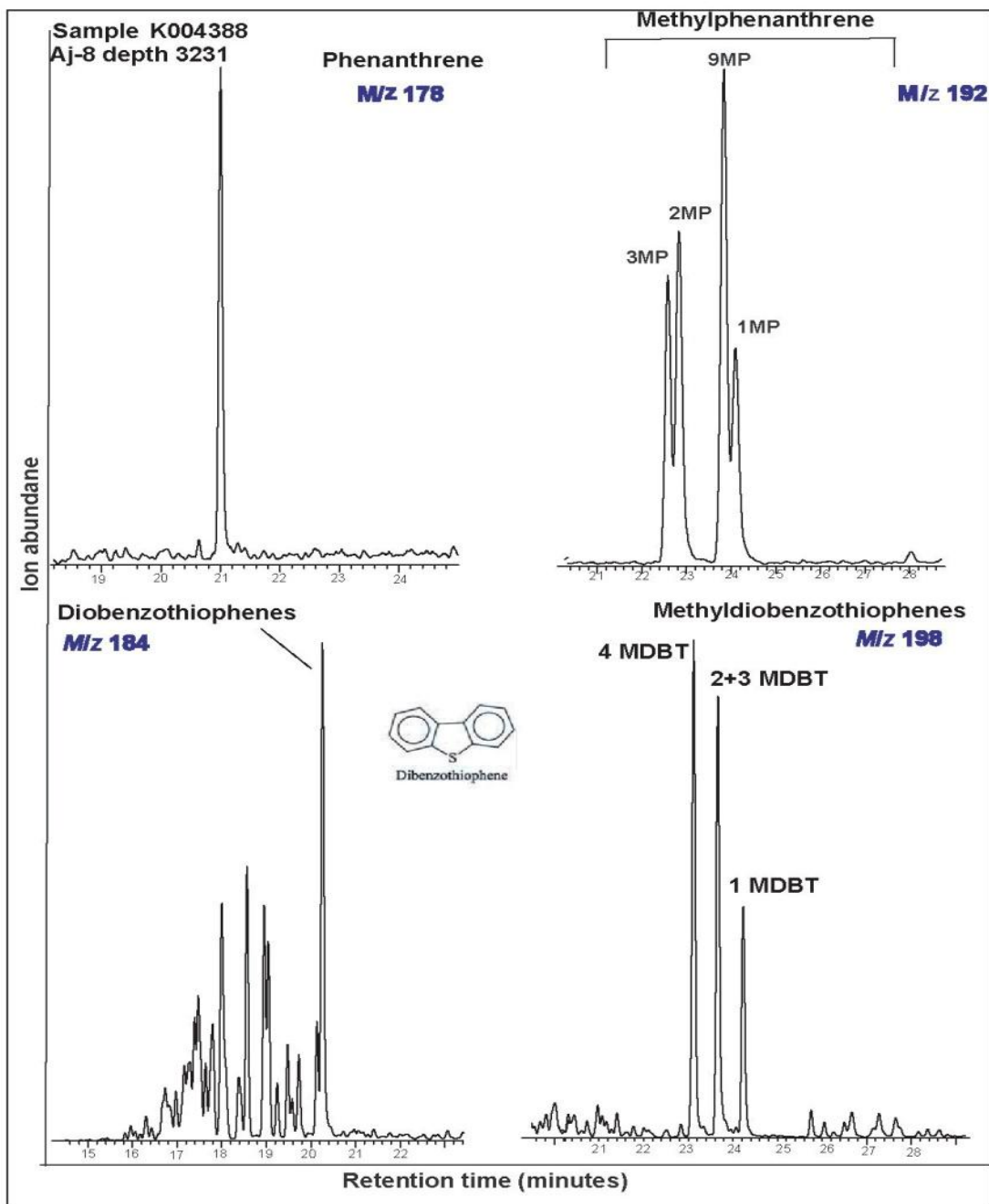


Fig3.10. Representative total ion chromatogram of aromatic fractions showing distribution 178m/z) phenanthrene, (192m/z) methylphenanthrene, (184m/z) dibenzothiophene and (198m/z) methylphenanthrene.

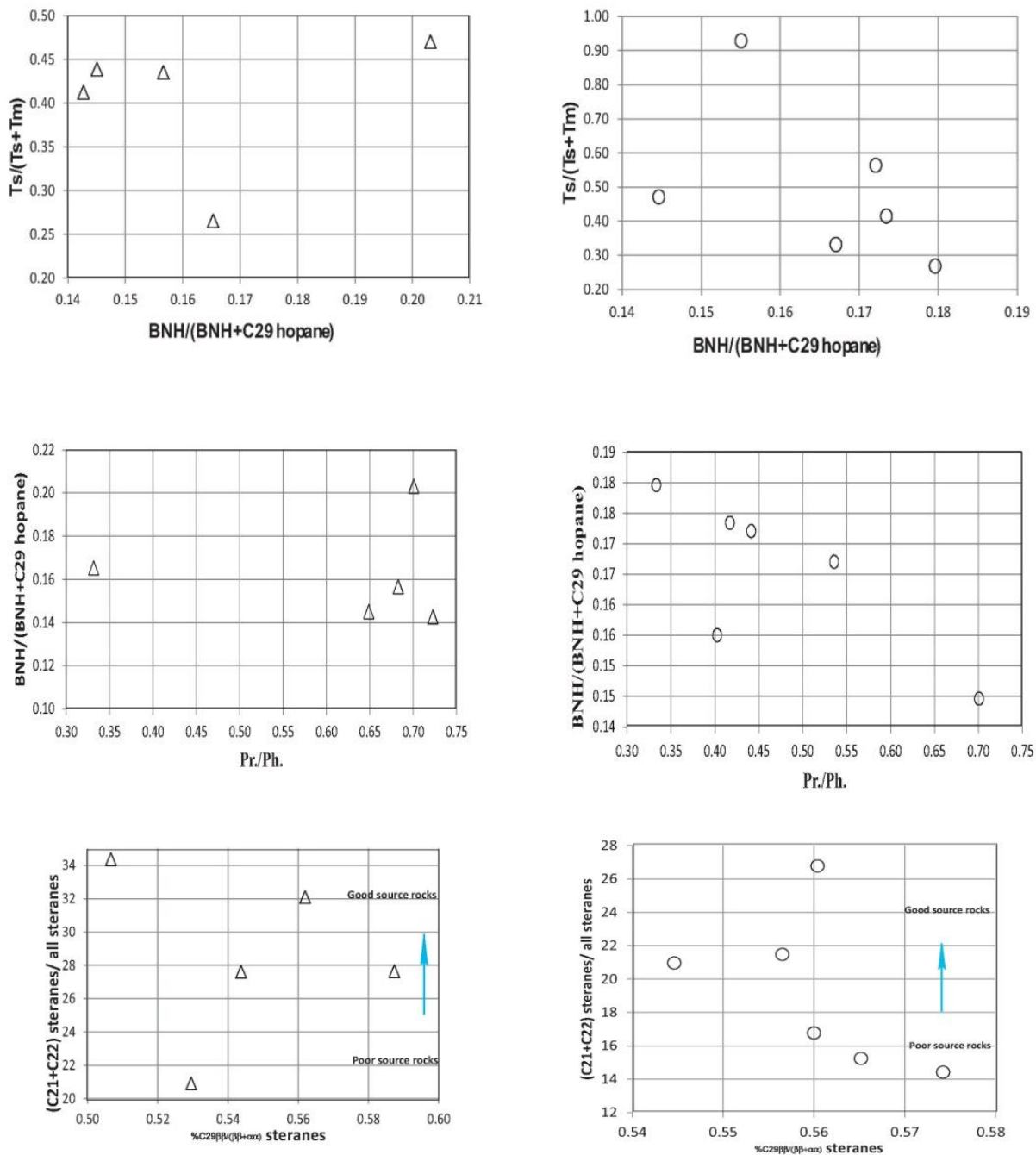


Fig. 3.11. Stable variations of calculated ratios with facies changes and clearly separation between Carbonate and Anhydrite layers. Samples from the wells (Aj-12 -circles and Aj-8- triangles) Gotnia Formation. From (A to d) $BNH/ (BNH+C29 \text{ hopane})$ versus: Ph/Ph and $Ts/(Ts+Tm)$. The plots (E and F) two steranes parameters show the poor and rich source rock in this Formation.

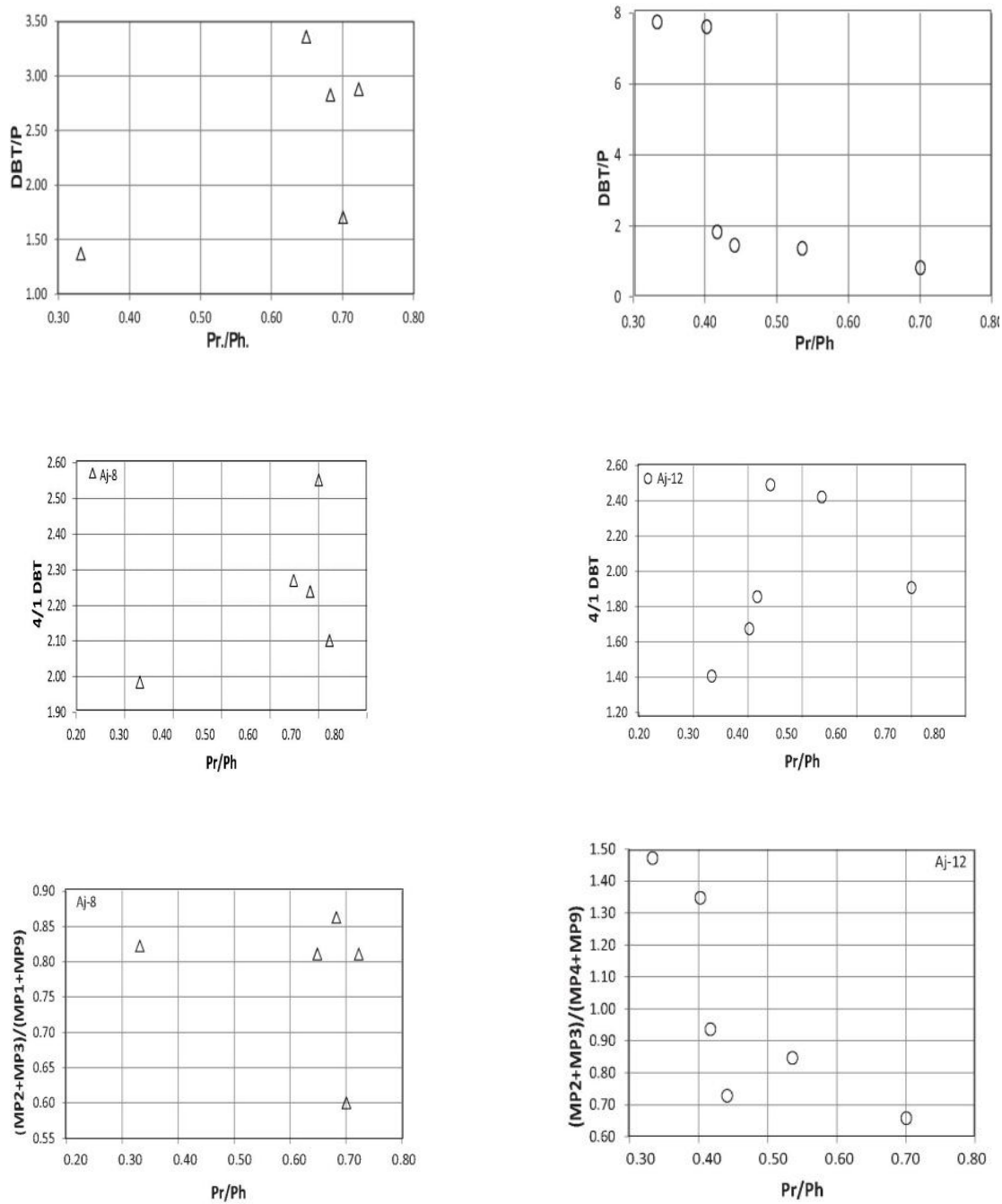


Fig 3.12. Stable variations of calculated ratios with facies changes and clearly separation between Carbonate and Anhydrite layers. Samples from wells (Aj-12 (circles) and Aj-8 (triangles)) Gotnia Formation. Data from gas chromatogram aromatic fraction (178m/z) phenanthrene, (192m/z) methylphenanthrene, (184 m/z) dibenzothiophene and (198m/z) methylphenanthrene. From (A to F) Pr./Ph ratio versus DBT/P, 4/1 DBT, (MP2+MP3)/(MP1+MP9).

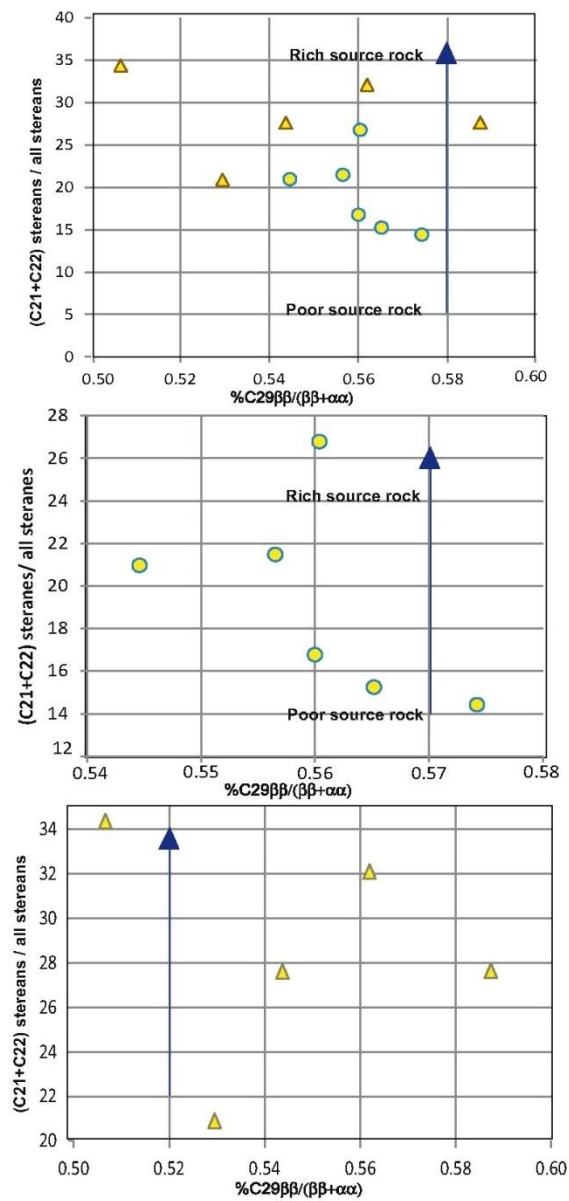


Fig. 3.13. Cross plots between two sterane parameters show the good and poor source rocks in Gotnia Formation.

Regional variation of Sabkha environments

Some bulk geochemistry data and biomarker parameters found in sabkhas in Iraq were compared with those of other sabkhas studied such as **marginal-marine sabkha sediments in Abu Dhabi, marine-fed Salinas (Santa Pola, Spain), sabkhas from Guatemala and the Aquitaine Basin (France)**. The sabkha in Abu Dhabi was studied by Butler et al. (1983) and Kenig et al. (1990). The Abu Dhabi sabkha continued to evaporate and was deposited in Iraq in the time of the deposited Gotnia Formation. The sedimentology and petrology of these sediments was described by Warren and Kendall (1985). Organic facies in the Abu Dhabi sabkha represent mixtures and variations and commonly contain intercalated beds of algal peat and algal mat sediments, and are suggested as source rock in a number of areas by Schreiber et al. (2001), who, in their study of selected samples from the Abu-Dhabi sabkha found these samples to have a TOC range from 2.37% to 5.31% and contain intercalated beds of algal peat and algal mat sediments. The aromatic fractions were dominated by C₂₀ and had a relatively high abundance of phytane and n-C₁₇, but pristane could not be detected. Gotnia samples were studied for both phytane and pristane. In samples from Santa Pola (marine evaporites), which are hypersaline, highly branched C₂₀ isoprenoid was detected. This is also present in lower concentrations in the gypsum and halite domains of the Santa Pola and Abu Dhabi salina, where gammacerane was absent in the original samples but present in the artificial maturation products.

Concluding remarks

Evaporate rocks should be studied in more detail. The analysis of the biomarkers present in evaporate rocks can lead to a better understanding of the origin and fate of the organic matter present there.

Sediments deposited under hypersaline conditions with transition zones between marine carbonates and evaporites are increasingly recognized as a potential source of oil. The environments that lie in waters with elevated salinities are good areas for high biological productivity.

Organic-rich sedimentary layers sandwiched between gypsum beds of Gotnia Formation sabkhas are all good candidates for the presence of amounts of sourced organic matter and could provide oil to reservoirs in the North of Iraq.

Equivalent formations to the Gotnia Formation in the countries surrounding Iraq (Iran, Kuwait, Saudi Arabia, Abu Dhabi and Qatar) should consider focusing on these, especially the carbonate layers between anhydrite layers because they could be good source rocks and could generate hydrocarbons.

Differences in biomarker behavior between the samples studied from the Gotnia Formation in well Aj-12 and well Aj-8 were due to the different well sites

6. Aliphatic and aromatic hydrocarbons

Introduction

In order to get information on the source characteristics of organic matter and to assess the depositional environment of the Formations studied, the biomarker structures used ranged from the simplest acyclic aliphatic components (e.g. *n*-alkanes, isoprenoids) to polycyclic components (e.g. steranes, triterpanes) and from simple aromatic hydrocarbons to those substituted with heteroelements (e.g. dibenzothiophenes). Biomarkers were further employed to assess the degree of thermal maturation based on the alterations of molecular maturity parameters. The figure (3.14) show the distribution of Bio/geomarkers for selected samples from the well Aj-12 from all the Formations studied.

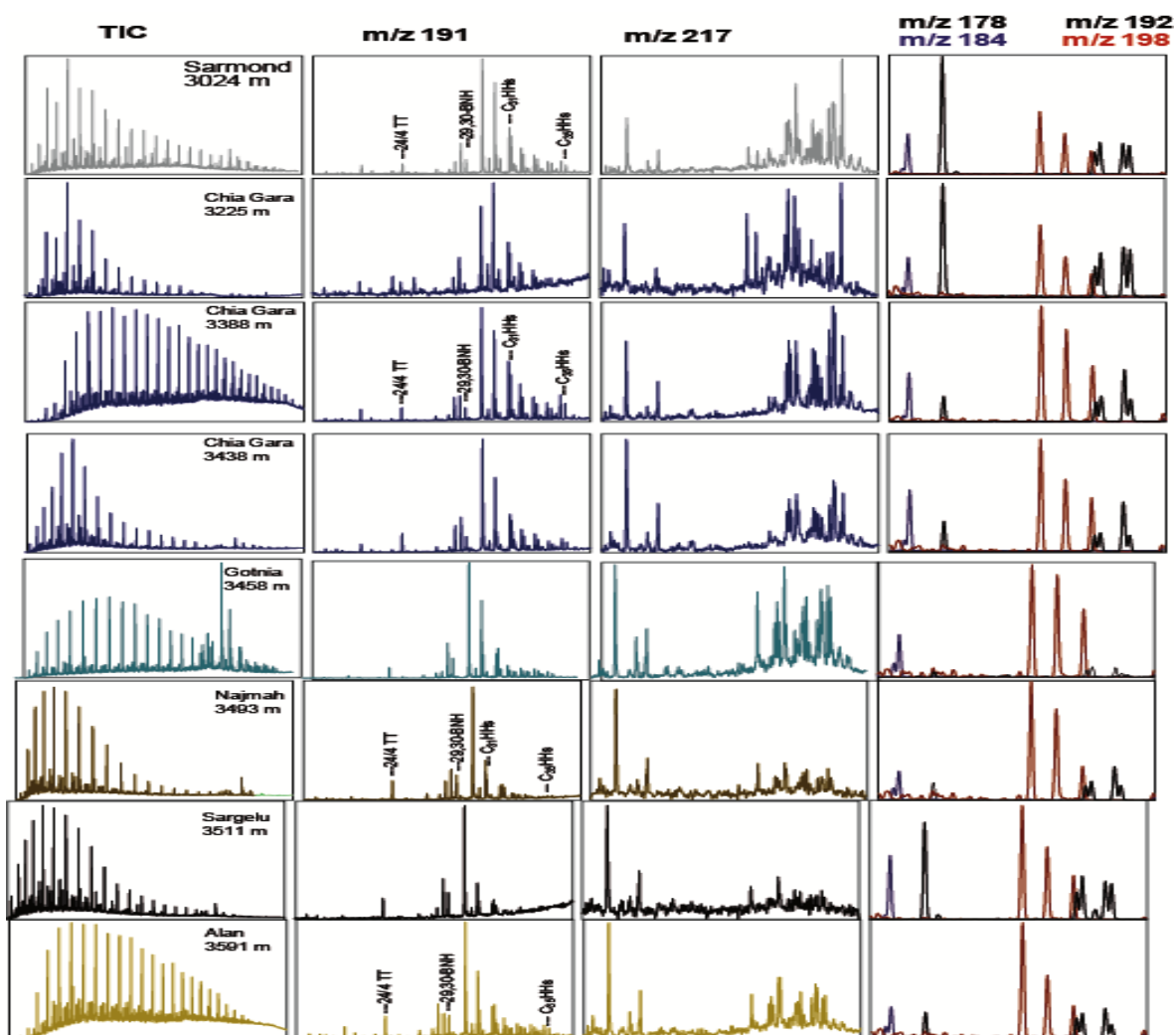


Fig.3.14. The figure show the distribution of Bio/geomarkers for selected samples from all the Formations studied. Samples from well Aj-12.

Aliphatic Hydrocarbons

Typical distributions of saturated hydrocarbons from the six Formations studied are shown in Figs() using the total reconstructed ion trace (TIC).The TIC was used to integrate peak areas for Pristane and Phytane and nearest *n*-alkanes to avoid bias due to mass spectrometric fragmentation patterns.

Acyclic Isoprenoid

- Pristane (Pr) and Phytane (Ph)

The isoprenoids Pristane (Pr) and Phytane (Ph) are acyclic isoprenoid hydrocarbons that contain 19 and 20 carbon atoms, respectively and frequently they are the most important biomarkers in terms of concentration (Powell and McKidy, 1973). The Pristane peak elutes after the C₁₇ *n*-alkane and the phytane peak elutes directly after the C₁₈ *n*-alkane on most gas chromatographic columns (Hughes et al., 1995; Peters et al., 2005)

Relative proportions of the regular isoprenoids pristane (Pr) versus phytane (Ph) have been used to get information about source rocks, depositional environments, maturity organic facies and oil source rock correlation (Peters et al., 2005).The ratio of (Pr/Ph) has been used as an environmental indicator (Michaelis and Albrecht,1979; Tissot and Welte,1984; Peters and Moldowan, 1993; Frimmel et al., 2004). The high values in this ratio (Pr/Ph) > 1 indicate dominance of oxidizing depositional while low values from this ration (<1) are associated with reducing depositional environments (Didyk et al.,1978; Tissot and Welte,1984; Ten Haven et al.,1987; Moldowan et al.,1985; Hughes et al.,1995). Most regular isoprenoids alkanes, which contain 20 or less carbon atoms, including both pristane and phytane during diagenesis originate primarily from the phytol side chain of chlorophyll (Peters et al., 2005,). When the conditions are more oxic phytol is oxidised mainly to phytanic acid, which then decarboxylates to form prist-1-ene, followed by reduction to form pristane In contrast under reducing conditions phytol is converted to dihydrophytol that upon dehydration forms phytane. For this reason the ratio of Pr/Ph can be applied as an indication of the depositional environment

Generally in both wells (Aj-12, Aj-8) studied, the Pr/Ph- ratio was low and less than 1 except for a few samples, most of them from Lower Sarmond Formation. The low values for Pr/Ph ratio for the Formations studied, is reflecting reducing conditions (Peters and Moldowan, 1993). The range of this value are as follows: in well Aj-12 the overall range is 0.33-1.67, with an average of 1.17 for the Lower Sarmond Formation, 0.87 for the Chia Gara Formation, 0.47 for the Gotnia Formation, 0.84 for the Najmah Formation, 0.74 for the Sargelu Formation, and 0.65 for the Alan Formation. In well Aj-8 the range is 0.27-0.92, with averages of 0.91 for the Lower Sarmond Formation, 0.63 for the Chia Gara Formation, 0.62 for the Gotnia Formation, 0.67 for the Naokelekan Formation, 0.67 for the Sargelu Formation and a single sample from Alan Formation with value 0.54. Pr/Ph-values showed relative variations which could be attributed to changes in lithofacies (carbonate, mixed carbonate, anhydrite and shale) as shown in Fig. XX.. A

second parameter which was used in graphical form to infer source rock depositional environments was the ratio of pristane and phytane, versus their nearest *n*-alkanes, i.e. *n*-C₁₇ and *n*-C₁₈, respectively (Lijmbach, 1975; Mathur et al., 1988). These ratios are also used as maturity or biodegradation indicators and indicate organic matter type. In this study, these plots have been applied to samples from the Formations in wells Aj-12 and Aj-8 (Fig xx). Accordingly, Pr/*n*-C₁₇ and Ph/*n*-C₁₈ ratio are less than 1 for all Formations in both wells (Aj-12 and Aj-8) with very low values for Pr/*n*-C₁₇ (0.09 and 0.1) for the Najmah Formation in well Aj-12. The plots indicate a marine source of organic matter, deposited under reducing conditions. This interpretation is supported by the Pr/Ph values and result in chapter 1 derived from Rock-Eval pyrolysis. The low ratio for Pr/*n*-C₁₇ and Ph/*n*-C₁₈ in most samples indicate that the samples are not biodegraded.

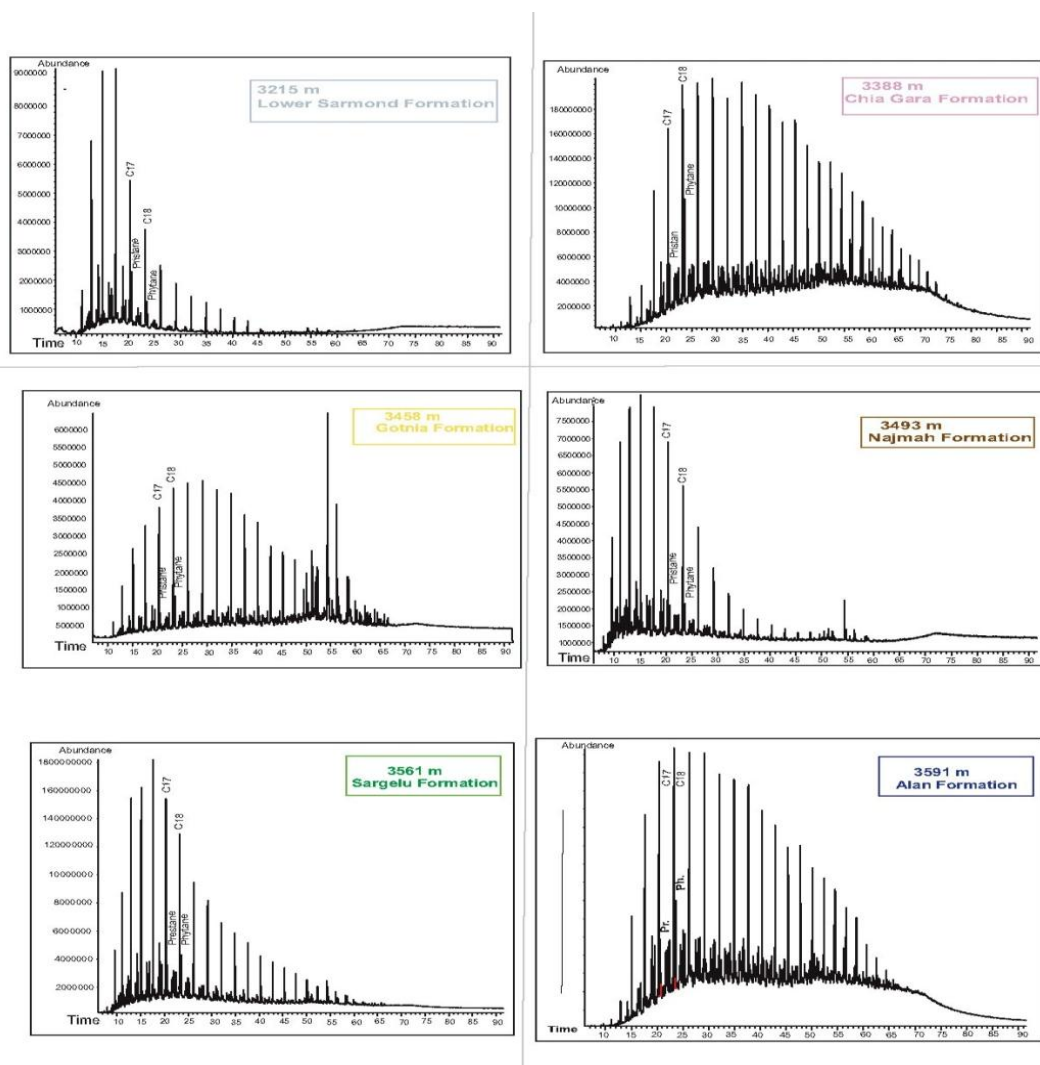


Fig.3.15. Representative saturate fraction gas chromatograms showing distribution of isoprenoids (pristane and phytane) for the Formations studied in well Aj-12.

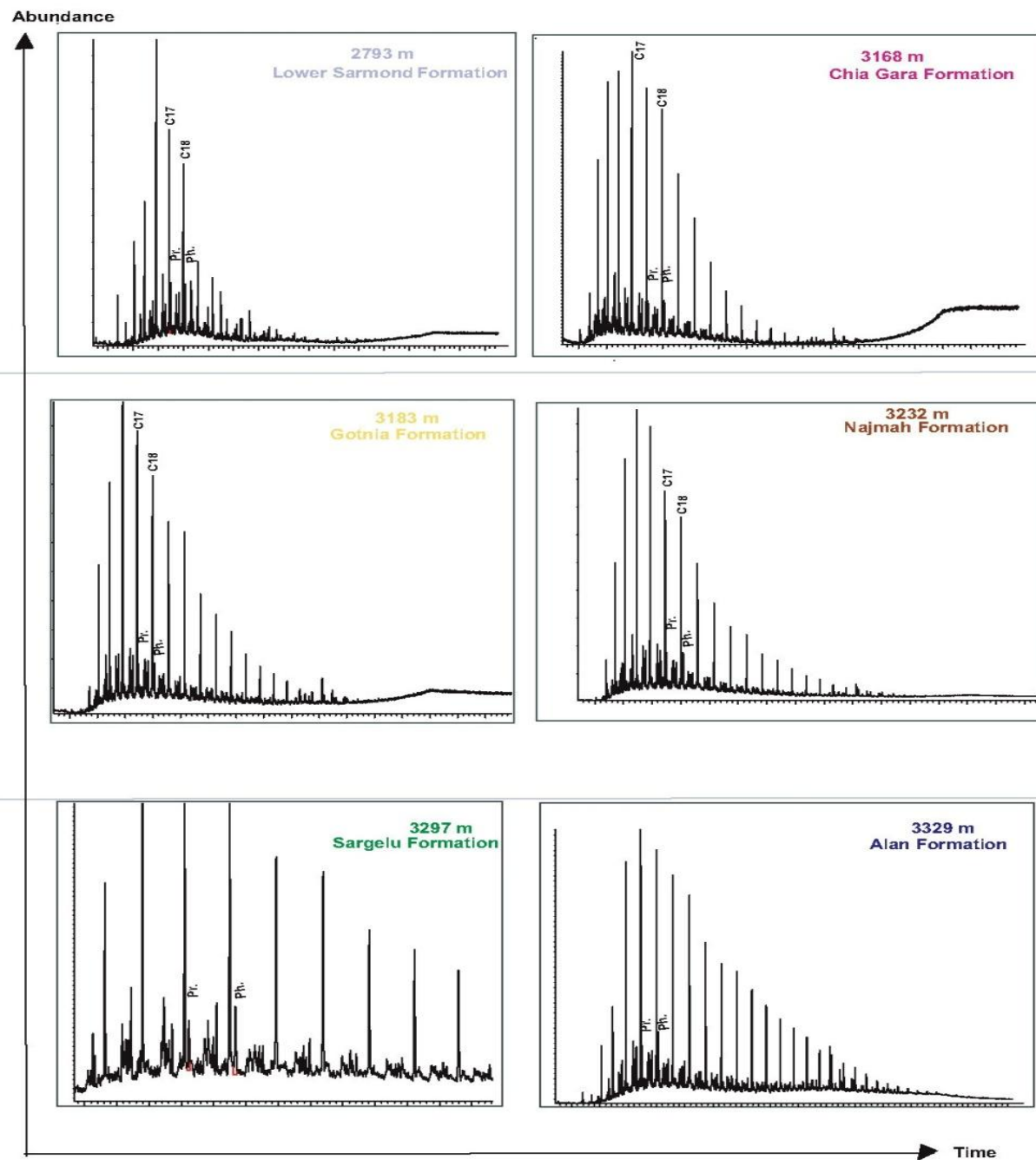


Fig. 3.16. Representative saturate fraction gas chromatograms showing distribution of isoprenoids (pristane and phytane) for the Formations studied in well Aj-8.

- N-Alkanes

The distributions of *n*-alkanes have been used for many years to determine many parameters in source rocks. Carbon preference index (CPI) is a maturity, organic matter type and depositional environment indicator for source rocks and oils (Peters et al., 2005) and its values are affected by type of organic matter as well as the degree of maturity (Tissot and Welt, 1984). This is a ratio formed by a summation of peak heights of 25, 27, 29, 31 and 33 carbon atoms per molecule for odd-carbon number and summation of the even-carbon numbers at 24, 26, 28, 30 carbon atoms per molecule. CPI values that are significantly higher (odd preference) or lower (even preferences) than 1 suggest a sample is thermally immature (Peters and Moldowan, 1993). Concentrations of *n*-alkanes increase at the less mature stage and then decrease with maturation. Bimodal *n*-alkane distributions and those skewed toward the range *n*-C₂₃ to *n*-C₃₁ are usually associated with terrigenous higher-plant source input (Philp, 1994). In contrast, abundant shorter-chain *n*-alkanes, particularly *n*-C₁₅ and *n*-C₁₇ are indicative for algal contributions to source rock (Blumer et al., 1971). Fig. 2.2 shows several selected examples of GC-MS-traces from hydrocarbon fractions from wells Aj-12 and Aj-8. In this application, CPI is calculated according to the equations: first (CPI-1) for long chain in the range of *n*-C₂₅ to *n*-C₃₃, and second (CPI-2) for short chain in the range of *n*-C₁₅ to *n*-C₂₃. A further equation is used to calculate odd-over-even predominance (EOP) according to (Bray & Evans, 1961). The results and the equations are listed in the Appendix). Carbon preference index (CPI) for samples for all Formations in both wells, Aj-12 and Aj-8 had variable values ranging between 0.85 and 1.24. D, with the variability primarily attributed to different lithologies and maturities. Long-chain *n*-alkanes (C₂₅ to C₃₃) showed a predominance of odd-over even-numbered molecules which is expressed by CPI values greater than 1. Predominance of short chain *n*-alkanes with low concentrations of long chain *n*-alkanes as noted in Chia Gara and Naokelekan Formations is indicative of high maturity. Values for *n*-C₁₇/*n*-C₂₇ were calculated to range from 0.28-24 for all Formations in both. High values for *n*-C₁₇/*n*-C₂₇ are typical for source rocks deposited under anoxic marine conditions with contributions from marine algae. Najmah Formation in Aj-12 at a depth range from 3492-3494 m were unsuitable to calculated values of *n*-C₁₇/*n*-C₂₇ due to the absence of long chain (C₂₅-C₃₃) analogues. This may indicate high maturity or intensive impregnation. Similar observations were made for the lower part of the Chia Gara Formation in Aj-8 and the upper part of the Sargelu Formation, where lower concentrations of long-chain *n*-alkanes are typical of high maturities. This conclusion is consistent with the results from Rock-Eval pyrolysis for Tmax analyses and CPI values as listed in the Appendix. The high CPI values in excess of 1, together with high concentrations for long-chain compounds and a predominance of odd/even alkanes as observed in Lower Sarmond, Alan Formations and the upper part of the Chia Gara and lower Sargelu Formations indicates low-to-moderate source rock maturity and some terrestrial biomass influx. Gotnia Formation show in some intervals revealed a predominance of even-chain-length *n*-alkanes in the C₂₀-C₃₀ range, which is known to occur specifically in evaporate basins (Peters et al., 2005).

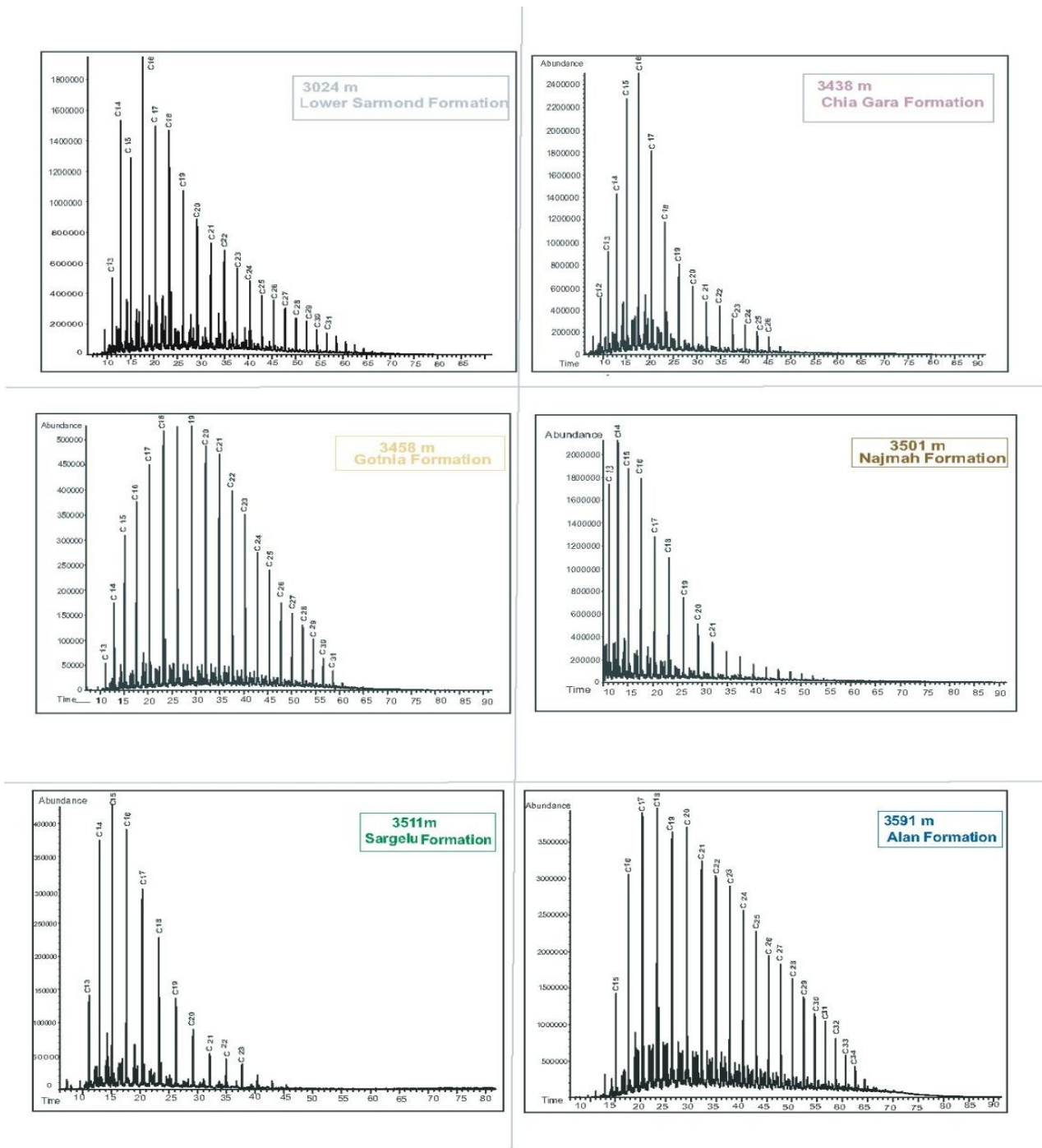


Fig 3.17. Representative saturate fraction gas chromatograms showing distribution of n-alkanes for the Formations studied in well Aj-12..

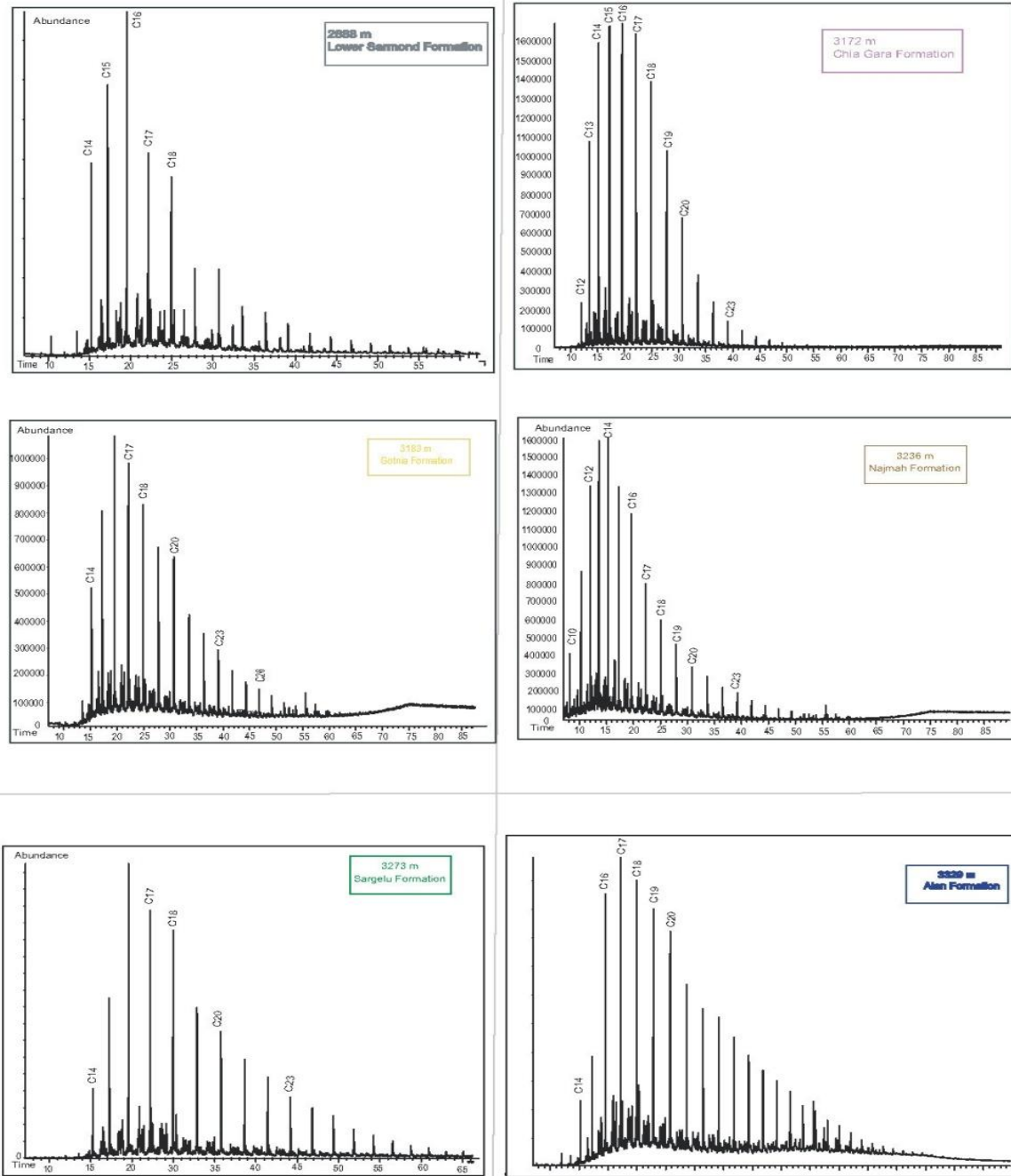


Fig .3.18. Representative saturate fraction gas chromatograms showing distribution of n-alkanes for the Formations studied in well Aj-8.

The relative amounts of terrigenous versus aquatic hydrocarbons in sediments or rock extracts (Peters et al., 2005). In this study, the TAR data indicate in general, that aquatic hydrocarbon is the major one in all studied samples with values less than 1 for all samples studied. Equation X used to calculate (TAR), with result shown in the Appendix.

Alicyclic (Steranes and Terpanes)

The composition of biomarker compounds, especially steroid and triterpenoid derivatives are of special interest because these compound may reflect the depositional environment, origin and diagenetic/maturation history of organic matter in sediments (Seifert and Moldowan, 1984; Peters and Moldowan, 1993). Steranes and pentacyclic triterpane biomarkers were cleaved in the ion source of the mass spectrometer to give the fragment ions $m/z=217/218$ and $m/z=191$, respectively. This fragmentation is independent of the nature of the side chain length X, which for C_{27} - to C_{29} steranes is C_8H_{17} to $C_{10}H_{21}$ and for a pentacyclic triterpane will be C_3H_7 . For full compound identification of sterane and pentacyclic triterpane biomarkers their molecular mass, mass spectra and GC retention time were employed.

Hopanes

Hopanoid are pentacyclic compounds usually in the C_{27} to C_{35} range, which dominate the triterpanes found in sediments and crude oils (Miles, 1994). Hopanoids are widely used for correlation of crude oils and source rocks (Hunt, 1996). A wide suite of hopanes was identified in this study (Table XX) and applied to estimate the maturity and depositional environment of the Formations investigated.

Steranes

The sterols in eukaryotic organisms are precursors of the steranes in source rocks and petroleum (Peters et al., 2005a,b). These compounds are derived from both plants and animals and found in the saturated hydrocarbon fraction. In this study, sterane biomarkers were used to assess different parameters. Tab. XX shows the identification of steranes used in this study.

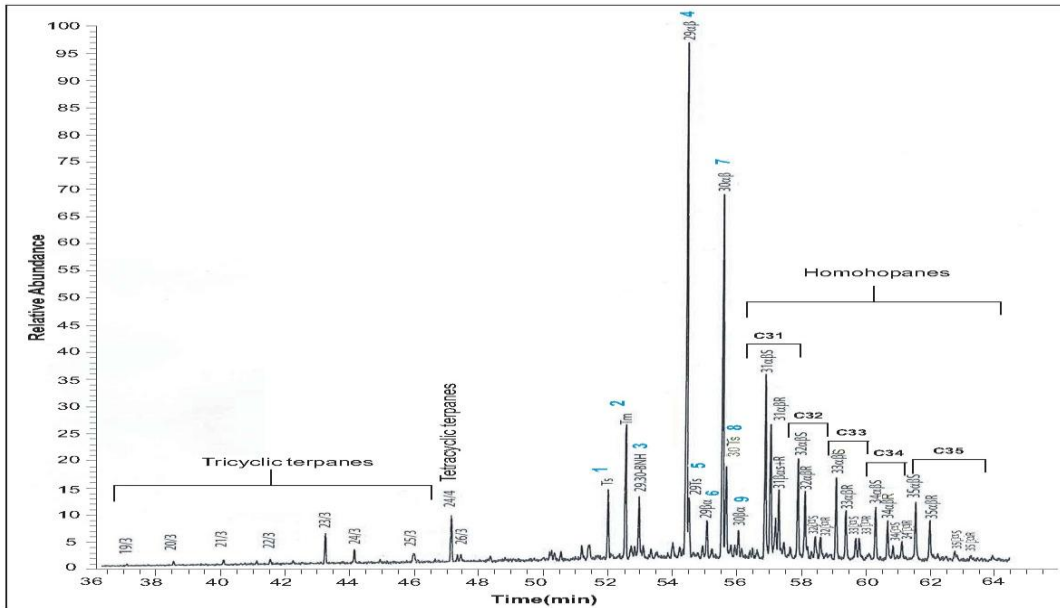


Fig.3.19. Representative saturate fraction gas chromatograms of the distributions of trepanes(191 m/z) with identification peak. The sample from Ajeel oil field.

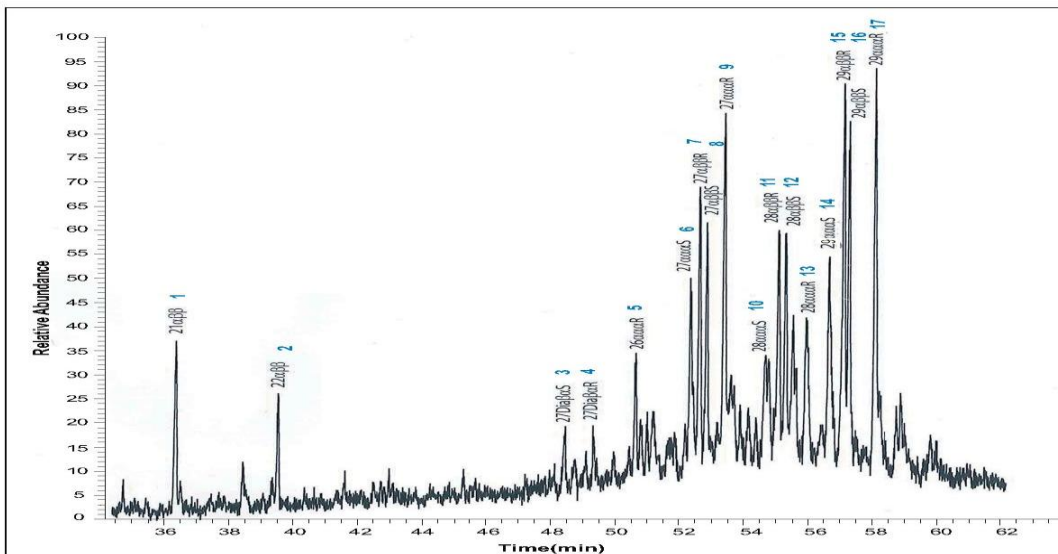


Fig.3.20. Representative saturate fraction gas chromatograms of the distributions of the steranes (217 m/z) with identification peak. The sample from Ajeel oil field.

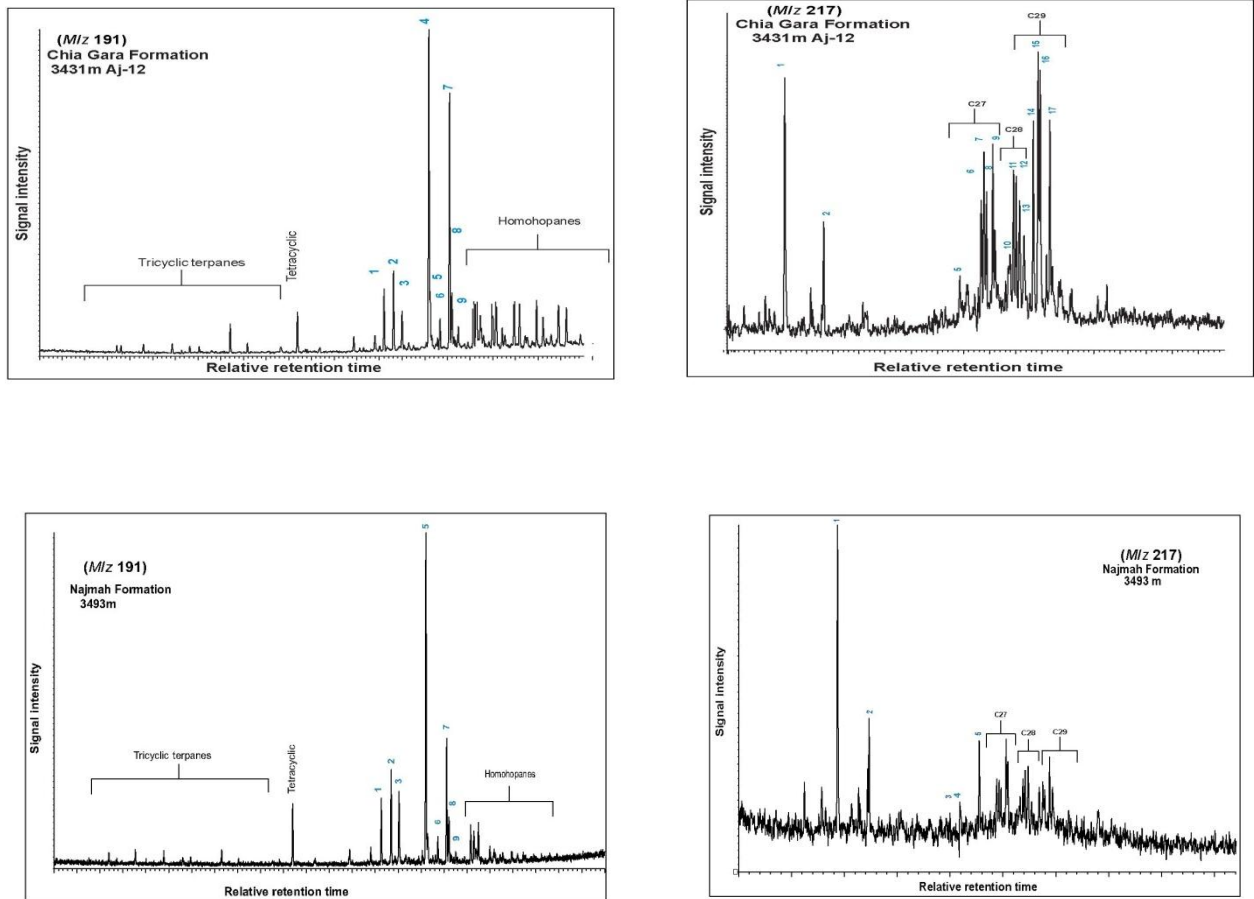


Fig.3.21. The m/z 191(left) and m/z 217 mass fragmentogram (right) of saturated hydrocarbon fractions of two select samples studied. The number related to the identification peaks in the Fig.(3.19)

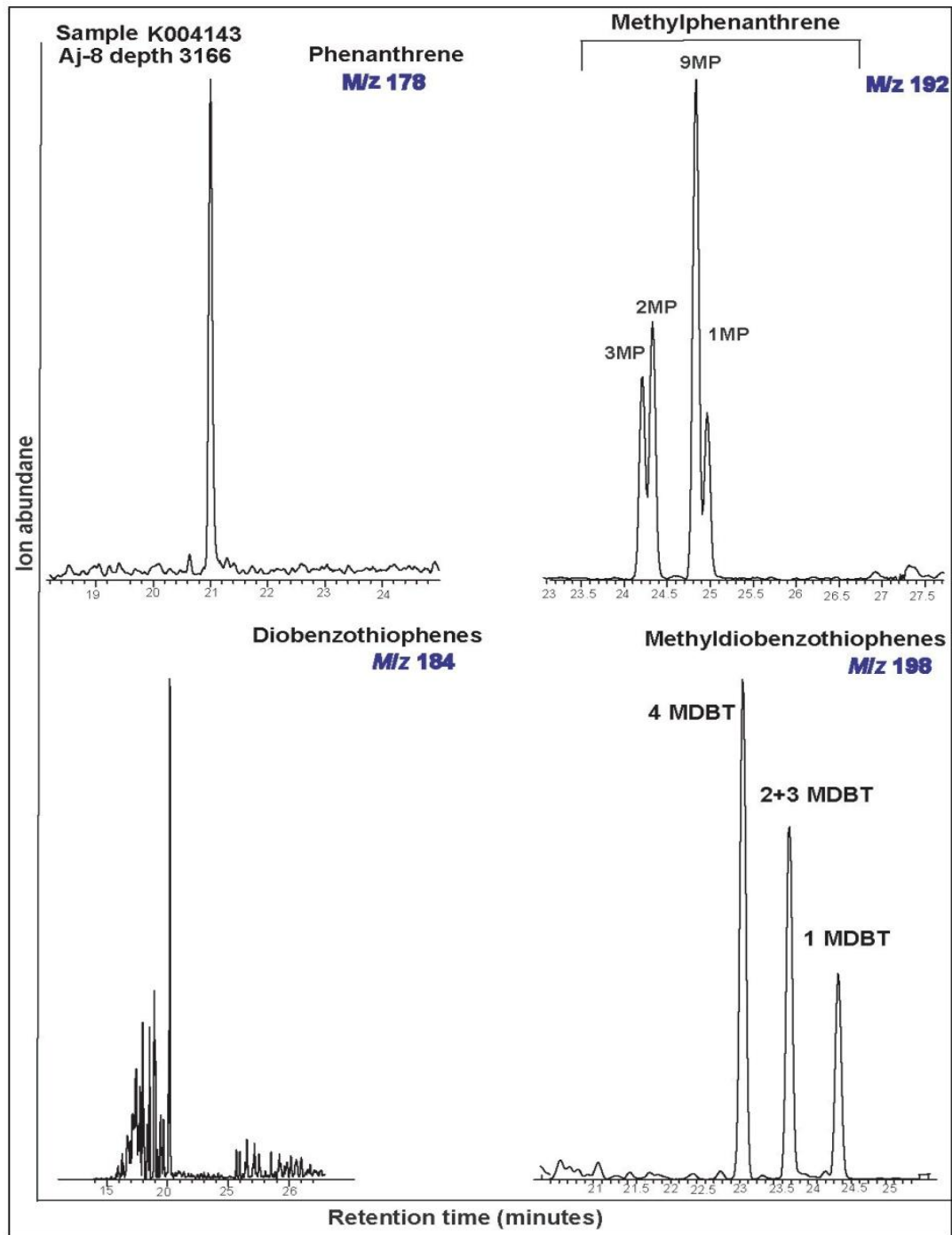


Fig.3.22. Representative aromatic fraction gas chromatograms showing distribution of phenanthrene (178 m/z), methylphenanthrene (192 m/z), diobenzothiophenes (184 m/z) and methyldiobenzothiophenes (198 m/z).

Maturity Parameters

Introduction

The maturity of source rocks and petroleum can be estimated by biomarkers ratio composed of compounds with different thermodynamic stability (Seifert and Moldowan, 1978). Maturity-induced biomarker modification is based on three types of reactions: configurational isomerization at certain carbon atoms, cracking reactions and aromatization. In this study several biomarker thermal maturity parameters are used.

Maturity parameters based on aromatic hydrocarbons

The distribution of aromatic compounds has been increasingly applied to problems of thermal maturation in the organic extracts of rocks, crude oils and coals. Aromatic parameters showed irregular variations, indicating significant influence of the organic facies and because of that their application should be used with caution.

Two groups of polycyclic aromatic and sulphur aromatic geomarker compounds were analyzed in rock extracts of the six Formations studied to evaluate the maturity levels and to interpret them in terms of depositional environment. These groups are: Dibenzothiophene (DBT) (m/z 184) and alkylated analogues methyl dibenzothiophenes (MeDBT) (m/z 198) (Chakhmakhchev et al., 1997; Chakhmakhchev and Suzuki, 1995), as well as Phenanthrene (P) (m/z 178) and alkylated analogues Methylphenanthrenes (MP) (m/z 192) (Huang et al., 2004).

Sulfur-compounds

The aromatic hydrocarbon fractions are dominated by sulfur-aromatic compounds, which are dibenzothiophene (DBT) and methyl dibenzothiophenes. Maturity assessment is mainly based on the methyl dibenzothiophene ratio (MDR), which calculates relative 4-/1-MDBT concentrations (Radke et al., 1986). This is useful for Type II and III kerogen maturity appraisal and it was reported by (Hughes, 1984) that 1-MDBT decreased relative to 2,3 and 4-MDBT with increasing maturity. Vitrinite reflectance calculated from measured values for MDR and then applying the empirical relationship between MDR and maturity for type I and Type II Kerogen by using the Eq (Radke, 1988) is listed in the Appendix. (App). The results are plotted versus the sampling depth in Fig. (8) and show relatively high maturity in the Lower part of the Chia Gara Formation and Najmah Formation and the Upper part of Sargelu Formation and a gradual increase in maturity with depth. The obtained maturity calculated from Vitrinite Reflectance equivalents based on MDR fits well with maturity determined from T_{max} from Rock-Eval pyrolyses (Fig. 8).

Phenanthrenes

Aromatic hydrocarbons that have been employed in the assessment of thermal maturity of source rocks and derived crude oils are phenanthrenes and methylphenanthrenes (Radke et al., 1982; Radke and Welte, 1983; Alexander et al., 1986). The Methylphenanthrene index (MPI-1), which is commonly used to assess the maturity of crude oils and rocks (Radke and Welte, 1983) was calculated according to Radke et al. (1982). The equation X for conversion of MPI-1 data to vitrinite reflectance equivalents ($\% R_c$) which is established strictly for source rocks of type III kerogen results and the resulting R_c -values for all samples is given in the Appendix. R_c -values ranging between 0.3% - 1.5 % appear to indicate that study rocks reveal from moderate to high maturity stage. Based on the distribution of methylphenanthrenes and similar to the MPI-1 ratio, another maturity index was introduced by Alexander et al. (1986) and later modified by Cassani et al. (1988). This is the methyl phenanthrene index PP-1 calculated according to equation X, with results shown in the Appendix. Maturity trends can be recognized on the basis of the PP-1 values but a facies and lithology influence is recognized when comparing PP-1 with sulfur content (Fig XX). The ratio of the maturity-related MP/P-proportion showed a trend of irregular variations with depth (Fig XX and Appendix), again attributed to a substantial facies control on aromatic distributions commonly expected to be maturity-dependent. The aromatic hydrocarbon fractions of source rocks samples are dominated by sulphur-aromatic compounds and minor abundances of phenanthrenes and methylphenanthrenes as expressed by the DBT/P and MDBT /MP ratios presented in the Appendix.

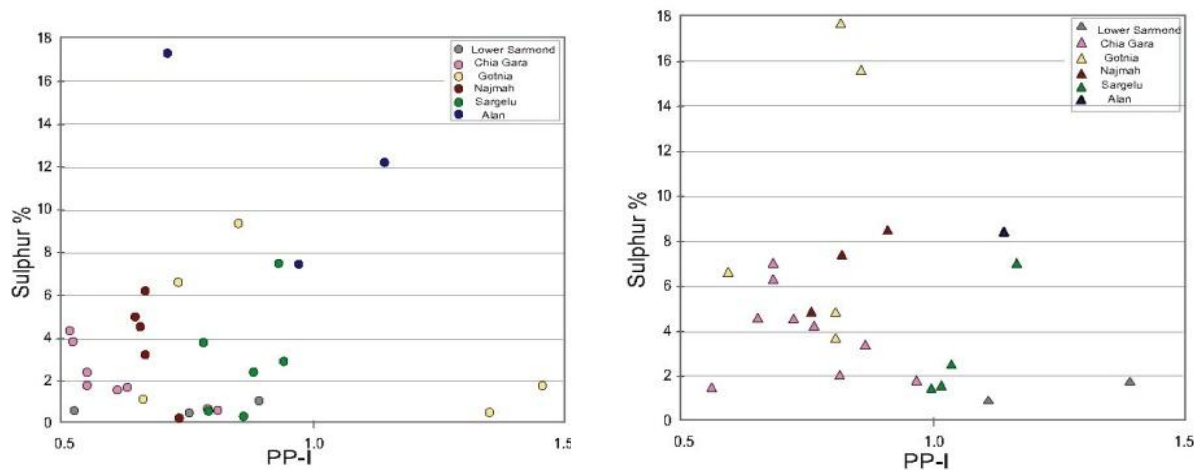


Fig.3.23. Relation between methylphenanthrene index PP-1 and sulfur abundance (weight %) for rocks samples inform well Aj-12(circles) and well Aj-8 (triangle). A negative covariance between these two proxies.

Maturity parameters based on saturated hydrocarbons

The saturated hydrocarbon fractions were generally representative of a larger proportion of the total soluble organic matter but consisted mainly of *n*-alkanes and acyclic hydrocarbons. The cyclic terpane fraction occurred in subordinate proportions but yielded a wide suite of components diagnostic of facies, maturity and biodegradation changes. Aliphatic biomarker distributions are applied more commonly than aromatic hydrocarbon distributions than the latter (Peters et al., 2005) in petroleum source and origin analysis.

Steranes parameters

The ratio of steranes have been used as the most frequently biomarker thermal maturity parameters (Seifert and Moldowan, 1980, 1986; Peters and Moldowan, 1993).

C_{29} $\alpha\alpha$ 20S / (20S + 20R)

As the maturity increases the isomerization at C-20 in the C_{29} -5 α (H),14 α (H),17 α (H)-20R-sterane takes place and compared to the 20R isomer, the 20S isomer increases in relative concentration. This causes 20S/(20S+20R) to rise from 0 to about 0.5 until an equilibrium condition is reached (C_{29} 20S/(20S+20R) ~ 0.55) (Peters et al., 2005). In this study a range of (0.20-0.57) values for C_{29} 20S/(20S+20R) was calculated in samples from wells (Aj-12 and Aj-8) with averages of 0.319 in the Lower Sarmond Formation, 0.46 for the Chia Gara Formation, 0.47 for the Gotnia Formation, 0.51 for Najmah Formation, 0.49 for the Sargelu Formation, and 0.46 for the Alan Formation. This indicates that the bitumen in the Lower Sarmond is thermally immature, whereas the other formations have reached the oil window.

C_{29} $\beta\beta$ / ($\beta\beta$ + $\alpha\alpha$)

As the source rocks maturity increases, the 5 α (H),14 β (H),17 β (H) steranes increase relative to the 5 α (H),14 α (H),17 α (H)-steranes with the former being more stable than the steranes with biological stereo-configuration. Isomerization at C-14 and C-17 in the C_{29} 20S and 20R regular steranes causes an increase in the ratio of C_{29} $\beta\beta$ / ($\beta\beta$ + $\alpha\alpha$) isomers from near to zero to values close to 0.7 until an equilibrium is reached (C_{29} $\beta\beta$ / ($\beta\beta$ + $\alpha\alpha$) ~ 0.75). In this study the range of this ratio was between 0.31 and 0.62 in wells Aj-12 and Aj-8 with averages for the Lower Sarmond Formation of 0.40, Chia Gara Formation of 0.51, Gotnia Formation of 0.55, Naokelikan Formation of 0.55, Sargelu Formation of 0.53, and Alan Formation of 0.57. The systematic and continuous increase in steranes with $\beta\beta$ -isomerization documents the progressive enhancement of thermal maturity reflected by this biomarker maturity parameter, which seems less affected by other processes related to biological input, preservation conditions or biodegradation, when compared to e.g. the C_{29} 20S/(20S+20R) ratio.

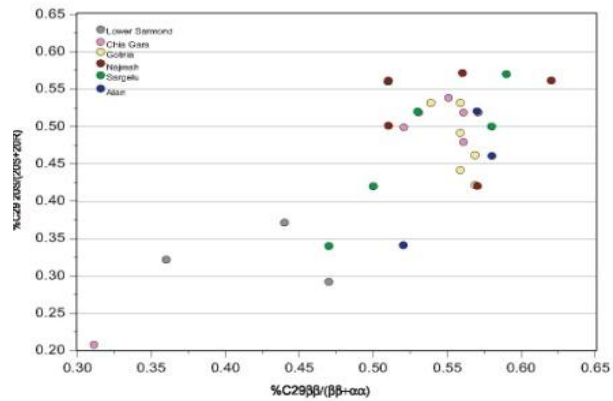
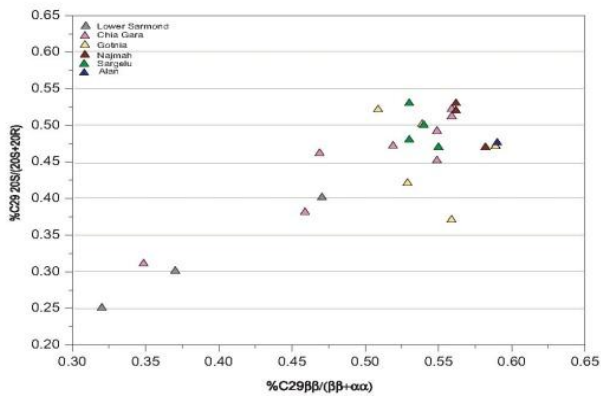


Fig. 3.24. shows relationship between two maturity parameters based on steranes. Samples inform well Aj-12 (circles) and Aj-8 (triangles).

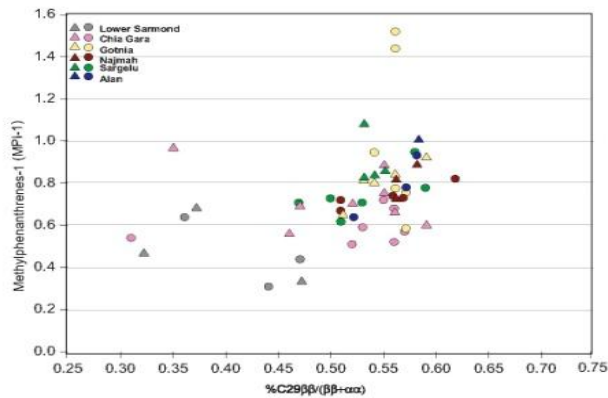
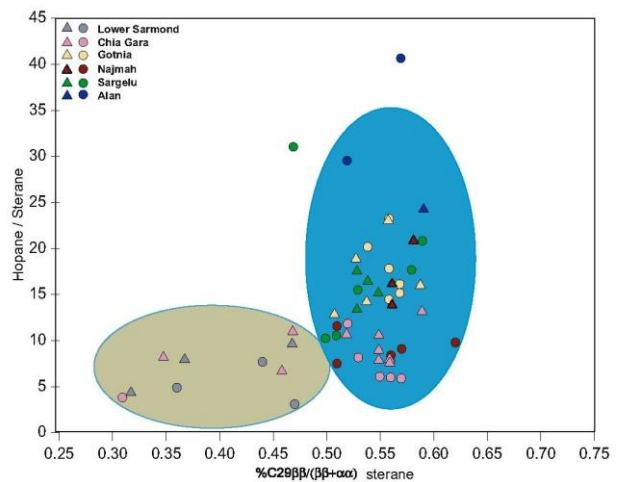


Fig. 3.25. show relationship between two maturity parameters (MPI-1) from aromatic fraction and C29 $\beta\beta$ / ($\beta\beta + \alpha\alpha$) steranes from saturated hydrocarbon (217 m/z) inform well Aj-12 (circles) and well Aj-8 (triangles).

Fig.3.26. Crossplot of C29 $\beta\beta$ / ($\beta\beta + \alpha\alpha$) sterane and hopane/sterane ratio showing maturity for the source rocks studied and high hopane/sterane ratio.



Hopane parameters

The tetracyclic terpanes (C₂₄)/penta hopane ratio, the ratio of tetracyclic terpanes to hopanes, increased in more mature source rocks and oils, indicating greater stability of the tetracyclic terpanes (biomarker volumes 2). Tetracyclic terpanes are also more resistant to biodegradation than hopanes and for this reason they are used in correlations of altered crude oils (Seifert and Moldowan, 1979). For the studied samples, the average in both wells studied (Aj-12 and Aj-8) for this ratio was as follows: For the Lower Sarmond Formation the average was 2.14, for the Chia Gara Formation it was 3.82, for the Gotnia Formation 3.46, for the Najmah Formation 5.25, for the Sargelu Formation 3.62, and 3.10 for the Alan Formation. Given the above, the Najmah Formation can be considered to have the most mature rocks of the formations studied in terms of this ratio. **The moretane/hopane ratio**, the 22S/(22S+22R) ratio for the C₃₁-C₃₅-17 α (H), 21 β (H) homohopanes are frequently used as a maturity indicator in the immature up to the onset of the oil window range. The ratio of moretanes (17 β 21 α hopanes) to (17 α 21 β hopanes) decreases with increasing maturity from 0.8 in immature bitumens to < 0.15 in mature source rocks (Seifert and Moldowan, 1980). In this study the ratio of moretane to their corresponding hopanes (C₂₉ and C₃₀) was calculated and the range for C₂₉ moretane/C₂₉ hopanes was 0.04-0.3 and for C₃₀ moretane/C₃₀ hopanes it was 0.04-0.28, indicating advanced maturity for all the samples. The higher values are generally from the Lower Sarmond Formation, indicating that the samples from this formation are less mature than the others. The cross-plot of Ts relative to Ts+Tm hopane ratios with a decrease in C₂₉ Moretane Index and an increase in maturity direction (Waples and Machihara, 1991), Fig (). **The Ts/(Ts+Tm) ratio** is a frequently applied hopane parameter and it is thought to be both maturity and source dependent (Peters and Moldowan, 1993). This ratio increases with growing maturity for source rocks and oils. The Ts/Ts+Tm ratio must be interpreted with caution, however, because Ts and Tm commonly co-elute with tricyclic or tetracyclic terpanes on the m/z 191 mass chromatograms, resulting in spurious values (Peters et al., 2005). For this study most samples generally have values of Ts/(Ts+Tm) of below 1 with a range of 0.07-0.93. Averages for the formations studied were as follows: 0.35 for the Lower Sarmond Formation, 0.45 for Chia Gara, 0.45 for Gotnia, 0.36 for Najmah, 0.55 for Sargelu, and 0.58 for the Alan Formation. The high averages values for the Sargelu and Alan Formation and the low value of Ts/(Ts+Tm) for the Najmah Formation may be influenced by source lithology (Seifert and Moldowan, 1978; Moldowan et al., 1986). Furthermore, this ratio appears to be sensitive to clay-catalyzed reactions, resulting in oils from carbonate source rocks having unusually low values for this ratio compared to samples of equal maturity but derived from shale (Peters et al., 2005). These result are unreliable as maturity parameters from pyrolysis indicate that the Alan Formation is immature with low Tmax average of (439 c) for the same samples (Ts/(Ts+Tm) calculated for them. The high PI 0.39 argues for impregnation of anhydrites with migrated oil so the high value for (Ts/(Ts+Tm) may be due to lithology for this formation. For the Najmah Formation, the maturity parameter from pyrolysis indicates that the basal unit from this formation (with the lowest value for (Ts/(Ts+Tm)) is impregnated by migrated oils from the high Tmax value with an average of 447 C and PI 0.2 for the same samples run for biomarkers.

Lower values occur for carbonate intervals from this formation in comparison to shale intervals. lithology for these intervals is obtained by calculating different parameters from elemental analysis (TIC/TS, TOC/TIC, TOC/TS ratios), and the results show that the basinal unit from this formation has carbonates (85-90%), so the result from biomarkers fits with that of the elemental analysis. The plots for TIC/TS, TOC/TIC, TOC/TS ratios with the plots for the Ts/(Ts+Tm) ratio show how this ratio changes with the change in lithology, shown in the Appendix. As mentioned above, the Ts/(Ts+Tm) ratio is controlled by variations of facies and depositional environments (Bakr and Wilkes, 2002). According to this, the variability in the formations is related more to differences in facies than to differences in maturity. **C₂₉TS/ C₂₉ hopane** ranges between 0.02-0.24 for samples studied with averages for the Lower Sarmond Formation of 0.14, 0.10 for Chia Gara, 0.06 for Gotnia, 0.04 for Naokelekan, 0.08 for Sargelu, and 0.06 for the Alan Formation. **C₃₀TS/C₃₀ hopane** ranges between 0.14 and 0.44 for the samples studied, with averages for the Lower Sarmond Formation of 0.14, 0.23 for Chia Gara, 0.36 for Gotnia, 0.44 for Naokelekan, 0.42 for Sargelu, and 0.39 for the Alan Formation. The highest value in these samples indicates that the samples from the Naokelekan Formation are the most mature.

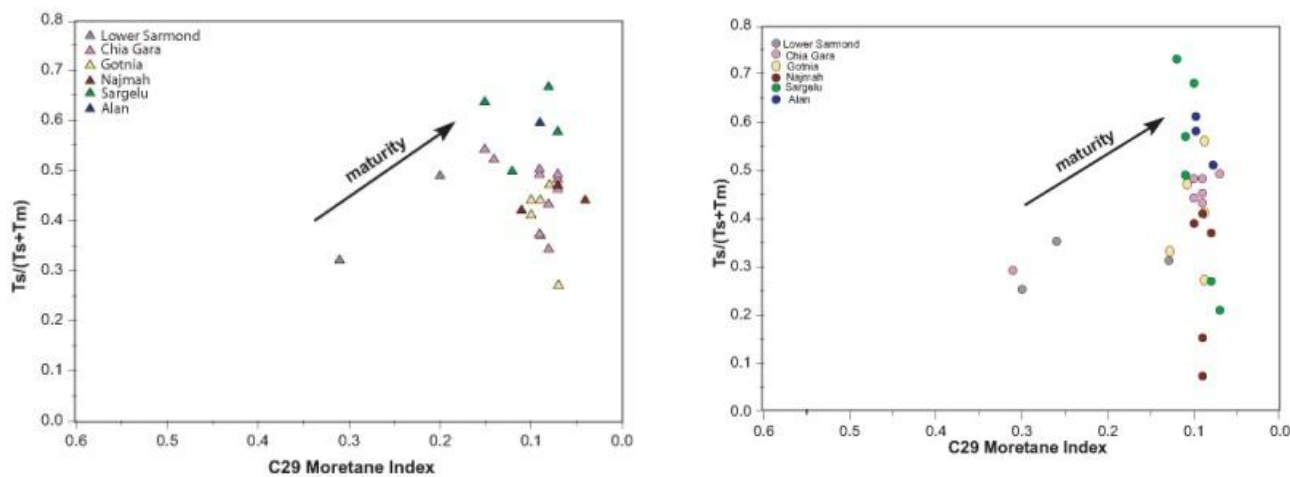


Fig.3.27 Cross-Plot of terpane maturity parameters (after Johnson et al., 2003) indicating high maturity of maturation of rock samples. Samples from well Aj-12 (circles) and well Aj-(triangles) from Ajeel oil field.

8. Type of source rocks

The C_{27} dia/(dia + reg) steranes ratio was calculated and plotted versus the Pr/(Pr+Ph) ratio. The plots show carbonate source rock for the samples studied (Fig). **Abundant C_{24} tetracyclic terpane** in petroleum and source rocks appears to indicate carbonate and evaporite source rock setting (Connan et al., 1986). **The ratios of tricyclic terpane C_{22}/C_{21} versus tricyclic terpane C_{24}/C_{23}** were calculated for the samples studied and plotted on the basis of equivalence with data points after Peters et al. (2005), and suggest a carbonate source rock. The average of the C_{22}/C_{21} ratio for the formations studied is 0.25 for the Lower Sarmond Formation, 0.43 for Chia Gara, 0.43 for Gotnia, 0.38 for Najmah, 0.42 for Sargelu, and 0.36 for the Alan Formation. The C_{22}/C_{21} ratio in the studied samples has the following averages: 0.63 for the Lower Sarmond Formation, 0.75 for Chia Gara, 1.11 for Gotnia, 0.75 for Najmah, 1.37 for Sargelu and 0.65 for the Alan Formation (Fig). **The ratios of Tricyclic Terpane C_{26}/C_{25} versus Hopane $C_{31}R/C_{30}$ ratios** were used to identify the kind of source rocks and were plotted on the basis of equivalence with data points after Peters et al. (2005). The average values for the studied formations in both studied wells (Aj-12 and Aj-8) are as follows: 0.59 for the Lower Sarmond Formation, 0.78 for Chia Gara, 1 for Gotnia, 0.62 for Najmah, 0.75 for Sargelu and 0.84 for the Alan Formation (Fig). **C_{29}/C_{30} hopanes ratios:** In oil generated from organic rich carbonates and evaporates, the (C_{29}/C_{30}) hopanes ratios are generally high (>1) (Connan et al., 1986). In this study the range of this ratio is 0.76-3.45, with averages for the formations studied in both wells as follows: 0.97 for the Lower Sarmond Formation, 1.41 for Chia Gara, 1.62 for Gotnia, 2.61 for Najmah, 2.12 for Sargelu, and 2.14 for the Alan Formation. These values with a predominance of C_{29} hopane are typical of carbonate source rocks and evaporates and thus consistent with the lithofacies analyzed. **The Diasterane/Sterane ratio:** This ratio is commonly used to distinguish carbonate from clay-rich source rocks (Mello et al., 1988) which correspond predominantly to C_{29} norhopane. The relative contents of diasteranes in samples studied are very low and the diasterane/regular sterane ratio ranges from 0.02 to 0.16. This ratio has generally been used as a maturation index. Previous studies showed that carbonate derived oils contain a relatively low amount of diasteranes due to the absence of clay minerals to catalyze the sterane rearrangement (Peters and Moldowan, 1993). The amount of diasteranes could decrease in highly reducing non-carbonate environments with increasing salinity (Philp et al., 1991) which is the case of samples studied from anhydritic formations.

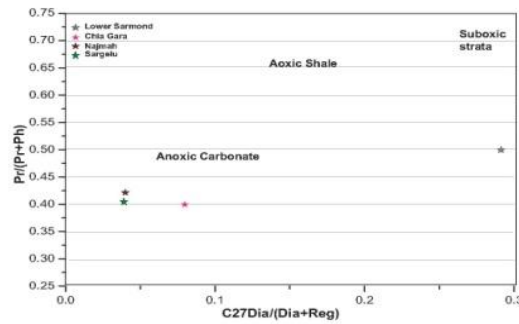


Fig.3.28. Relationship between $Pr/(Pr + Ph)$ and $C_{27} dia / (dia+ reg)$ suggesting a carbonate source rock for formations studied in both wells (Aj-12 and Aj-8), modified after (Peters et al., 2005).

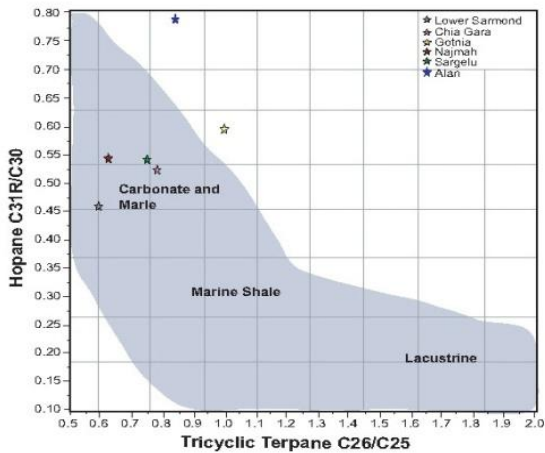
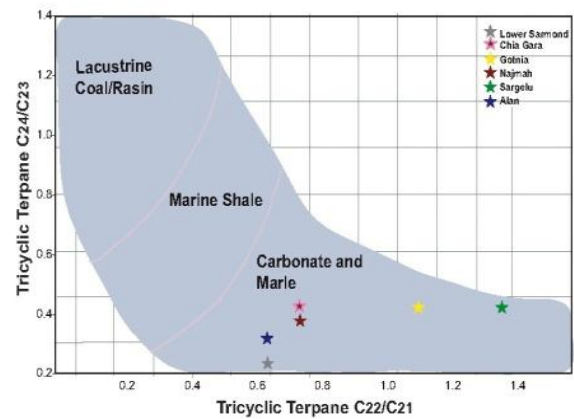


Fig.3.30. Cross-Plot of tricyclic terpene ratios (C_{26}/C_{25} versus hopane $C_{31}R/C_{30}$ ratio) suggesting a Carbonate source rocks for formations studied in both wells (Aj-12 and Aj-8), based on equivalence data from (Peters et al., 2005). The plots show the average values in both wells studied.

Fig. 3.29. Cross-Plot of tricyclic terpene ratios (C_{22}/C_{21} versus C_{24}/C_{23}) suggesting a Carbonate source rocks for formations studied in both wells (Aj-12 and Aj-8), based on equivalence data from (Peters et al., 2005). The plots show the average values in both wells studied.



Environment and deposit conditions

The Pr/Ph ratio is commonly used as redox indicator. Pr/Ph ratios < 1 indicate anoxic conditions whereas values > 1 indicate suboxic to oxic environments (Didyk et al., 1978). The Pr/Ph ratios for samples studied varied from 0.27 to 1.67, most high values came from the Lower Sarmond Formation.

The DBT/Ph versus Pristane/Phytane diagram shows the relationship between the Pr./Ph. and the dibenzothiophenes/phenanthrene. Fig. shows the origin of the studied samples, generally plotting between marine carbonate and marine marl sulfate-rich, with a few samples plotting marine carbonate organic poor from the Lower Sarmond Formation and the upper part from the Chia Gara and Sargelu Formations. **The $C_{31}R/C_{30}$ hopane ratio** has been used to distinguish between marine and lacustrine environments. The ratio is generally higher than 0.25 for marine environments (which is the case of the samples studied) but often lower for lacustrine settings (Peters et al., 2005). $C_{31}R/C_{30}$ hopane ratios of the studied formations extracts have an average range from 0.4 to 0.92, the high average values coming from evaporitic formations. The cross plot of this parameter against (Pr/Ph) ratios (Fig.) clearly supports sediment deposition in marine environments.

The cross plots of the Pr/n- C_{17} and Ph/n- C_{18} are also used in graphical form to infer source rock depositional environments (Lijmbach, 1975; Mathur et al., 1988). In this study, this plot has also been applied to the studied samples and confirms the depositional environment and the type of organic matter for the studied samples which plot in the field of marine Algal Type II/III Kerogen, with a few samples plotting in transition environments with mixed organic matter; these different samples again come from well Aj-12, while all studied samples from Aj-8 are plotted in marine environments which show different environmental condition between these two wells (Fig). Generally, similar conclusions concerning the depositional environment of these formations for the whole of Iraq have recently been reported by Aqrawi and Badics (2015). **Pr/n- C_{17}** : Limbach (1975) and Mathur et al. (1988) noted that oils from source rocks deposited under open-water conditions have Pr/n- C_{17} lower than 0.5, while those from inland peat swamps have ratios greater than 1. **Pr/Ph ratios**: This ratio varies from 0.27 to 1.67, indicating that marine organic matter is prevalent during the time of deposition, as shown in the appendix. However, some of terrestrial materials were also involved. **The CPI varies** from 0.75 to 1.24 and exhibits both a relatively high level of thermal maturation and the input of primary marine organic matter during deposition. **The sulfur content of bulk samples** can also be used to discriminate marine from freshwater environments. Kerogen with high sulfur content is indicative of carbonate rocks deposited in a marine environment, while the low sulfur content is typical of a freshwater lacustrine environment (Berner and Raiswell, 1983; Moldowan et al, 1985; Mohialdeen et al., 2013). The sediments of samples studied which were collected from carbonate/evaporate cycles have relatively high sulfur with highest values from anhydritic formations. Fig. () shows plots of sulfur content vs. TOC (wt%) for samples studied which plot along a line with a positive intercept on the sulfur axis and generally show marine environment with few sample plots in

lacustrine environments. Again samples plots show more lacustrine environments for samples studied from well Aj-12 compared with samples studied from well Aj-8, which again improve a little differently in environmental deposition conditions. Additionally the lithological descriptions and TIC-determinations are in perfect agreement with biomarkers parameters. The high sulfur value plot for the sample from the Najmah Formation in well Aj-12 (Fig) is at a similar depth to that found in the Gotnia Formation and there are 5 more samples from Gotnia and Alan Formations with very high sulfur values (18-22 wt%) not included in (Fig) for more illustrated reason.

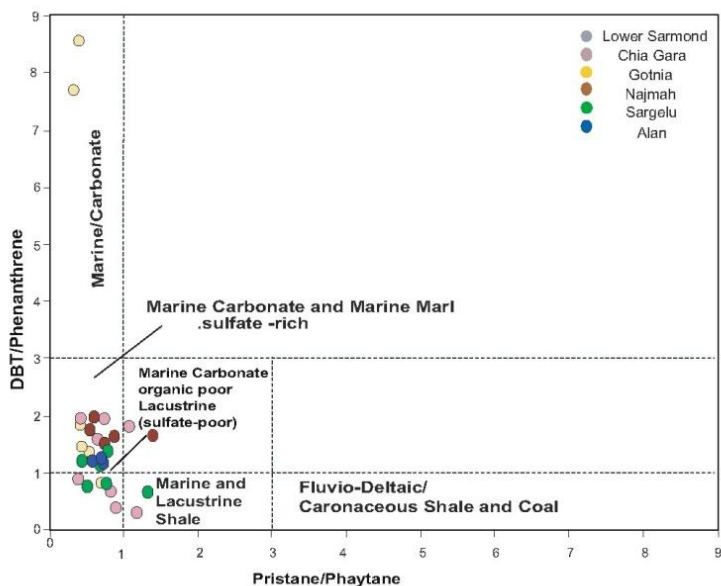
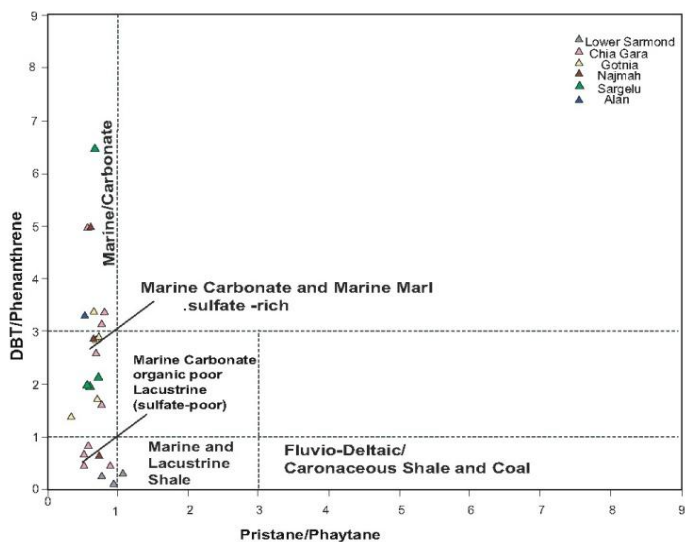


Fig.3.31 Cross-Plot of dibenzothiophene/phenanthrene-(DBT/P) vs.Pr./Ph. The (upper) samples from well Aj-12(circles) and the (lower) samples from well Aj-8(triangles) most plots show marine Carbonate sulfate rich. After (Hughes et al., 1995).



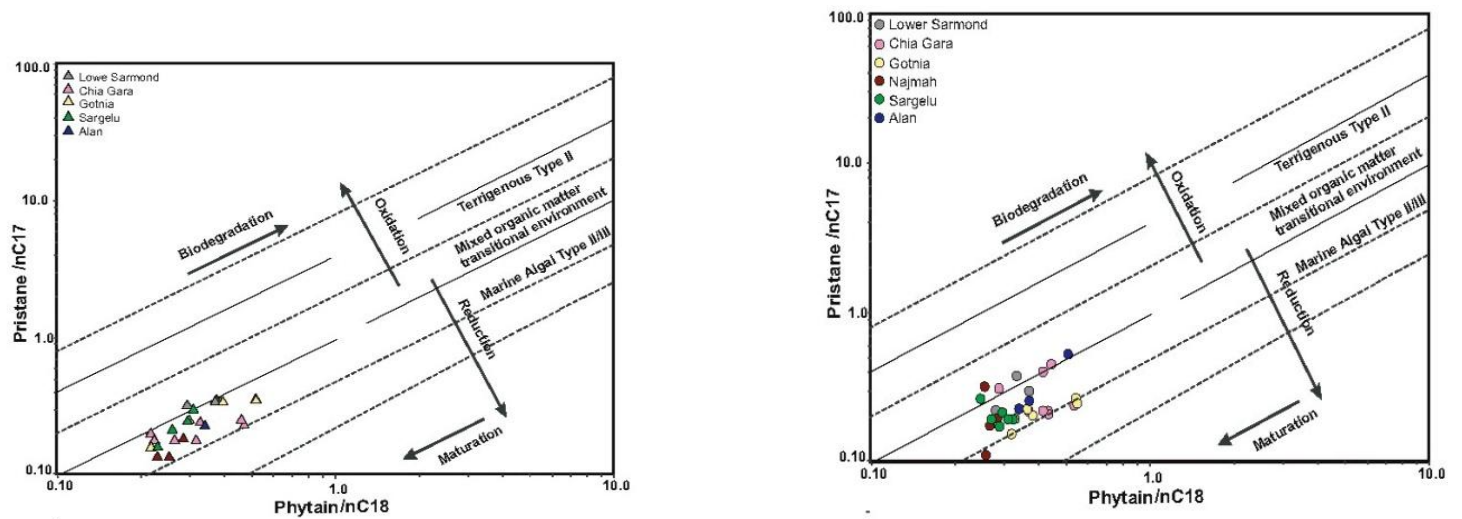


Fig. 3.32 Relationship between Pr/n-C₁₇ and Ph/n-C₁₈ for rocks samples suggest reduction deposited condition and marine algal organic matter. The left plots (circles) inform well Aj-8. The right plots (triangles) inform well Aj-12. The measurement carried out by (85 m/z) and Tic.

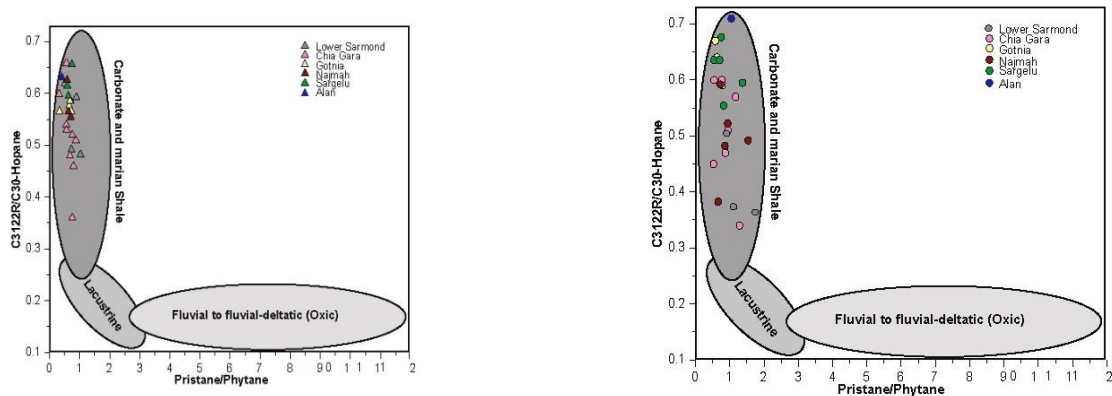


Fig. 3.33 Hopane and isoprenoid Pr./Ph. ratios of extracts sediments. The left inform well Aj-8 (triangles) and the right inform well Aj-12(circles) modified after (Peters et al., 2005).

10. Origin of Organic Matter and quality of source rocks

It has been assumed originally that predominance of **C27 steranes** in oil and extract rock would signify an algal or marine input, while **C29 steranes** signified the presence of higher plant or terrestrial input. This simple interpretation published in early literature has now been revoked and it has been clearly established that the presence of C₂₉ steranes does not necessarily mean an input of higher plant material because C₂₉ sterols as biological precursors to C₂₉ steranes can also have an algal source (Philip et al., 1995). In the study bitumen samples revealed C27 steranes to range from (26-44%) with average 33% in Aj-12 and from (23-44%) with average 37% in Aj-8, while the C₂₉ steranes ranged from (27-47%) with an average 39% in Aj-12 and a range from (29-50%) with an average of 38% in Aj-8. **Ternary diagram of regular steranes (C₂₇-C₂₉)** the relative distribution of C27, C28 and C29 steranes is represented in the form of a regular steranes ternary diagram in Fig(). The original classification of this diagram related C27 steranes to strong algal influence and C29 steranes to strong higher plant influence (Huang and Meinschein, 1979). The samples extracts are composed of C27-C29 regular steranes which is an indicator of the mixed marine/terrestrial origin (e.g. planktonic-bacterial land plant) as indicated by regular sterane ratio ternary diagram (Huang and Meinschein, 1979). **C₂₇/C₂₉ regular steranes versus pristane/phytane**, these plots used to study the origin of the organic matter and the deposit conditions. The result from these ratio is support the result from the other ratios and show anoxic deposit condition for the samples studied in the wells studied (Aj-12 and Aj-8). The extract from the samples studied in the well Aj-8 show relatively higher values from C₂₇/C₂₉ ratios comparing with the samples from well Aj-12 which indicate more from red algae for the organic matter in this well (Aj-8) and open marine deposit environment and more from green algae with estuarine environment deposit in the well Aj-12 (). **The diasterane index which is diasterane/sterane ratio** is used to distinguish carbonate from clay-rich source rocks (Mello et al., 1988) and it can indicate further, whether sediments were deposited in environments with high algal productivity (Peters and Moldowan, 1993). Samples studied are very low and diasterane/regular sterane ratio range from 0.02 to 0.16. **The present of C27 diasteranes** indicates that the Formation deposited in an environment with high algal productivity. **The low Pr/Ph ratios (<1) and carbon preference index (CPI < or equal to 1)**, indicating free algal/bacterial organic detritus in the kerogen (Hanson et al., 2000, Collister et al., 2004).

For study quality of the source rocks two steranes parameters are used to show the quality of the source rocks for the samples studied which are (C₂₁+C₂₂) steranes/all steranes ratio versus **C₂₉ ββ / (ββ + αα)** ratio. The plots in general show good source rocks for the samples studied and high quality source for samples from Najmah, lower part from Chia Gara and Sargule Formations and poor source for the samples from the Lower Sarmond and upper part from Chia Gara Formation. The ratio of the (C₂₁+C₂₂) steranes range from (6 to 44), most highest values from the Najmah and the lower part from Chia Gara Formation, while the lowest values from the Lower Sarmond and lower part of Chia Gara Formation.

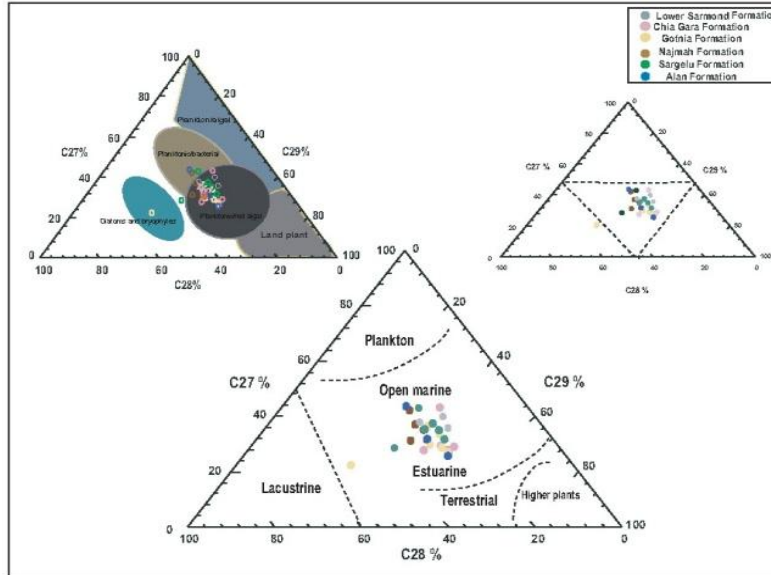
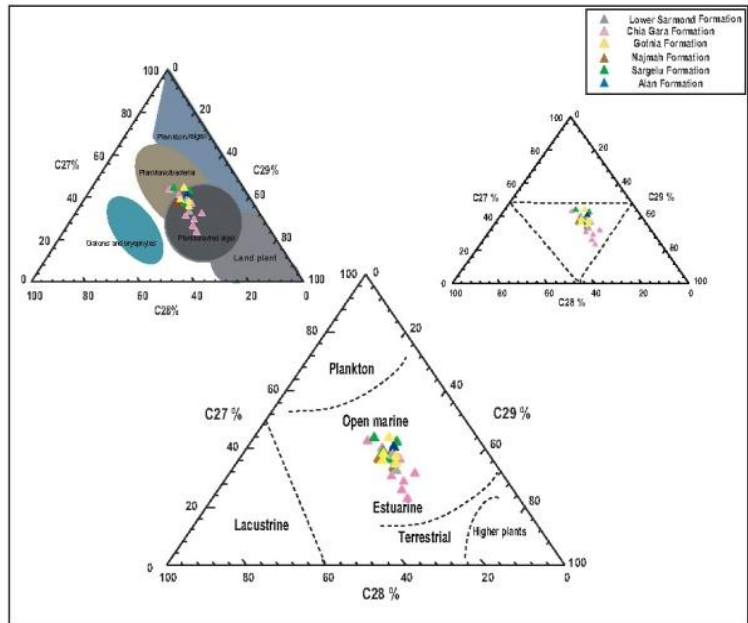


Fig. 3.34 Different triplot providing the composition of the C27-C29 regular steranes of the samples studied the plot suggest open marine environment with organic matter derived from algae. The upper plots(circles) inform well Aj-12. The lower plots(triangles) inform well Aj-8. The measurement from (217m/z) .

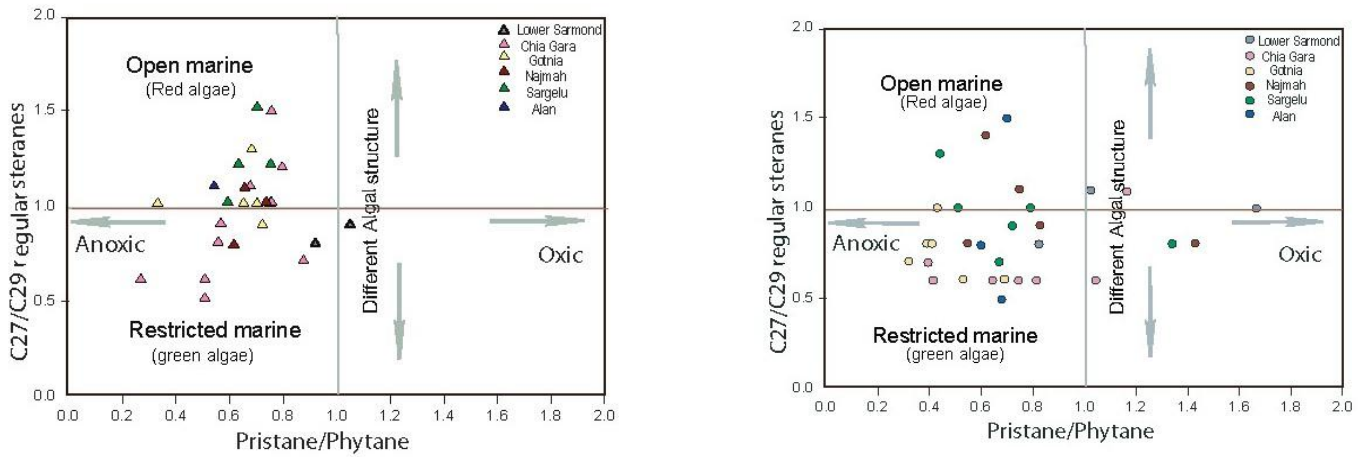


Fig. 3.35 Pristane/Phytane ratio versus C27/C29 regular steranes plot, indicating organic matter input and depositional conditions for samples studied. The left inform well Aj-8(triangles)and the right inform well Aj-12 (circles). The plots show also the different algae structure in the two wells and the environment.

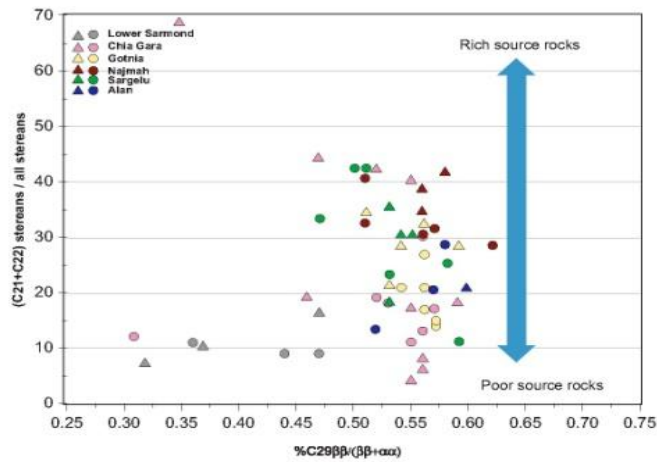


Fig.3.36 Two steranes parameters from saturated hydrocarbon (217m/z) show the poor and rich source rocks for the samples studied from wells Aj-12 (circles) and Aj-8(triangles).

-Hypersaline depositional environment

The samples studied were collected from Carbonate/Anhydrite sequence which is indicate hypersaline depositional environment for the extract studied samples. The high amount from the sulfur content (TS wt%) from bulk analysis which reach around 20% in some samples from Gotnia Formation another indicator for the salinity. The low ratio of Pr/Ph ratio and a strong dominance of hopanes over steranes are also indicate hypersaline environment. High relative abundance of C34+C35 homohopanes, suggesting the source rocks derived from hypersaline depositional environment (Moldowan et al., 1985; Fu et al., 1986; Philip et al., 1991). High ratio from the DBT/P which is reached around 7 in some samples from Gotnia Formation is good indicator for the hypersaline environment Fig(). Gammacerane has been proposed to be derived from reduction of tetrahymanol and it is an accepted biomarker for both highly saline marine and no marine (continental) depositional environments (Peters and Moldowan, 1993) was absent in all extracts samples.

11. Age of the source rock

C₂₈/ C₂₉ steranes : In marine petroleum the relative content of C₂₈ steranes increase and the C₂₉ steranes decrease through geologic time (Grantham and Wakefield, 1988). C₂₈/ C₂₉ steranes is <0.5 for lower Paleozoic and older oils, 0.4-0.7 for Upper Paleozoic to Lower Jurassic oils, and greater than 0.7 for Upper Jurassic to Miocene oils (Grantham and Wakefield, 1988). The studied samples have an average values as follows: for the Alan Formation 0.69, for the Sargelu Formation 0.75, for the Naokelekan Formation 0.81, for the Gotnia Formation 0.83, for the Chia Gara Formation 0.68, for the Lower Sarmond Formation 0.64. Based in (Grantham and Wakefield, 1988) classification these values generally are in the range of Lower Jurassic-Lower Cretaceous age for the Kerogen of the samples studied, the values of Najmah and Gotnia Formations are higher than 0.7 but is still in the range of classification. For the Sargelu, Chia Gara Formations the values of this study is very near to the values in Al-Ameri et al and Sachsenhofer et al in their study for the same Formations.

Tricyclic terpanes ratio (tricyclic/ (tricyclic + pentacyclic) is used also to identified the age of Kerogen for the samples studied the average of this ratio was as follows: Lower Sarmond Formation of 0.05, Chia Gara Formation of 0.07, Gotnia Formation of 0.04, Najmah Formation of 0.05, Sargelu Formation of 0.06, Alan Formation of 0.05. The low values for tricyclic terpanes ratio (< 20%) indicate the Lower Jurassic to early Cretaceous age for samples studied.

Oleanane in extract rock and oil is indicator for both source input and geology age. Oleanane originates from betulins, taraxerene and other pentacyclic triterpenoids produced by angiosperms flowering land plants (Peters et al., 2005). Oleanane is not detected in samples studied indicates that the kerogen for these source samples are from pre-Cretaceous age, or earliest Cretaceous age, a time period when angiosperms did not exist. This interpretation is restricted while the absent of Oleanane can mean no Oleanane was present in the source rock. Moreover, Oleanane

has been detected in some Mesozoic and Paleozoic non-angiospermous fossils (Taylor et al., 2006).). The increasing maturation from Cretaceous to Jurassic intervals appears in this study which is also supported by Aqrabi and Badics (2015) study. Sulfur and carbon isotopic measurements and mass-balance modeling there is evidence that during the Phanerozoic the sizes of the various carbon and sulfur reservoirs have changed relative to their present values such as mass of sedimentary pyrite in the world was increasing while that organic matter was decreasing which is observations of modern sedimentary pyrite formation (Veizer et al., 1980; Garrels and Lerman, 1981).

12. Different in the Biomarker distribution and behaviors and preservation condition in the central and margin of the Sedimentation basin

The studied wells are located in the low folded zone of the Zagros Fold Belt with transition towards the northern part of the Mesopotamian Foredeep Basin in the centre and at the margin of sedimentation basin. The Figure () is simple structure map for the two wells studied and show the location of these wells. The well Aj-8 in near to the center and the well Aj-12 is near to the margin which due to the varying in biomarker distribution and quality of the organic matter.

The aim of this part from this study to discuss the difference between the two wells studied in distribution of some biomarkers which is also noted in some bulk analysis in the precede chapter(chapter 1). The reason for differences not relate to the different in maturity level, because of , the maturity parameters from biomarker (saturated hydrocarbon and aromatic) are relatively the same in both wells and the same result can be notes from bulk analysis. The pr/ph ratio which is most useful indicator to reflect environment is lower than 1 in both wells studied (Aj-12 and Aj-8) which indicate that both wells deposit in marine environment, but at the same time (**open marine environment**) is the deposit environment for the well Aj-8, and more from (**estuarine environment**) for the samples studied in the well Aj-12.

The C27/C29 sterane ratio versus Pr/Ph ratio (Fig 2.31) show that the origin for the organic matter in this well mostly from red algae reflect by high C27 sterane, while high green algae in well Aj-12 which is reflect by high C29 sterane and it is also indicate that autochthonous marine organic matter was deposited in the central part where the well Aj-8 is located and at the margin mixed organic matter were deposit where the well A-12 is located. The result from biomarkers were compared with bulk analysis for the type of Kerogen in both wells from different plots (TOC% versus S2 from rock Eval pyrolysis and HI values) which indicate more from mix Kerogen II/III in the well Aj-12 with low from HI values (comparing with the HI values in the well Aj-8) which reflect mixing organic matter is the origin for this type of Kerogen. The bulk analysis show more from Type II Kerogen with more high values from HI in the well Aj-8 which is indicate autochthonous phytoplankton and zooplankton is the origin for this organic matter (plots present in chapter 1).

preservation conditions were different in the both wells studied. In the central (where the well Aj-8 near located) the preservation conditions were best with more anoxic condition, while in the margin (where the well Aj-12 near located) was more oxic condition.

The ratio of relative concentrations of BNH/(BNH+C29 hopane) is here considered to be the main parameter reflecting differences in chemical characteristics of the organic matter deposited in different location to the basin deposit.

BNH/(BNH+C29 hopane) ratio plots versus $T_s/(T_s+T_m)$ and versus Pr/Ph ratio for the extract samples in both wells studied(Aj-12 and Aj-8)the plots show inverse trend in the both wells studied. The BNH/(BNH+C29 hopane) ratio show different trend in the both wells studied with relatively same values for the same Formations in both wells (Aj-12 and Aj-8) which is (0.15 to 0.2) generally for the Jurassic Formations (Sargelu, Najmah, and Gotnia) with inverse trend distribution in the two wells studied. The plots of sulfur content (weight %) versus the methylphenanthrene index PP-1 for rocks samples in the two wells studied (Aj-12 and Aj-8) show the same result above (inverse trend between the two wells) as shown in the Fig(3.32).

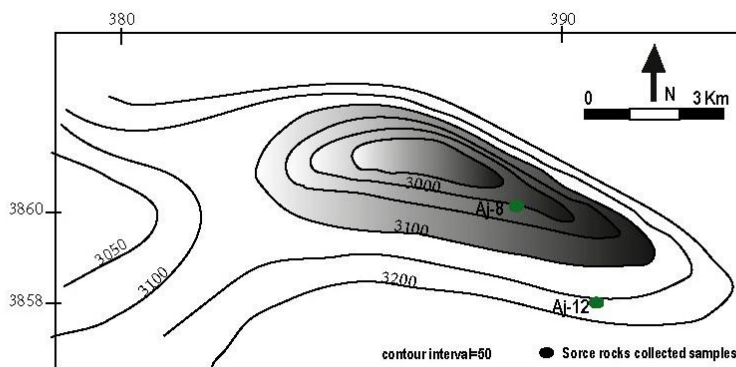


Fig. 3.37 Simple couthure map show the location of the well Aj-8 which is near to the center of the basin and the well Aj-12 which is near to the margin .

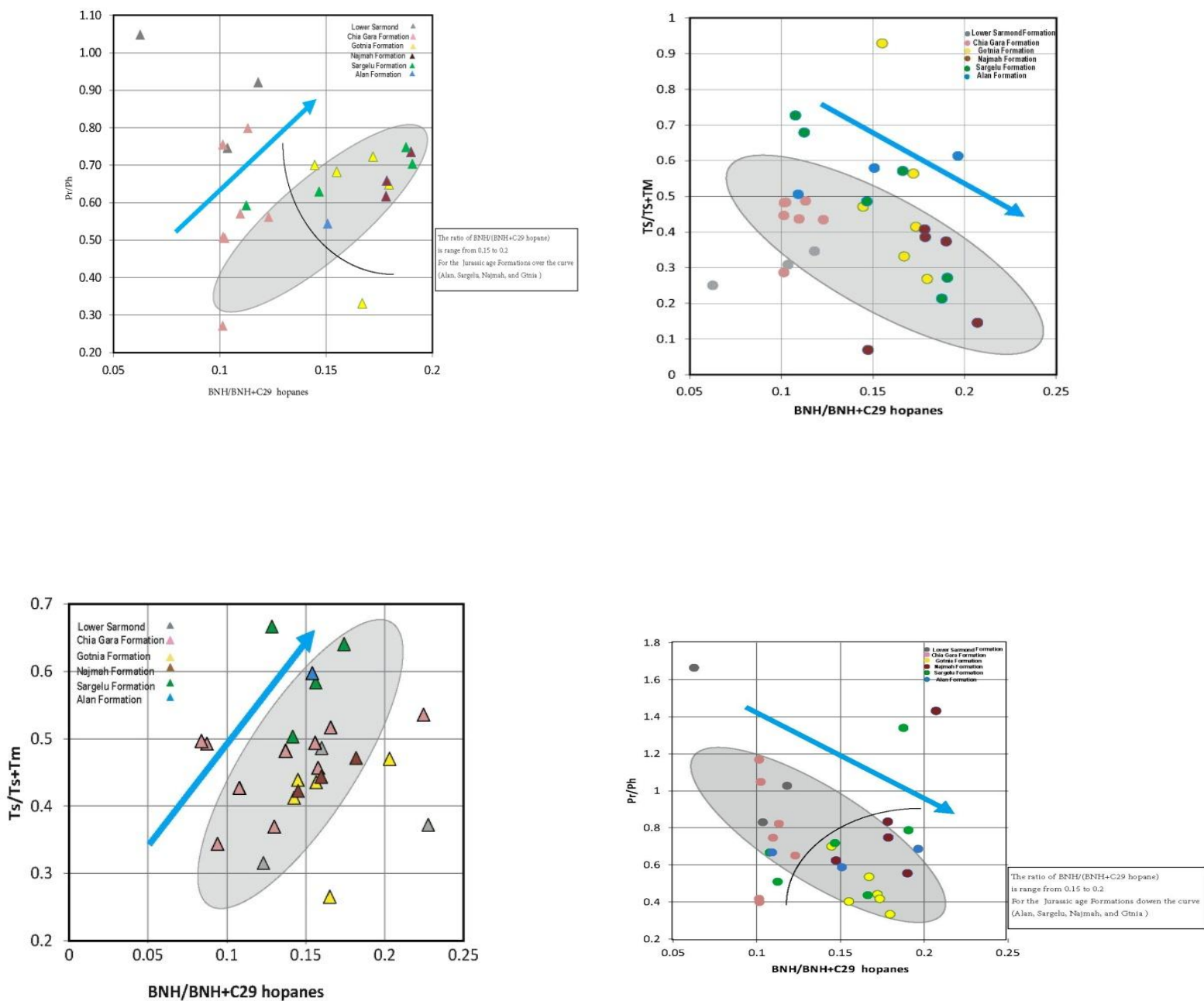


Fig. 3.38 Cross plots for different calculates ratios show different in biomarkers distribution related to the location of the wells studied .

13. Sulfur content and Biodegrading

Understanding the origin of sulfur in petroleum and Kerogen is necessary to make reliable interpretations regarding source input and depositional environment (Peters and Moldowan, 1993). Most primary sulfur in oils and bitumen originates from early diagenetic reactions between the deposited organic matter and aqueous sulfide (S^{2-}) such as hydrogen sulfide (H_2S) or polysulfide (e.g., Francois, 1987) and some sulfur may be derived from amino acids in the original contributing organic matter in sediments. Sulfides are produced by sulfate-reducing bacteria, primarily in highly reducing to anoxic (low Eh) marine sediments. If H_2S migrates upward from an anoxic into an oxic environment in sediment or the water column, it is rapidly oxidized back to sulfate by aerobic bacteria (Orr and Gaines, 1974). Even in anoxic environments, sulfide ions produced by sulfate reducing bacteria can be oxidized back to sulfate during periodic mixing of oxic and anoxic water layers an overall reaction representing by Garrels and Lerman, 1981). Hydrogen sulfide in petroleum reservoirs comes from two main source first: thermal degradation of labile S compounds, (COS , CS_2) (including asphaltenes and NSO compounds), which results in an isotopic composition that is close to its parent oil (Orr, 1986), and the second source is reduction of sulfate minerals in evaporate deposits, resulting in an isotopic composition close to that of seawater sulfate. Burial of organic matter under euxinic marine conditions can result in different amounts of reduced sulfur being buried with the organic matter. In marine sediments, the reduced sulfur is present predominantly as pyrite. High- and low-sulfur crude oils are derived from high- and low-sulfur Kerogens, respectively (Gransch and posthuma, 1974) and under this condition; much of the sulfide becomes incorporated into the Kerogen. Thus, many high-sulfur Kerogens and oils originate from clay-poor, marine rocks (e.g., carbonates or anhydrites) deposited under highly reducing to anoxic conditions (Peters and Moldowan, 1993). In this study, bulk geochemistry and geomarker are used to study the sulfur and the relationship between it and the deposit condition and its origin. The samples studied are collected from carbonate/anhydritic cycle which makes some of these samples be rich in sulfate minerals (Gotnia and Alan Formations) and these minerals could produce sulfides in highly reducing to anoxic conditions.

Bulk geochemistry analysis could use understanding the origin of sulfur in Kerogen, sulfur/Organic-carbon (S/C) relationship could use to assess the oxygen level of bottom water, based on the covariance of organic carbon and sulfur, which result from concomitant reduction of sulfate reducing bacteria to form hydrogen sulfide (H_2S) that reacts with iron to form pyrite in the sediments (Hofmann et al., 2000; Leventhal, 1987). The sediments deposited under oxic marine conditions generally have S/C ratios of 0.36, while this ratio would be higher than 0.36 in anoxic environments (Berner, 1984). For samples studied this ratio generally have range (0.4- 4.2 wt%) with very high values from Anhydritic Formation studied reach to (61wt%) and few samples have values lower than 0.36 most of these samples are from the upper part of the Chia Gara Formation and the Lower Sarmond Formation. In addition the sulfur content vs. TOC (wt %) were plotted for the sediments of samples studied which collect from carbonate/evaporitic cycles

and they are relatively high in sulfur with highest values from Anhydritic Formations. The samples are plotted along a line with a positive intercept on the sulfur axis indicating deposition under a H_2S containing water column with same samples plots in oxic condition which are generally from Lower Sarmond and the Upper part from Chia Gara Formation fig()and there are few samples from Gotnia and Alan Formations have very high sulfur values (18-22 wt%) did not included for more illustrated reason.

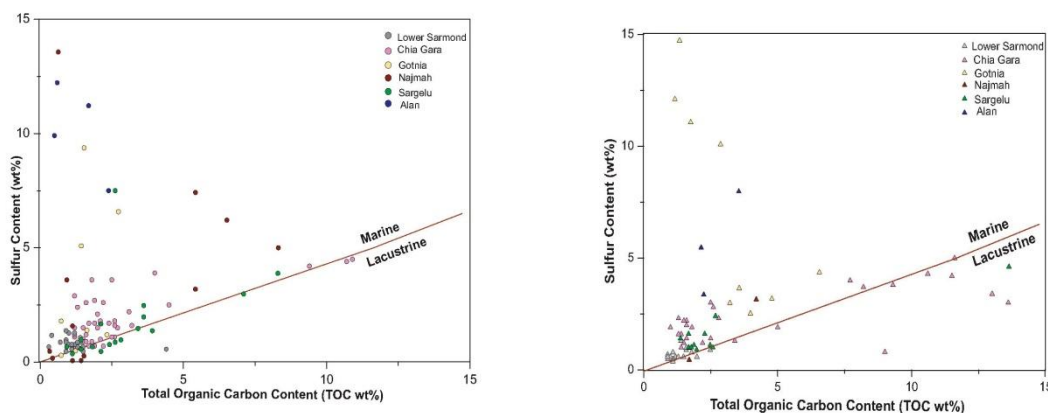


Fig. 3.39. Sulfur content (wt%) plotted against (TOC wt%) for samples studied in well Aj-12 and well Aj-8, suggesting that the depositional environment was dominantly marine environment with few samples plotted in lacustrine environment. Modified after Berner and Raiswell, 1983. The figures show also more oxic condition in well Aj-12.

Sulfur compound from the aromatic hydrocarbon fractions are used to understanding the origin of sulfur in the Kerogen and the environment conditions and to signify the H_2S produced in the organic layers. For samples studied reduction of sulfate minerals in evaporate deposits, resulting amount of the H_2S produced in the organic layers but the sulfate reduction could not fixed as pyrite resulting in significant amounts of free H_2S and only a small portion of this H_2S was incorporated in organic matter. The ratio of the C29/C30 hopane is the fixed ratio which is used for the samples studied (high values from this ratio indicate more anoxic condition) versus different calculated ratios as follow:

(4+1)/(2+3) MDBT ratios versus C29/C30 hopane, for the samples studied 4+1/2+3 MDBT ratio range from 1.54 to 3.57 most high values were from Lower Sarmond and Upper Chia Gara Formations and the C29/C30 hopane ratio has range values from 0.91 to 2.83. The higher values from this ratio indicate more anoxic condition and the higher values from this ratio for the

samples studied were from the Najmah and Sargelu Formations which indicate more anoxic condition in these two Formations.

P/MP ratios versus C29/C30 hopane, the high values from this ratio indicates the higher oxic condition. In general the samples studied have low values from this ratio (less than 1) which indicate anoxic condition in general for all the Formations studied with few high values most of them from the Lower Sarmond and the Upper Chia Gara Formations. The range of this values for the samples studied was (0.14 to 0.89) with three values more than 1 from the Lower Sarmond Formation.

Hopanes/regular sterane versus C29/C30 hopane, the Formations studied are Carbonates and Anhydrite Formation for this reason the hopane /regular sterane ratio was high in Anhydrite Formations (Gotnia(in Anhydritic layers) and Alan Formations.

Bulk geochemical analysis (TOC/TIC ratio from elemental analyzer) versus Biomarker parameter ratio (C29/C30 hopane) for the samples studied are plotted and show the same result more oxic condition from Lower Sarmond and Upper Chia Gara Formations and more anoxic with sulfide in Najmah and Sargelu Formations. From above it can be concluded that the Formations studied in general deposit under anoxic_ sulfatic and H₂S containing water column and samples studied from Lower Sarmond and Upper Chia Gara Formation in general deposit under oxic condition and the other part from the samples studied which are from Najmah and Sargelu Formations deposits under anoxic_ sulfidic condition where the reduced sulfur is present as pyrite.

14. Conclusion remarks

This chapter reports the distribution of biomarker and geomarker hydrocarbons and distribution of n-alkanes and isoprenoid (Pr and Ph) from selected lower Jurassic-Early Cretaceous sediments. Terpane biomarker and aromatic geomarker signatures reveal origin from similar source and facies regimes concordant with Carbonate/evaporitic cycles. The maturity parameter from the saturated hydrocarbon and from aromatic show high and regular in maturity for the Jurassic Formations with the lower part of the basal Cretaceous Chia Gara Formation the upper part from Chia Gara Formation Fig(3.41) and the Lower Sarmond Formation show low in maturity comparing with the other Formations studied. The Formations studied were deposited in marine, carbonate rich, anoxic environment with more oxic condition deposited for the upper Chia Gara and Lower Sarmond Formations it could be said there is gradational changes in the redox conditions from anoxic condition (for the Jurassic Formations with the Lower part from Chia Gara Formation) to oxic condition (for the Cretaceous Formations). The algae input is the origin for this organic matter and no biodegradation notice. The samples studied were collected from Carbonate/Anhydrite sequence which is indicate hypersaline depositional environment supported by high ratio from DBT/P for the Formations studied. Difference in the trend for some biomarkers distribution noticed between the well Aj-12 and Aj-8 related to the site of these

wells near to the central basin(Aj-8) and near to the margin(Aj-12). Preservation conditions were best in Lower Chia Gara and Upper Sargelu Fmormatons Fig(3.41,42). Highest source potential occurs in the basal Chia Gara, the Najmah/Naokelekan and uppermost Sargelu Fms. The central Chia Gara and Lower Sargelu Fm. contain less effective source units.

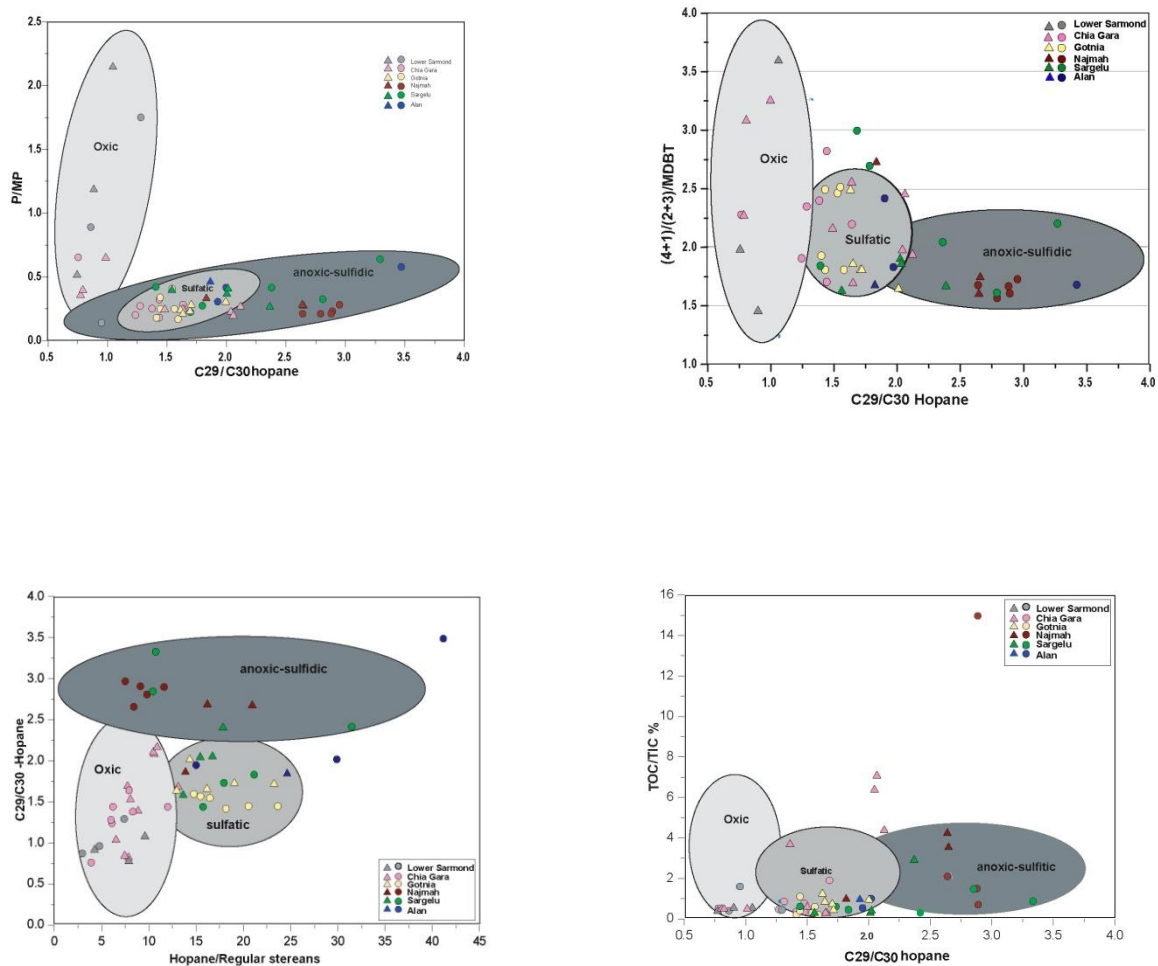


Fig.3.40. C29/C30 hopane ratio versus different calculate ratio: (a and b) aromatic ratios P/MP and (4+1)/(2+3) MDBT. (c) versus hopane/regular sterane ratio.(d) TOC/TIC ratio from bulk analysis. The suggest three group for the samples studied. The first group where most samples are plots is sulfatic condition and the second group which is content some samples from Najmah and Sargelu Formations reflects sulfidic condition and the third group which is content some samples from Lower Sarmond and upper part from Chia Gara Formation which reflect oxic condition.

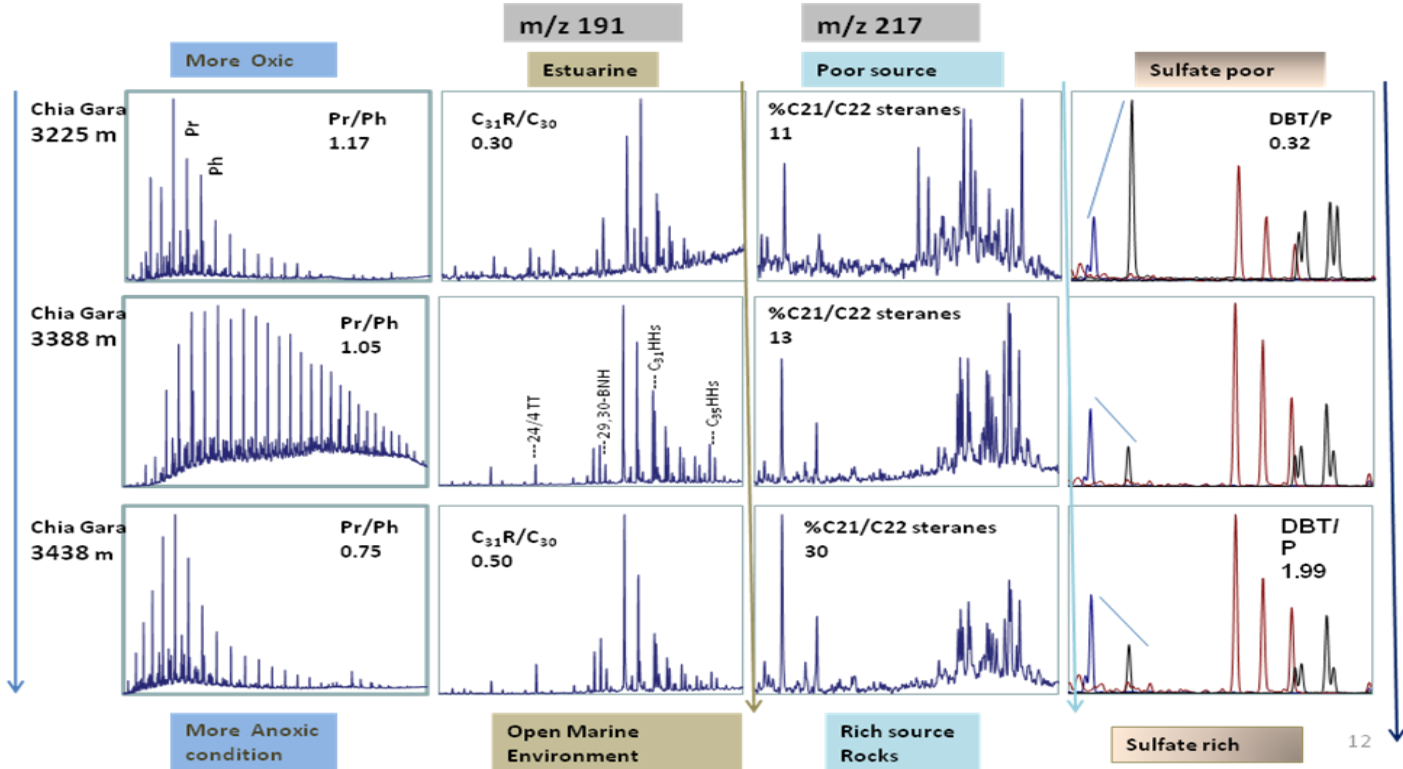


Fig. 3.41. Different between the upper part and the lower part from Chia Gara Formation in Bio/geomarkers distribution. The figure show more oxidic condition, poor source rock and poor sulfate in the upper part from this Formation, while very strong anoxic condition with excellent source rock and sulfate rich in the lower part from this Formation.

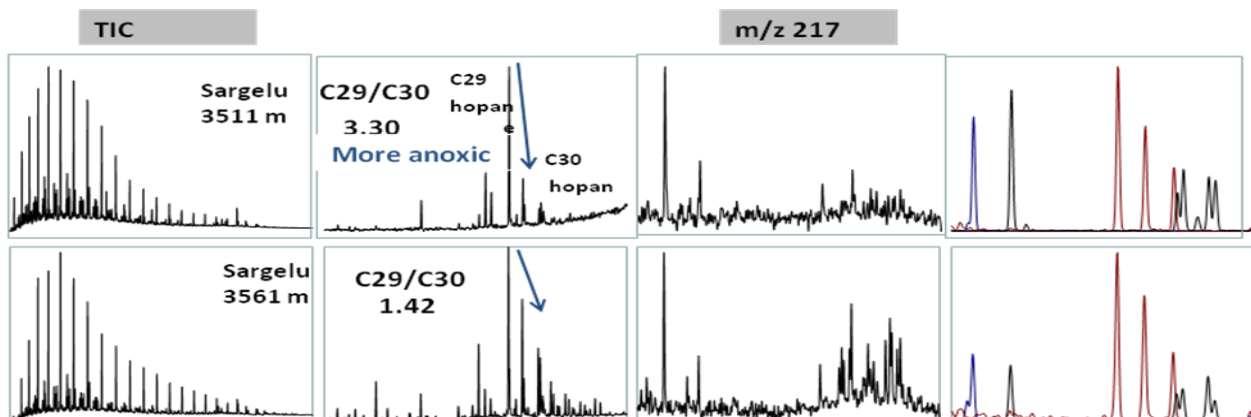


Fig. 3.42. more anoxic condition in the Upper part from Sargelu Formation with high source potential incomparing with the lower part from it.

Chapter 4

Geochemical, biomarkers distribution for the reservoirs solid bitumen and crude oils of the Miocene reservoirs NE Iraq and comparison with source origins

Introduction

Little is known about the potential molecular fractionation of bitumen residing in reservoir rocks and few data exist on the comparative organic geochemistry of hydrocarbons formed in reservoir rocks and the bitumen in the pore space (Wilhelms et al., 1996). In recent years, reservoir geochemistry has developed rapidly, being applied to solve exploration, appraisal and production problems (L. Schwark et al., 1997). From a reservoir evaluation perspective, however, reservoir solid bitumen remain as well known but poorly understood organic deposits (Hwang et al., 1998), neutron logs record it as porosity and resistivity logs may record it as conventional oil (pay). The presence of solid bitumen reduces porosity and permeability of reservoirs because it is cement, and it is close pore throats and filling pore space (McFadzean, 1977; Lomando, 1992)

Geochemical comparison of solid bitumen with various origins from reservoirs was studied to provide insight into their formation processes and their chemical properties. Sequential extraction studies have been reported for reservoir rocks (Ghenima, 1993; Wilhelms, 1993). Reservoir solid bitumen are referred to organic matter found in reservoir rocks which are products of reservoir alteration processes of once- liquid petroleum (Curiale, 1986) and the formation of solid bitumen in reservoirs from liquid petroleum has been mainly attributed to natural processes including, thermal alteration, and biodegradation (Hwang et al., 1998).

1. Geological background

After the deposition of upper Oligocene rocks in the lower lying parts of Oligocene basin, a further regression, dated approximately at the Oligocene- Aquitanian transition, preceded the commencement of lower Miocene sedimentation (Dunnington, H. V., 2005). By the early Miocene, laterally extensive shallow-water carbonate platforms had developed on the margins of the Mesopotamian Basin, and included the Asmari Limestone and Qum Limestone of Iran, and the Kirkuk Group of Iraq which are restricted to the axial part of the foreland basin (Aqrabi et al., 2010). At this time, a continuous marine connection existed around the northern edge of the Arabian Plate from the Eastern Mediterranean to the Hormuz Straits. In the mid- Miocene time regional tectonic subsidence occurred in Iraq with the deposition of the Lower, Middle and Upper Fars Formation throughout NE Iraq. In the Late Miocene time, intense compression propagated into the Middle Miocene foreland basin and resulted in the growth of large-scale Zagros anticlines. In this study geochemical comparison of solid bitumen were studied in Four Miocene age Formations (Euphrates, Dhiban, Jeribe, Transition Beds) in four wells from Ajeel oil field as follows: (Aj-12, Aj-8, Aj-10, Aj-88) and two wells from Harman oil field (Hr.39 and Hr.40).

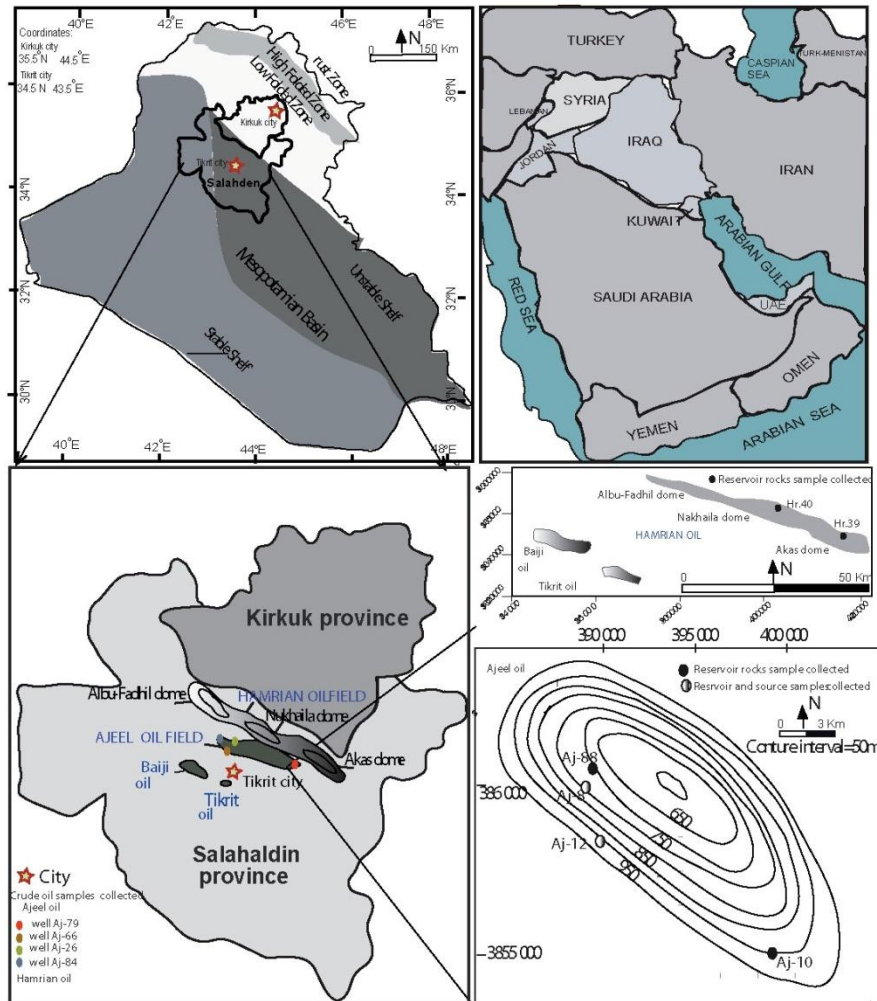


Fig 4.1. (a) a simplified map showing Iraq site with the Arabian plate (b) Regional tectonic setting of Iraq (modified from Jassim and Goff, 2006) and show two province boundaries where samples studied were collect. (c) Location map showing oil fields and wells where the crude oil samples are collect.(d) structure contour map for Ajeel oil field and location map for Hamrin oil field showing the wells where the source and reservoir samples where collect.

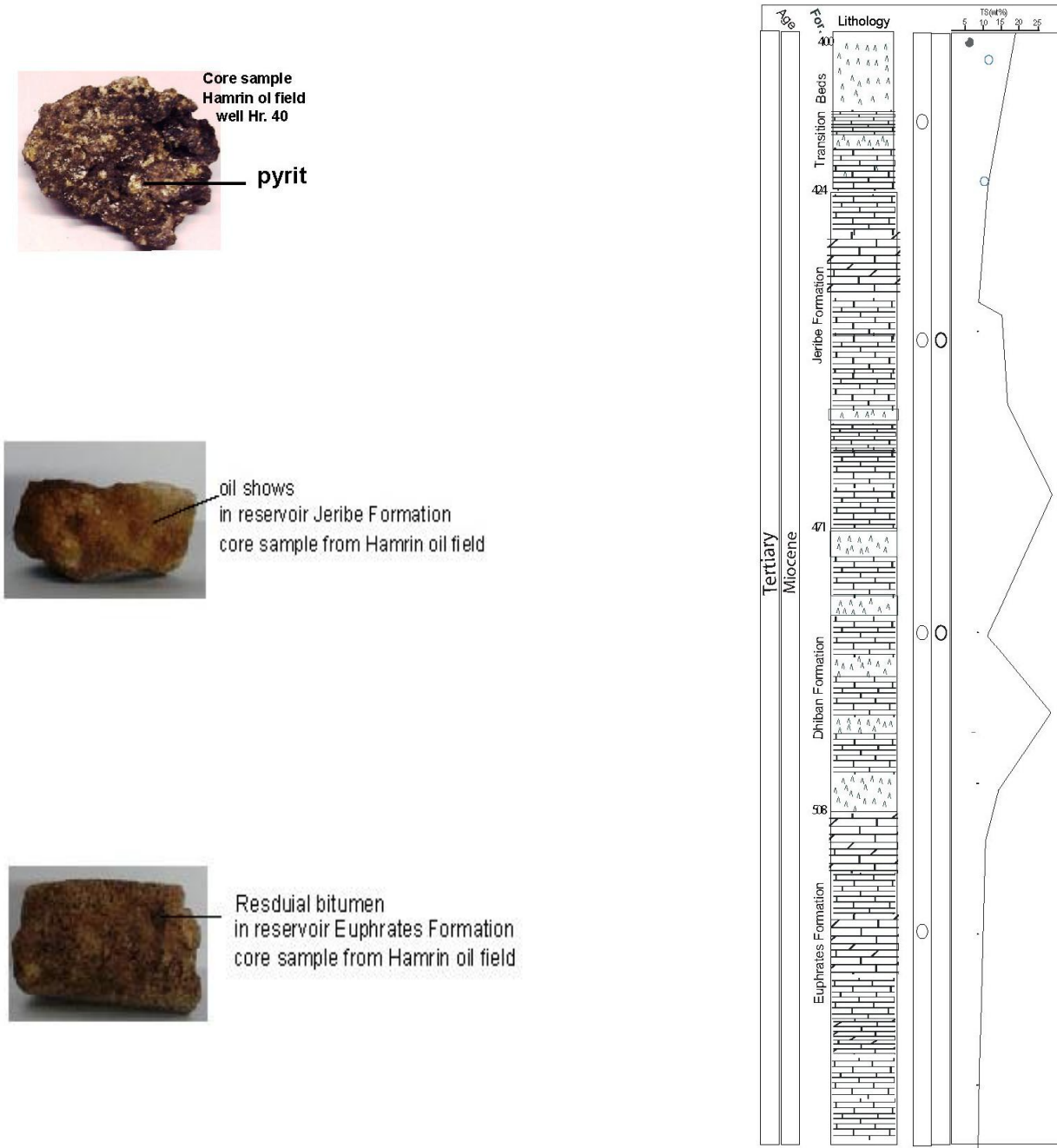


Fig 4.2. Lithostratigraphy for Hamrin oil field from the well Hr. 39 studied. the photos are core collected samples from the Hamrin oil field.

The Euphrates Formation

The Euphrates Formation was originally described by De Boeckh in 1992 and later amended by Bellen in 1957. The formation consists mainly of Limestone with textures ranging from oolitic to chalky. It is conformable with Dhiban Formation and uncomfortably overlies Oligocene and Eocene Formations. It is again Limestone and Dolomitic in character, but contains less anhydrite than the Jeribe and Dhiban Formations. The Formation is 75-85 m thick and has the reservoir quality in Ajeel and Hamrin oil fields. The Euphrates Formation is of early Miocene age and it is deposit in carbonate inner shelf. Uncomfortably overlies Oligocene and Eocene Formations. In the type area the basal beds of the formation comprise conglomerates and residual clays which infill an uneven surface at the top of the Oligocene Anah Formation. Lower Miocene Limestone in Syria is referred to the Euphrates Formation by Dubertret (1966) and in the SE of Iran the Euphrates Formation is equivalent to part of the Asmari Limestone. The Euphrates Formation passes laterally into continental clastics in Saudi Arabia, represented by the Hadrukh Formation (Powers et al., 1966).

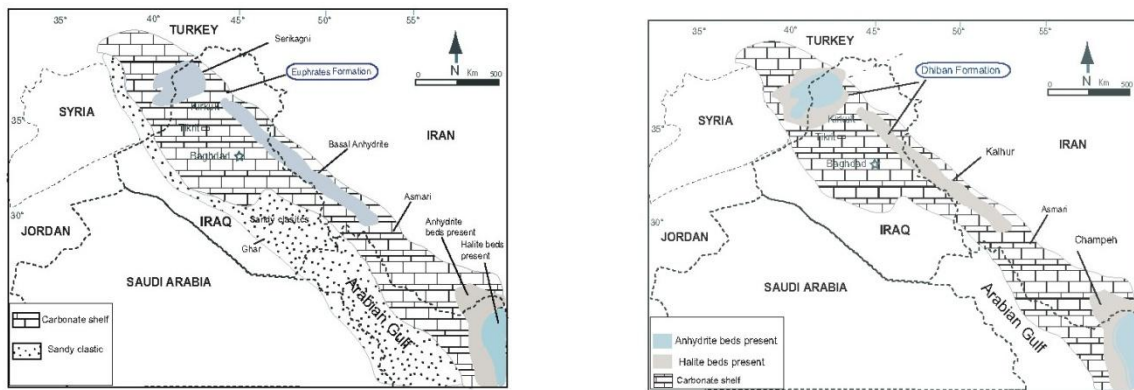
The Dhiban Formation

The Dhiban Formation was defined by Henson in 1940 and amended by Bellen in 1957 (Bellen et al., 1959) from the type area near Dhiban village in the Sinjar area of the Foothill Zone of NW Iraq. The formation comprises 72 m of gypsum, thin beds of marl and brecciated recrystallised limestone and deposit in evaporite lagoons environment. Between Mosul and Qaiyarah the anhydrites in Dhiban Formation are replaced by (chemical) limestone (Bellen et al., 1959) due to bacterial reduction and sulfur Formation. Early Miocene is the age of Dhiban Formation and it is conformable overlain the Jeribe Formation and it has essentially the same character as Jeribe Formation, but contains a high concentration of anhydrite nodules, especially towards its base. For this reason, it is mainly a poor reservoir unit. The Dhiban Formation occurs in NE Syria and the Kalhur Gypsum of SW Iran is equivalent to it.

The Jeribe Formation

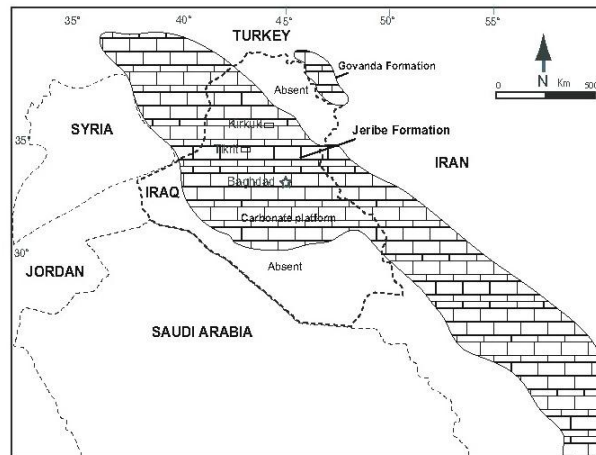
The Jeribe Formation conformably lying below the Transition Beds is a slightly argillaceous dolomitic unit with abundant anhydrite nodules. It is 23-32 m thick and its reservoir quality is generally fair to good. For reservoir simulation purposes, the formation has been subdivided into three layers, which roughly correspond to the three layers of the previous report. Aqrabi et al. (2010) noted that the Jeribe Formation is of Early Miocene age and it was deposited relatively uniformly throughout the Mesopotamian Basin. A maximum thickness of 63 m was recorded at Injana field by Al-Juboury et al. (2007). In the basin center, cycles up to 10 m thick occur in which porous open-marine carbonates are interbedded with relatively tight, restricted marine carbonates and evaporate. The Jeribe Formation is equivalent to the upper part of the Middle

Asmari and the upper Asmari Formation of Iran (as defined by Jasmes and Wynd, 1965 and Aqrawi et al., 2010). The Jeribe Formation is overlain by the anhydrites of the Middle Miocene Fars Formation which forms a regional seal.



(B)

(A)



(C)

Fig.4.3. Paleogeographic maps for the study Formations (a) Euphrates Formation (b) Dhiban Formation and (d) Jeribe Formation (modified after Aqrawi et al., 2010).

Transition Beds

The Fatha (Lower Fars) Formation is one of the most aerially widespread and economically important formations in Iraq (Jassim and Goff 2006). The Lower Fars Formation in Iraq was subdivided into informal units. It comprises anhydrite, gypsum and salt, interbedded with limestone and marl (Belen et al., 1959) and the Transition Beds is the bottom of these units which is overlying Jeribe Formation. Transition Beds normally comprising beds of anhydrite, mudstone and thin limestone.

2. Harmin oil field and relationship between Ajeel oil field and Harmin oil field structures

Harmin oil field is part of many fields of structurally oriented NW- SE within northern part of adjacent to the low folded zone of the Zagros Fold Belt. Harman oil field is located 10 Km north of Tikrit city, and 80 Km south west of Kirkuk city, and to the northeast of the Ajeel oil field and parallel to it, and it is one of the geological structures visible on the surface which is extends on the (Fethia) on the Tigris River in the northwest of the Great River. Harman oil field is long asymmetric anticline with length of (100) km and width (4.5) with axis direction northwest southeast. The field consists of three domes they are as follow: from the northwest to the southeast (Akaz dome, with 34 km length and 4 km width, and Nukhaila dome, with 18 km length and 5 km width and Albu- fadhil dome with length 26,5 km and 4,5 km width), these domes are separated by two saddle , the first one is (Salt way saddel) which is separate (Abu- fadhil and Nukaila domes) and the second one is (Ein Nukhaila saddel) which is separate (Nukaila and Akaz domes). There is some index indicate that the Ajeel and Hamirn structures are separated by thrust fault. The index includes cross-section from NOC in well Hr.1, which is located to the NE of Ajeel oil field intersected a thrust and sudden loss of seismic reflectors just to the north of Ajeel oil field (north of the synclinal axis). Furthermore, on a surface geologic map by NOC, a thrust is shown to separate the Ajeel and Hamrin structures. In this study the residual bitumen were studied in two wells from this field (Hr.39 and Hr.40) from four Formations (Euphrates, Dhiban, Jeribe and Transition beds (Lower Fars Formation). Short descriptions of the studied field are given below:

Well Hamrin -39 (Hr.39)

This well is sited on the south west flank of Allas dome in Jabal Hamrin structure. Elevation ground level: 286, 24 m. 290 m RTKB.

Location:

The U.T.M coordinates are as following:

N: 3852 218.750 m E: 416 163.045 m

Transition Beds (400- 424 m) is composed of massive hard Anhydrite in the upper part and lower part from this formation alternate with marly pours Limestone. The Jeribe Formation (424- 471 m) is consist of pores pyritic Limestone. Dhiban Formation (471- 508 m) is consisting of Anhydrite with marly limestone layers. Euphrates Formation (508- 574 m) consists of pours Limestone with oil show and pours Dolomite in the lower part from it with no oil show

Well Hamrin -40 (Hr.40)

This well is sited on the south west flank of Nukhaila dome in Jabal Hamrin structure. Elevation ground level: 305.8 m. 310 m RTKB

Location:

The U.T.M coordinates are as following:

N: 3861 8391.1 m E: 400 416.31 m

There are no samples from the Transition Beds and Jeribe Formation in this well. Dhiban Formation (368-396 m) it consists of massive hard Anhydrite with layers of Limestone. Euphrates Formation (396- 482 m) consists of Dolomitic Limestone with oil shows and Marl Layers in the lower part from this Formation.

Ajeel oil field residual bitumen were studied in this field from the main reservoir units which are the Jeribe, and Euphrates Formations and Transition Beds with samples from Dhabian Formation, in four wells two from them the source formations are also studied in them which are (Aj-8 and Aj-12 in chapter 2) from this oil field. The four wells as follow:

Well Ajeel- 10 (Aj-10)

This well is located on the south eastern plunge of the structure with ground level is about 158m and 164 m RTKB.

Location:

The U.T.M coordinates are as following:

N: 3855 567.7m E: 399 398.5 m

Transition Beds in this well (922-1024 m) consists of alternating sequence of anhydrite beds and Limestone and Marl beds which had oil shows. Jeribe Formation (1024.5- 1052 m) it consists of Dolomitic Limestone and it is the main reservoir in this well. Dhiban Formation (1052- 1081 m) it consists of massive anhydrite beds alternating with thin Dolomitic Limestone beds. Euphrates

Formation (1081- 1173.5 m) it consider as reservoir formation it consists of Dolomitic Limestone.

Well Ajeel- 88 (Aj-88)

This well is located on the north eastern flank of the Ajeel field of the structure with ground level is about 185.46 m and 190 m RTKB.

Location:

The U.T.M coordinates are as following:

N: 3863 504.04 m E: 389 996.19 m

Transition Beds in this well had 126 m (978- 1104 m) and these beds consist of anhydrite with Limestone alternatively. Jeribe Formation (1104 - 1138.5 m) consists of Limestone and Marl with Dolomite and anhydrite nodules. Dhiban Formation (1138.5- 1155 m) with 16.5 m thickness consists of white hard and massive anhydrite with Limestone porous. Euphrates Formation (1155- 1155.5 m) with 0.5 m thickness consists of Limestone.

Well Ajeel- 12 (Aj-12)

This well is located on the SW of the structure, and it lies 2650 m SE of Ajeel-8 well. Elevation ground level 158 m and 164 m RTKB.

Location:

The U.T.M coordinates are as following:

N: 3858 116.5 m E: 390, 817.5 m

Transition Beds (957- 1079 m) it composed of alternative beds of light grey to light brown Limestone with white crystalline anhydrite beds. Jeribe Formation (1074 - 1119 m) it consists of yellow-beige Limestone with Dolomite and nodules of white anhydrite. Dhiban Formation (1119- 1134 m) it consists of Limestone slightly pyritic with anhydrite and nodules anhydrite. Euphrates Formation (1134- 1250 m), this formation consists of Limestone slightly porous at place with Dolomitic Marly at bottom.

Well Ajeel- 8 (Aj-8)

This well is located on the SW flank of the structure and on the crest maxima of the cretaceous, and of 163 m above sea level.

Location:

The U.T.M coordinates are as following:

N: 386, 000 E: 389, 050

Transition Beds (827- 943.5 m) consist of Dolomitic Limestone to Marl Limestone alternative with anhydrite beds. Jeribe Formation (943.5 - 972 m) it composed pour vague Limestone with Dolomitic Limestone in part from it. Dhiban Formation (972- 998 m) it composed of anhydrite in the upper and lower part from it and anhydritic Limestone in the middle part from it. Euphrates Formation (998- 1090 m) it consist of pour Dolomitic Limestone with Marl in some part of it.

3. Methods

In this part from this study **108** (core and cutting) samples were select from six wells in two oil fields (Ajeel oil field and Hamrin oil field) from four Formations (Transition beds (Lower Fars Formation), Jeribe Formation , Dhiban Formation and Euphrates Formation), to study their solid bitumen and comparison with source origins. While, the main propos for this part from this study is compared solid bitumen in reservoir rocks with source rocks, the same analyzed methods are used for (bulk geochemical, extraction, gas chromatography and molecular geochemical parameters) and the same identification peak for biomarkers(hopane(191 m/z), steranes (217m/z) and aromatic). which are showing in chapter 2 from this study.

Bulk geochemical analysis

Reservoir core extracts are usually enriched in compounds containing nitrogen, sulfur and oxygen compared with oils produced from the same reservoir zone (Leythaeuser and Ruckheim, 1989; Larter et al., 1991; Horstad et al; 1990; Stoddart et al., 1995). After cleaning and crushing the 108 reservoir rocks samples were run in Elemental Analyzer in two module first to determined Carbon (C), Nitrogen (N), and Sulfur (S) the Carbone here represent the total carbon content (**TC**), the second module is a **TIC** module o determined inorganic carbon, then total organic Carbon (TOC) was calculated by subtracting the TIC from TC.Measured Rock-Eval parameters (S1, S2, S3 and Tmax) are shown in Appendix ().

Extraction and Gas-Chromatography- Mass Spectrometry (GC-MS).

Depending on the highest TOC values and the other bulk parameters and geological information 25 samples from the 108 reservoirs samples were selected for extraction. Extraction was carried out using the same method and the same solvent which used for extract the bitumen in source rocks are used for reservoir rocks samples. Dichloromethane solvent (DCM) a temperature of 75°C and a pressure of 50 bars, the static extraction phase was set to 20 minutes (more details in chapter 1 from this study). The soluble organic matter for reservoir samples show different

colors (Fig.). The extracts were separated into saturated fractions, aromatic and a polar hydrocarbon fraction. The fraction was analyzed using gas chromatograph-mass spectrometry (GC-MS). The same peaks that used for source rocks were integrate for reservoir samples

4. Bulk geochemical parameters result and soluble organic matter extraction

The samples show TOC contents varying between 0.2 and 6% and the Miocene Euphrates Formation show higher TOC contents than Jeribe Formation with average 1.5 % in Ajeel oil field and 1.95 % average in the Hamrin oil field. The Jeribe Formation shows 1.6 % TOC average in the Ajeel oil field and 2.3 % in the well Hr.39 in Hamrin oil field. Preliminary analysis of log parameters (GR, FDC, CNL, DLL, and MSFL) confirms the Euphrates and Jeribe Formations as the main pay zones in the Ajeel and Hamrin oil fields. Rock-Eval parameters (S1 relative to S2) lend supporting evidence for migration of hydrocarbons has been nearly entirely released from source rock (Peters, 1986). Generality, solid bitumen samples have S1 pyrolysis yields greater than the corresponding S2 pyrolysis yield that is indicative of migrated hydrocarbons, while the source rock samples have high S2 pyrolysis yield than the associated S1 pyrolysis yields which is indicative of sedentary organic material although degraded bitumen can appear as S2 hydrocarbons (Peters, 1986). To estimate the nature of the hydrocarbon products (generated or migrated) the production index (PI) and pyrolysis T_{max} were also used. High production index values are due to migrated hydrocarbons (HasenhuEttla et al., 2011). The production index (PI) and pyrolysis T_{max} values of the solid bitumen represent within the pore space of the reservoir Formations indicate that the solid bitumen could have been generated from an effective source rocks Formations and subsequently migrated into the reservoir rocks as shown in Fig(). The evaluation of thermal maturity from bulk parameters of the residual bitumen in the Formations studied was carried out using pyrolysis Tmax and show range average from 415°C to 431°C for with small variation in in Ajeel and Harmin wells with higher values in Jeribe Formation in well Aj-8. The extraction has be done for selected samples from the reservoirs studied Formations. The extract samples selected from the 4 wells studied in Ajeel oil field and generally, covered all the reservoirs Formation studied and from the 2 wells studied in Hamrin oil field. The method of that used for extraction is the same method that used to extract samples from the source rocks. The extract samples show in generally, dark color, especially, the extract samples from Hamrin oil field as shown in photo (Fig.). The amount of soluble organic matter has been calculated the values listed in Appendix () and it is range from 38 to 12937, 05 ppm for the studied samples. The Fig () show that Euphrates Formation in Hamrin oil field has the highest values from soluble organic matter. The soluble organic matter in samples with solid bitumen is represented mainly by asphaltenes. The high asphaltene content is commonly due to the presence of solid bitumen within the pore spaces of the Limestone and Dolomite of the studied samples. The solid bitumen from Euphrates Formation in Harmin oil field is highly extractable (23695.3ppm) and generally,

the Formations studied in Harmin oil field show high in extractable comparing with the same Formation in Ajeel oil field which also supported by the dark color from the extract. The Figure() show the averages values from the extraction in (ppm) for the samples studied in both oil fields and average values for the reservoir studied Formation in every oil in Hamrin and Ajeel oil fields with photo show the color from extraction for some samples.

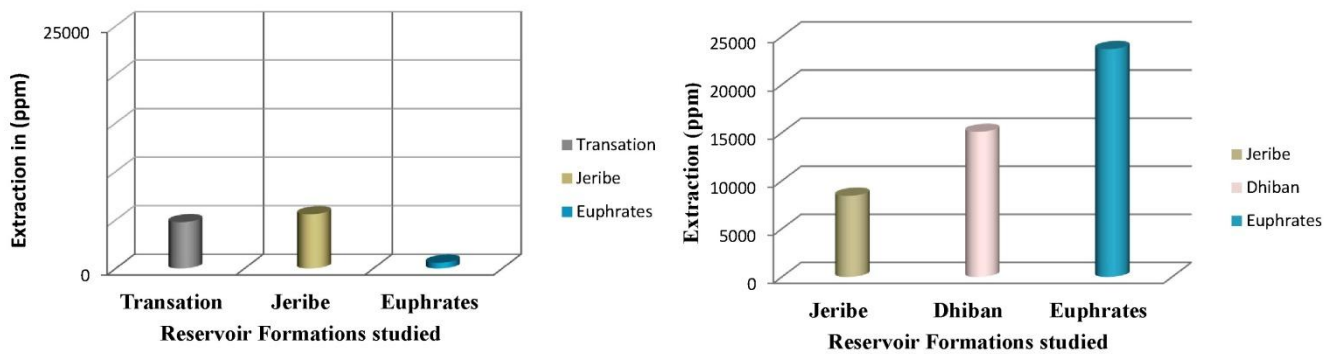


Fig 4.4. Distribution of extract yield in ppm (average values) for the Formations studied. The (left)Ajeel oil field and the (right) Harmin oil field, show high extract from Euphrates Formation in Harmin oil field and low extract from this Formation in Ajeel oil field .

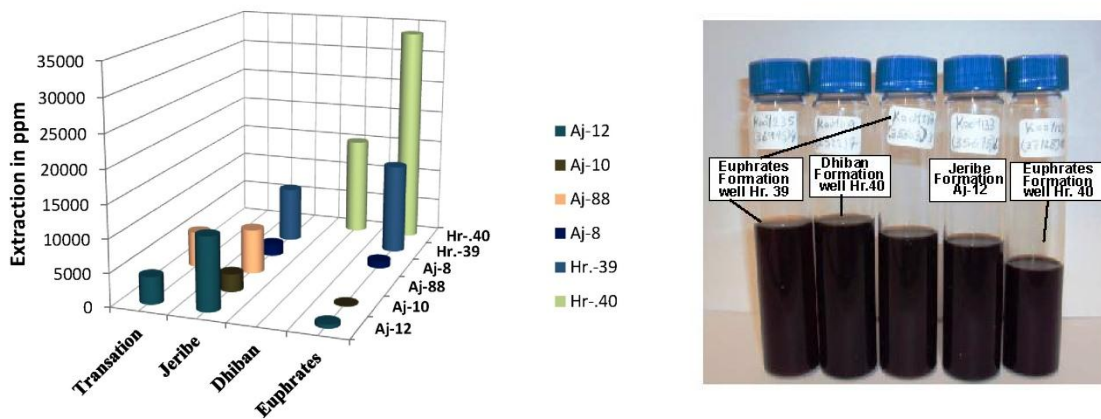


Fig .4.5. Distribution of extract yield in ppm for the Formations studied in Ajeel and Harmin oil fields for all the wells studied. The values here are the average values in every well. The photo show extract for select samples.

5. Biomarker distribution of the saturated fraction

Triterpanes and steranes

The relative abundance of n-C₂₉ norhopane is generally higher than that of n-C₃₀ hopane in most of the studied samples, with C₂₉/C₃₀ ratios in the range of 0.15-2.7 Appendix (). The predominance of n-C₂₉ norhopane is frequently associated with carbonate source rocks (Waples and Machihara, 1991). The homophones are dominated by the C₃₁ homophone and decrease with increasing carbon number which is indicate that the solid bitumen was derived from marine source rock deposited under anoxic and suboxic conditions (Peter and Moldowan, 1991), which is also consistent with the source rocks of the analyzed solid bitumen samples. All solid bitumen samples consisted low Ts /Tm ratios (0.15-0.77). Ts and Tm ratio are known to be influenced by maturation, type of organic matter and lithology (Modowan et al., 1985; Seifert and Moldowan, 1979). Considering the lithology of the reservoir analyzed samples are mostly the same; the Ts/Tm ratios thus appear to be more strongly influenced by maturity rather than lithology or source input. The relative homophone abundance decreased from C₃₁ to C₃₅, which is similar to what we seen in the extract from source rocks studied.

The distribution of regular steranes (C₂₇, C₂₈ and C₂₉) is shown by the m/z 217 ion chromatograms. Peaks assignments are shown Fig (), and the derived parameters are listed in Appendix (). The distribution of C₂₇-C₂₉ regular steranes can be used to indicate depositional setting (Philp, 1985). For samples studied suggested marine depositional environment. The low ratios of sterane/hopane ranging between 0.15 and 1.48 which is other indicator for marine depositional environment which is consistent with observation for the source rocks studied. In addition, these samples have C₂₉ 20S/ (20S+ 20R) and the C₂₉ ββ / (ββ + αα) ratios in the range of 0.28-0.45 and 0.31-0.61, respectively, suggesting that the solid bitumen is thermally mature.

C 29 ααα 20S / (20S + 20R) steranes ratio was calculated for the studied Formations this ratio increase with maturity increasing. For samples studied the average for this ratio was calculate and the averages were as follow: for the Jeribe Formation the average was 0,417, for the Euphrates Formation the average was 0,31 for the Transition beds the average was 0,37 in Ajeel oil field. In Hamrin oil field the range for this ratio was as follow: for the Jeribe Formation the average was 0,40, for the Euphrates Formation the average was 0,43 and one sample from Dhiban Formation with 0,46 value. These values suggesting that the solid bitumen in all Formations studied generally is thermal mature. The Jeribe Formation in Ajeel oil field is the most mature Formation with short filling history, while Euphrates Formation in this oil field show variety in maturity from low to high with long filling history. The Euphrates Formation show high maturity with short filling history in Hamrin oil field and the Jeribe Formation show variety in maturity in Hamrin oil field with long filling history in Hamrin oil field. The figure (3.5) the range averages

The Hopanes/Regular sterane ratios were calculated for the Formations studied in both oil fields studied (Ajeel and Harmin). This ratio was relatively high in all Formations studied which suggest that solid bitumen was derived from algae organic matter input which is similar for the source rock studied. The ratio of hopanes /regular steranes for the Formations studied was as average as a follow: for the Jeribe Formation the average was 5,37, for the Euphrates Formation the average was 4,15 and for the Transition Beds the average was 3,7 in Ajeel oil field. In the Harmin oil field this ratio as average was for the Jeribe Formation 5,02, for the Euphrates Formation was 6,4 and one sample from Dhiban Formation with value 5,8.

The tricyclic/hopanes ratio calculated for the Formations studied in Ajeel and Harmin oil fields and the result was as follow: the Jeribe Formation show high value from this ratio in Ajeel oil field with average value 0,1 and 0,064 was the average value from this ratio for the Jeribe Formation in Harmin oil field. These observations indicate that different from this ratio for the Jeribe Formation in Ajeel and Hamrin oil field. The Euphrates Formation has 0,05 average value in Ajeel oil field and average value 0,045 in Hamrin oil field. The Transition Beds in Ajeel oil field the average value was 0,1 and one sample from Dhiban Formation in Hr. 40 well with 0,0486 value from this ratio (Fig). The tricyclic/hopanes ratio generally compared in both oil fields studied (Ajeel and Harmin oil fields) and Ajeel oil field shows high from this ratio, while in the Harmin oil field this ratio was low.

The BNH/(BNH+C29 Hopane) ratio for the Formations studied was calculate for the formations studied in both oil fields and the average values were as a follow: in Ajeel oil field Jeribe Formation has average value 0,44 , for the Euphrates Formation the average value was 0,29 and for the Transition Beds the average value was 0,17. In Harmin oil field the average values from this ratio was as follow: for the Jeribe Formation the average was 0.117, for the Euphrates Formation the average was 0,074 and one sample from Dhiban Formation with 0,097 values. The bisnorhopane to bisnorhopane+norhopane ratio can be used to provide information on the redox condition and the organic matter input for the oils. The high concentrations of BNH indicate deposition of source rocks under anoxic conditions (Katz and Elrod, 1983; Mello et al., 1988; Curiale and Odermatt, 1989). The extract from reservoir Formation studied in Ajeel oil field show high values from the ratio of the BNH/(BNH+ C29 hopane) comparing with values from this ratio in Hamrin oil field and there is inverse relationship between the DBT/P ratio and BNH/(BNH+C29 hopane). The samples studied in Hamrin oil field show high values from DPT/P ratio and low values from BNH/(BNH+C29 hopane) ratio and Ajeel oil field show low values from DBT/P ratio comparing with Hamrin oil field and high values from BNH/(BNH+C29 hopane) ratio.

Biomarkers oil field's correlation, the main biomarker parameters in both oil fields studied were compared. The abundances of the tricyclic trepans are high in Ajeel oil field and it is very low in Hamrin oil field. The relative high BNH/(BNH+C29 hopane) ratio in Ajeel oil field

comparing to this ratio in Hamrin oil field and high DBT/P ratio in this field which indicate more from sulfur content in Hamrin oil field, which may indicate different source rocks or different ratios from the same source rocks provide these oil fields.

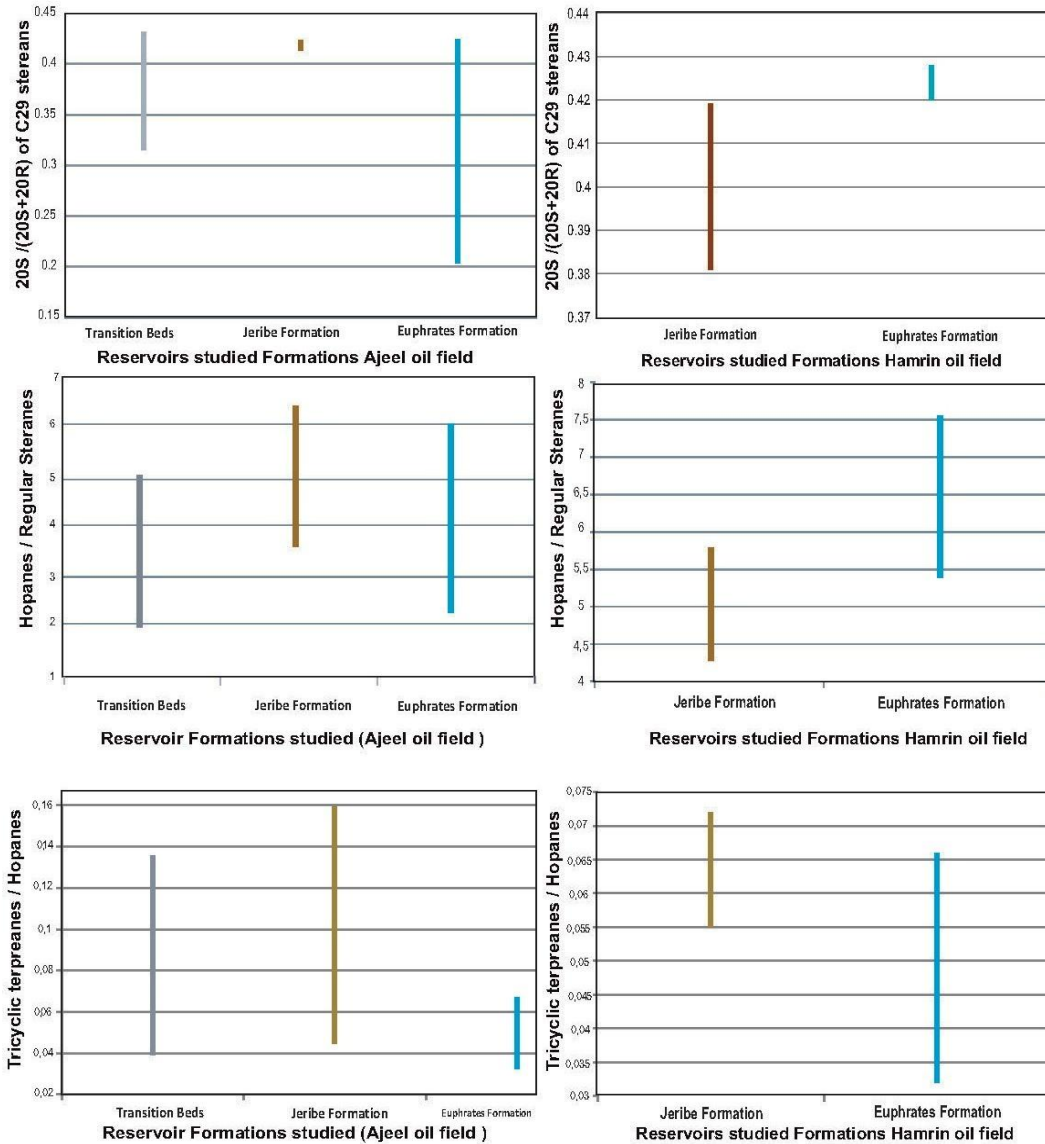


Fig .4.6. Distribution of some biomarker composition in Ajeel and Harmin oil fields. 20S/(20S+20R) of C29 steranes and hopane /regular steranes and tricyclic terpane/ hopanes. The data are from 191m/z mass fragment. The data show the range averages values for the calculated ratios in all wells studied for each oil fields studied. The wide range of variation in values indicates more filling history.

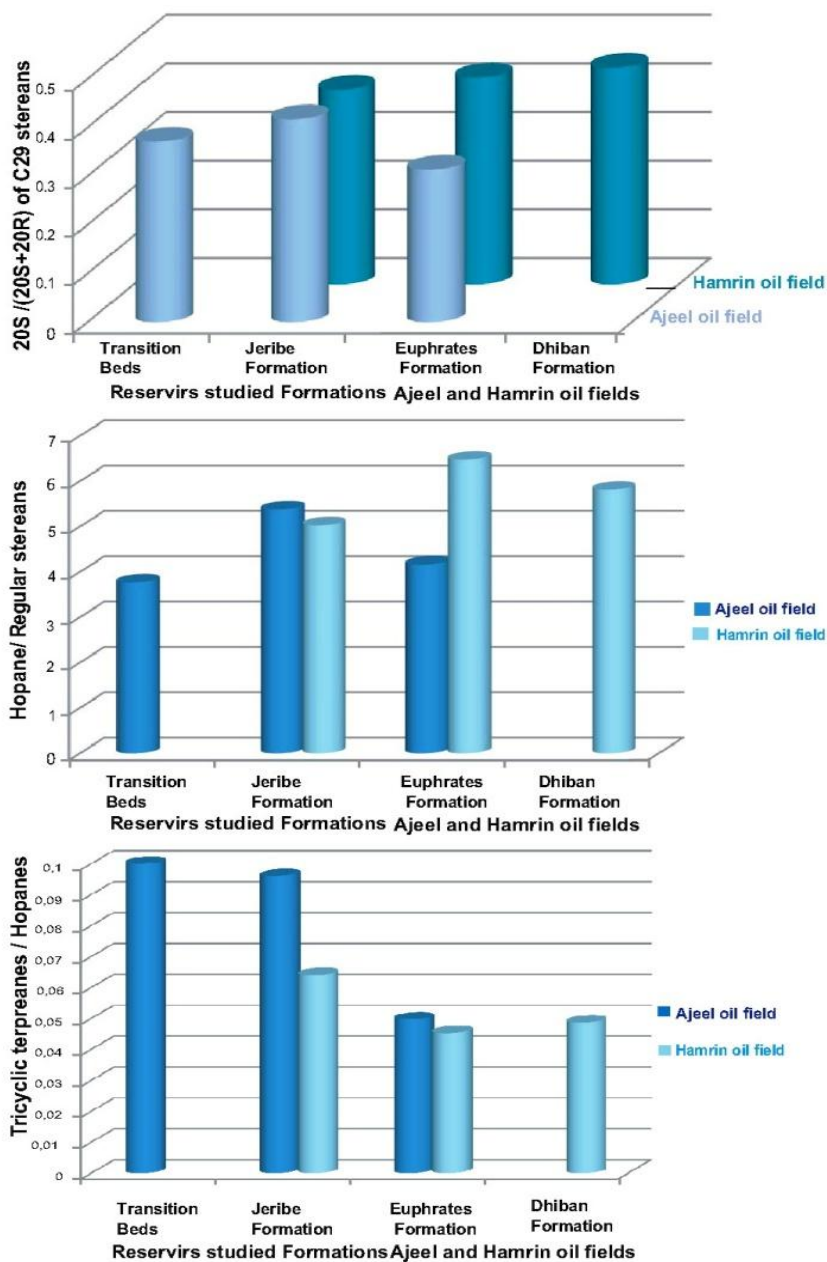


Fig. 4.7. Distribution of some biomarker composition in Ajeel and Harmin oil fields. 20S/ (20S+20R) of C29 steranes and hopane /regular steranes and tricyclic terpane/ hopanes. The data are from 191m/z mass fragment. The figure show the calculate averages from these ratios in all oil field and for the both oil fields studied (Ajeel and Harmin oil fields).

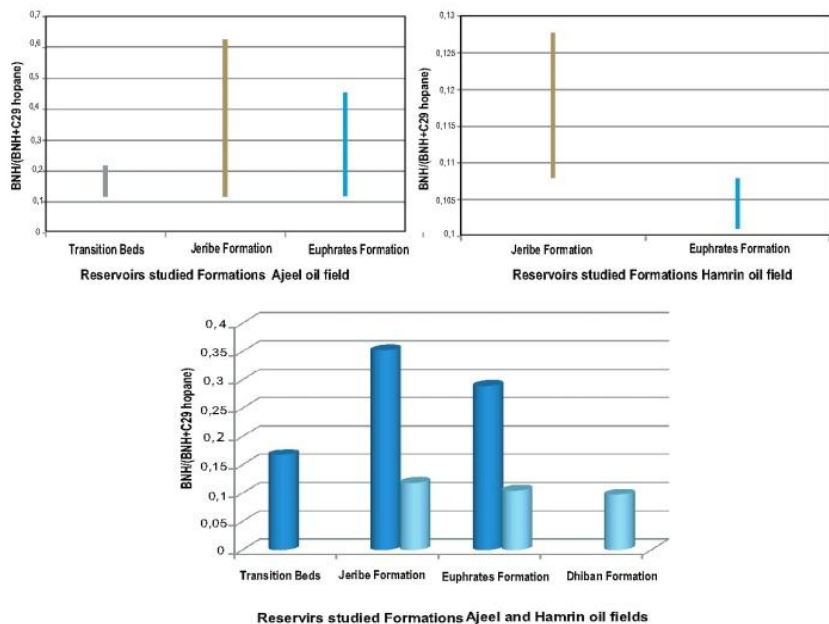


Fig.4.8. Distribution of BNH/ (BNH+C29 hopane) biomarker composition in Ajeel and Harmin oil fields. The data are from 191m/z mass fragment. The figure show the calculate averages from this ratio in all oil field and for the both oil fields studied (Ajeel and Harmin oil fields).

6. Biomarker distributions of the aromatic fraction

The aromatic hydrocarbon fractions for study samples are dominated by sulfur-aromatic compounds which are dibenziothiophen and methyl dibenzothiophene. The DBT/P ratio was calculated for the Formations studied and it was as average in Ajeel oil field for the Transition Beds 1,185, 0,873 for the Jeribe Formation and 1 for the Euphrates Formation. The DBT/P ratio in Harmin oil field was as average for the Formation studied as follow 1,48 for the Jeribe Formation 1,3 for the Dhiban Formation and 1,29 for the Euphrates Formation. The extract from solid bitumen in Hamrin oil field show high from DBT/P ratio than Ajeel oil field which indicate high sulfur content in this bitumen.

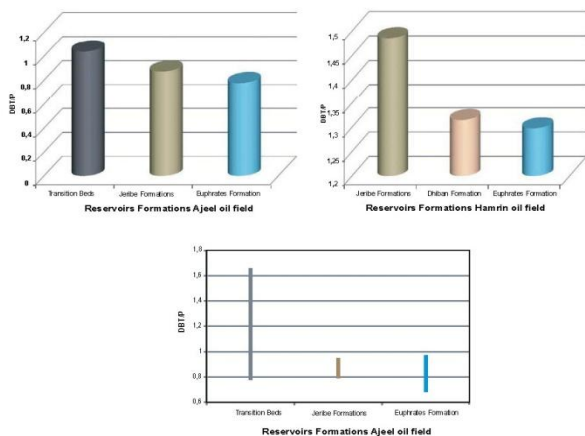
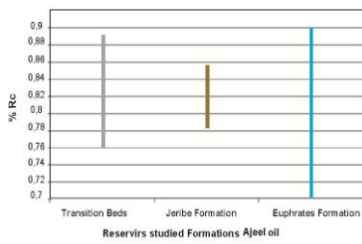
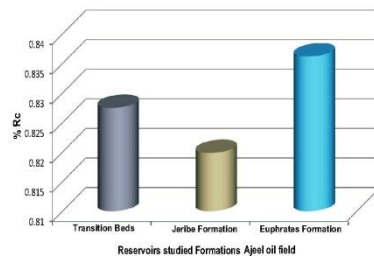


Fig. 4.9. Distribution of DBT/P average ratio in Ajeel and Harmin oil fields and the(down) figure show the range averages from this ratio in Ajeel oil field.

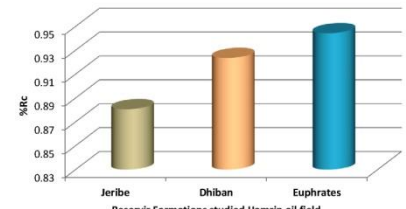
Methylphenanthrene index(MPI-1) is generally accepted maturity parameter and appears useful as vitrinite reflectance (Radke et al., 1982). The $\%R_c$ calculated by using the methylphenanthrene ratio (MPI-1) and by using Radke,1988 equation ($0,60*MPI-1+0,40$) for the studied samples and the $\%R_m$ calculated by using the methylidibenzothiophene ratio (MDR) and by using Radke,1988 equation ($0.073*MDR+0,51$) to study the maturity for the formations studied in both oil fields. The Euphrates Formation show high value average from Rc reach 0.944 in Hamrin oil field comparing with it is average value in Ajeel oil field which is 0.83. The Jeribe Formation has almost similar values from Rc average in Ajeel and Hamrin oil field which is (0.819 and 0.88) respectively. A plot is draw between the calculated vitrinite reflectance values obtained from MPI-1 and MDR Rm and Rc to show the and it shows that Miocene bitumen had peak oil generation window thermal maturity(Fig 3.10).



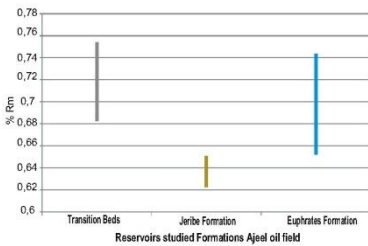
(a)



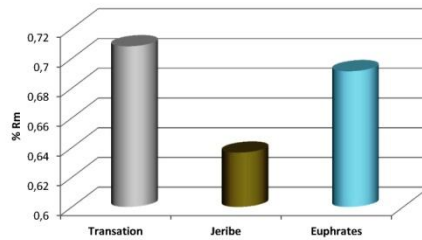
(b)



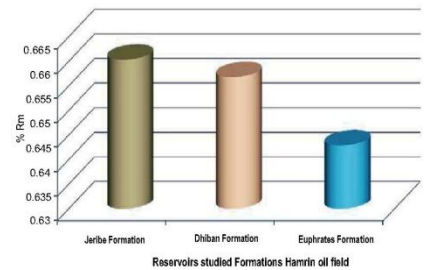
(c)



(d)



(e)



(f)

Fig. 4.10. Show Distribution of calculated vitrinite reflectance values, Rc and Rm obtained from MPI-1 and MDR aromatic maturity parameters respectively. The figures(a,b,d,e) inform Ajeel oil field and(c,f) inform Hamrin oil field.

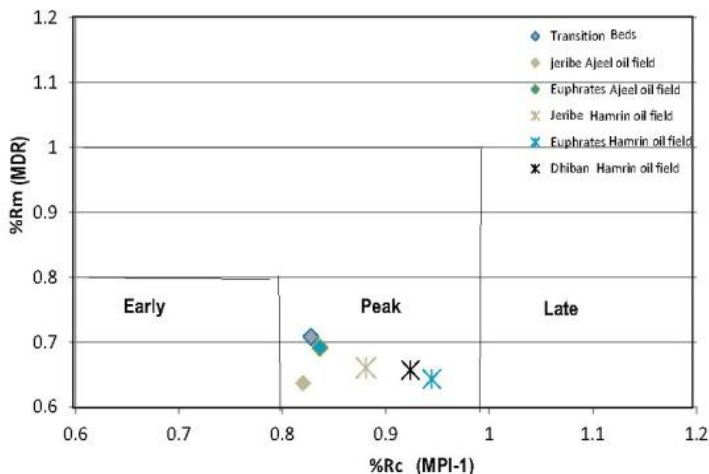


Fig. 4.11. Plots between calculated vitrinite reflectance values, R_c and R_m obtained from MPI-1 and MDR aromatic maturity parameters respectively. The plots show that the bitumen studied is in the peak oil generation.

7. Conclusion remarks

The result from these discussions of biomarker parameters indicates that the solid bitumen was derived from a source rocks that was deposited in anoxic conditions and contained marine organic matter. Different in maturity and distribution of biomarkers indicate that the solid bitumen studied is derived from mixing source rocks.

Difference in the biomarkers ratios in the two fields studied (Ajeel and Hamrin oil fields). The Formations studied generally show high amount from extraction in (ppm) in Hamrin oil field comparing with it in Ajeel oil field. High DBT/P ratio in Hamrin oil field with low from BNH/(BNH+C29 hopane) ratio comparing with Ajeel oil field which indicate high sulfur content in Hamrin oil field. The abundance of the Tricyclic in the Ajeel oil field, while slight from Tricyclic in Hamrin oil field. From above can be infer that the solid bitumen studied in the Ajeel and Hamrin oil fields is derived from mixing source rocks.

Difference in the maturity and amount of extraction in (ppm) and the biomarkers distribution for the Euphrates Formation in the fields studied (Ajeel and Harmin oil fields). very high amount from extraction in (ppm) with dark color for the solid bitumen extract from Euphrates Formation in Hamrin oil field(Fig) and low amount from extraction in(ppm) with light color from this Formation in Ajeel oil field indicate different source rocks are the origin for the bitumen studied

The Euphrates Formation show high maturity in Hamrin oil field, while this Formation show low maturity in Ajeel oil field depending on different maturity parameters from bulk analysis and biomarker parameters. High average for the C 29 $\alpha\alpha\alpha$ 20S / (20S + 20R) steranes ratio and high hopane/regular steranes ratio indicate that the solid bitumen in Euphrates Formation in Harmin oil field is mature. DBT/P calculate ratio for samples studied from Euphrates Formation in

Hamrin oil field is high comparing with samples studied from this Formation in Ajeel oil field(Fig). From above could be said that different source rocks provide Euphrates Formation in the two oil fields studied or different ratio from the same source rocks. The Jeribe Formation also show little different in behaved in both oil fields studied. In Ajeel oil field the Jeribe Formation is the most mature formation comparing with the Euphrates Formation and the Transition Bed, while the Euphrates Formation is the most mature formation in Hamrin oil field comparing with the Jeribe Formation after the Dhiban Formation which contains a high concentration of Anhydrite nodules. For this reason, it is mainly poor reservoir unit.

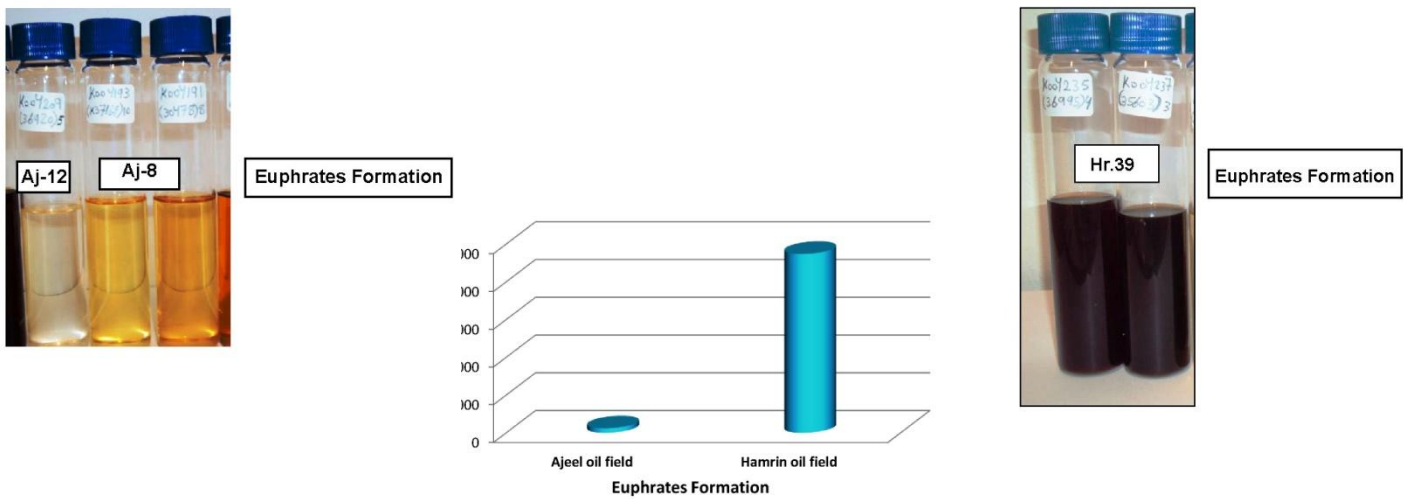


Fig. 4.12. Bar chart show the high extraction in(ppm)from the Euphrates Formation in Hamrin oil field and the lower from it in the Ajeel oil field with select photos the (left) extract from Hamrin oil field and the(right) from Ajeel oil field.

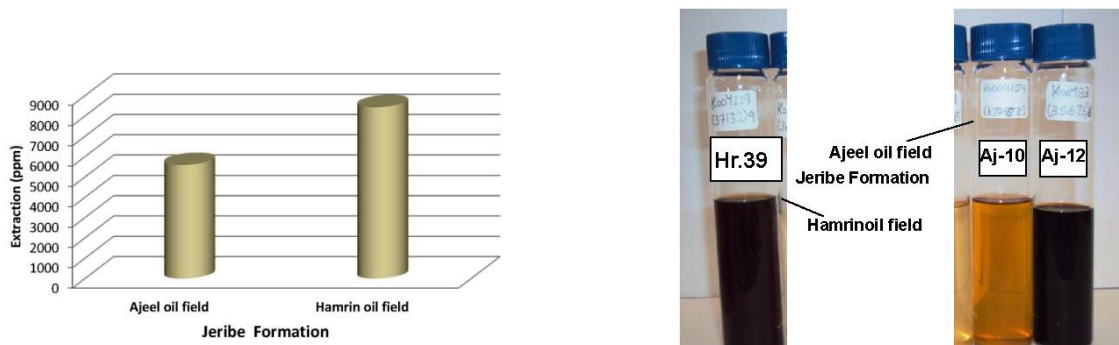


Fig.4.13. Bar chart show the extraction from Jeribe Formation in Hamrin oil and Ajeel oil field with select photo for extraction from this Formation in both oil fields.

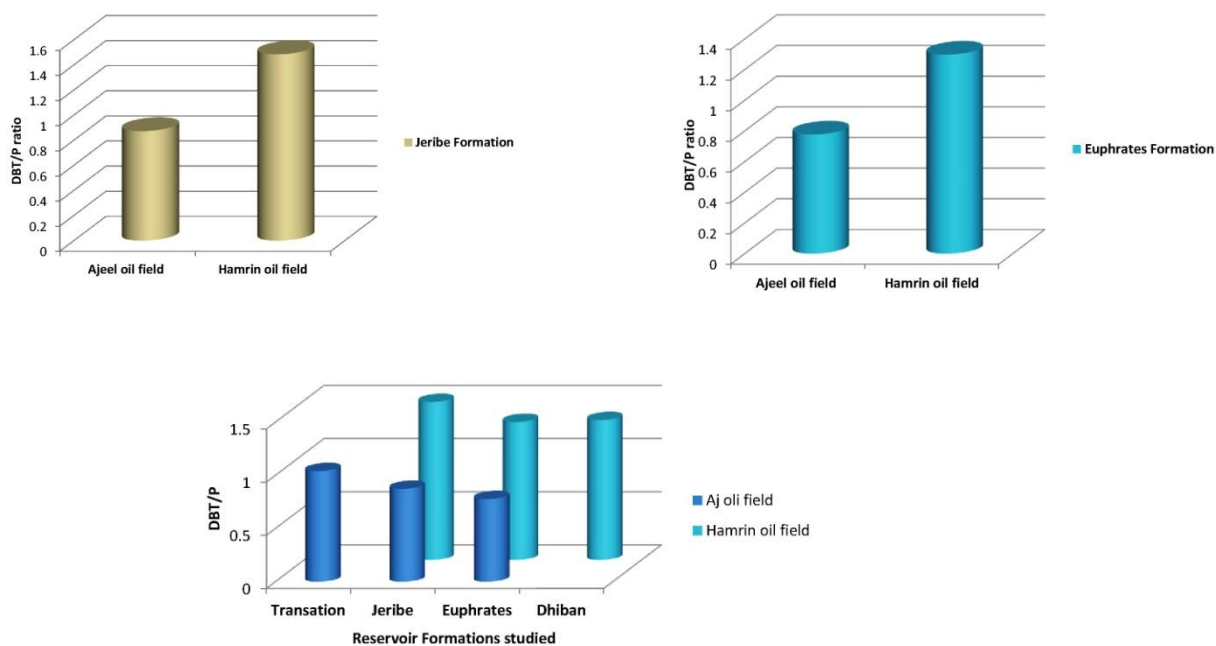


Fig . 4.14. DBT/P ratio for the Jeribe Formation (Left) and for the Euphrates Formation (right) in both oil field studied and show the high from this ratio in Hamrin oil field for the Jeribe and Euphrates Formation. The down figure show the DPT/P ratio in both fields studied.

8. Geochemical Correlation

Introduction

The relationship between oil (liquid and solid oil) and its source rock is of interest for scientific and economic reasons, and understanding this relationship is a major goal of organic geochemistry and successful oil-source rock correlations require knowledge of petroleum generation, expulsion, migration, and entrapment (Curiale, 1993). Geochemical correlation can be used to establish petroleum systems to improve exploration success, define reservoir components to enhance production, and identify the origin of petroleum contaminating the environment (Peters et al., 2005). The differences in the chemical composition of the oil and the soluble organic matter in the source rock are a function of migration fraction (Leythaeuser et al., 1987). Several processes alter both the oil and the organic matter remaining in the source, for the source rock, further altering the chemical composition of both the Kerogen and the bitumen, and the oil is affected by migration fraction and postmigrational alteration which is occurring after the oil has reached a reservoir. Both of these factors will change the chemical character of the organic matter in the source rock or the oil.

It has become increasingly clear that a simple set of chemical correlations between oil and the extractable organic matter in a proposed source is not sufficient to establish an oil- source rock correlation. Geologic data supporting are also necessary. To investigate the link between solid bitumen and source rock extracts correlation have been proposed, using both bulk geochemical data and molecular distributions .

9. Solid bitumen-Source rocks correlation

9.1 Correlation basis of bulk properties

Correlation between solid bitumen and its related source rock is difficult to establish on the basis of bulk properties. For this study the **production index (PI)** which is represents the ratio of distillable organic matter to total amount of organic matter generated from a sample by pyrolysis and pyrolysis T_{max} were used to estimate the nature of the hydrocarbon products (i.e., generated or migrated Hunt, 1996). The high production index values are generally due to migrated hydrocarbons (Fig) show that the solid bitumen could have been generated from the source Formations studied and migrated into to the reservoir Formations studied. **S₁ relative to S₂** lend evidence for migration of hydrocarbons and the depletion of the S₂ pyrolysis yield indicates that hydrocarbons have been nearly released from source rock (Peters, 1986). Generally, for this study most of the solid bitumen have S₁ pyrolysis yield greater than the S₂ pyrolysis yield which is indicate of migrated hydrocarbons, while the source rock samples have a high S₂ pyrolysis yield than S₁ pyrolysis.

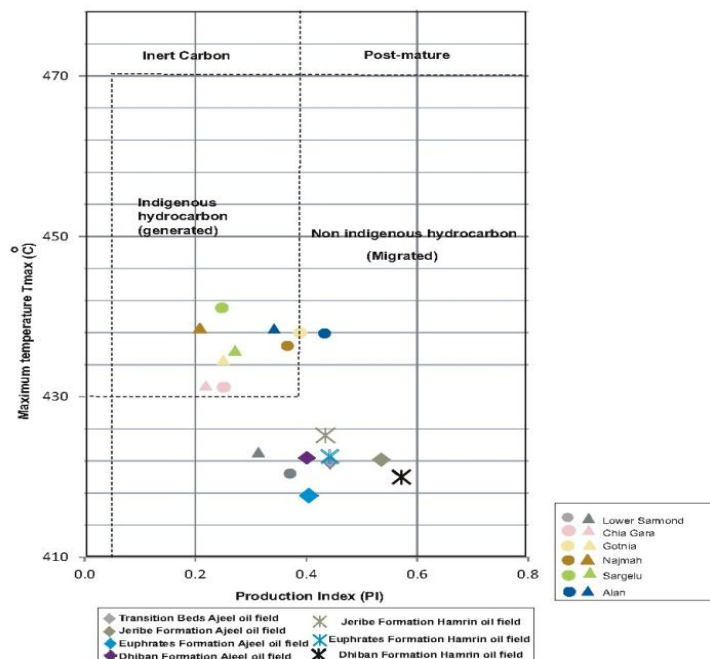


Fig. 4.15. Plot of pyrolysis T_{max} versus production index (PI), showing the maturity and nature of hydrocarbon products of the solid bitumen and source rocks samples.

9.2 Biomarker ratios for correlation:

Biomarker ratios and patterns are used mainly in the correlation which is one the most important advantages for them, because they are strengths resistance to biodegradation (Hunt, 1996). There are many biomarkers ratios used in geochemical correlation. For this study some of the more resistant and commonly used ratio is used. This work is based on 27 extracts reservoir samples studied. Biomarker analysis of the extracts solid bitumen appeared that the solid bitumen has multiple source rocks.

The degree of the thermal maturity of oil over the time is called thermal maturity and reflects expulsion maturity and cracking after accumulation (Peters and Cassa, 1994) and it can be determined by ratio of composition of biomarkers alternating with increasing thermal maturity (Philp, 1985). **The cross plots of steranes biomarker parameters C 29 Sterane 20S / (20S + 20R) and $\alpha \beta \beta$ ($\alpha \beta \beta + \alpha \alpha \alpha$) ratios** are used as indicators of maturity and can be used in source rock-migrated material correlation as well. The samples show a range of values with average for the Formations studied in Ajeel oil field for the C 29 Sterane 20S / (20S + 20R) as a follow: for the Transition Beds the average is 0.37, for the Jeribe Formation is 0.41, for the Euphrates Formation is 0.31 and for the Formations studied in Harmin oil field as follow: for the Jeribe Formation is 0.40, for the Dhiban Formation, 0.44 and for the Euphrates Formation is 0.424, while the average from $\alpha \beta \beta$ ($\alpha \beta \beta + \alpha \alpha \alpha$) sterane maturity ratio for the Formation studied in Ajeel oil field as a follow: For the Transition Beds the average is 0.47, for the Jeribe Formation is 0.49 and for the Euphrates Formation is 0.4 and the average from this ratio for the Formation studied in Hamrin oil field was as follow: for the Jeribe Formation is 0.49, for the Dhiban Formation is 0.49 and for the Euphrates Formation is 0.48. The cross-plots suggest that the solid bitumen is thermally mature and it is less mature than the source rocks derived from them. The maturity from biomarker sterane ratios is compared with maturity from the bulk analysis which is show in(Fig 3.14) and the same result observed. The reslut from bulk analysis and biomarker show also different in maturity for the Euphrates Formation in both oil field studied and show that the Euphrates Formation is less mature in Ajeel oil field, while it is high mature in Hamrin oil field.

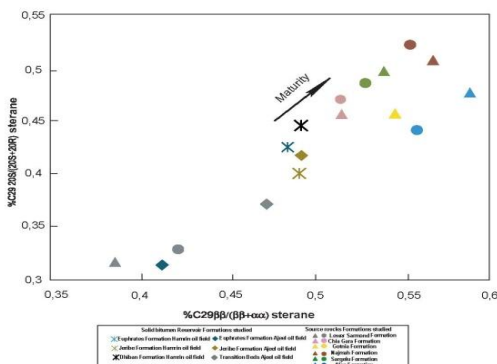


Fig. 4.16. Plot of two steranes parameters to correlated the maturity of the solid bitumen and the extract from the source rocks studied. The plots show that the solid bitumen is lower in maturity than the source origin.

Based on the saturated hydrocarbon distribution of the hopane (**191 m/z**) and steranes (**217 m/z**) as well as tricyclic terpanes (m/z 191), tetracyclic (m/z 191) for the solid bitumen extract and the source rocks extract were compared and show strongly reflect a close genetic relationship between the solid bitumen and the source rock (Fig 3.15,16). The distribution of aromatic compound in the solid bitumen was applied for solid bitumen source rocks correlation. Based on the Aromatic sulfur compound dibenzothiophene (DBT), methyl dibenzothiophene (MDRT) from the (**184 and 198 m/z** mass fragmentograms) respectively, and phenanthrene (**178 m/z**), methylphenanthrenes (**192 m/z**) were compared for the extract solid bitumen and source rocks extract Fig (3.17, 21) and show relationship between the solid bitumen and the source rocks.

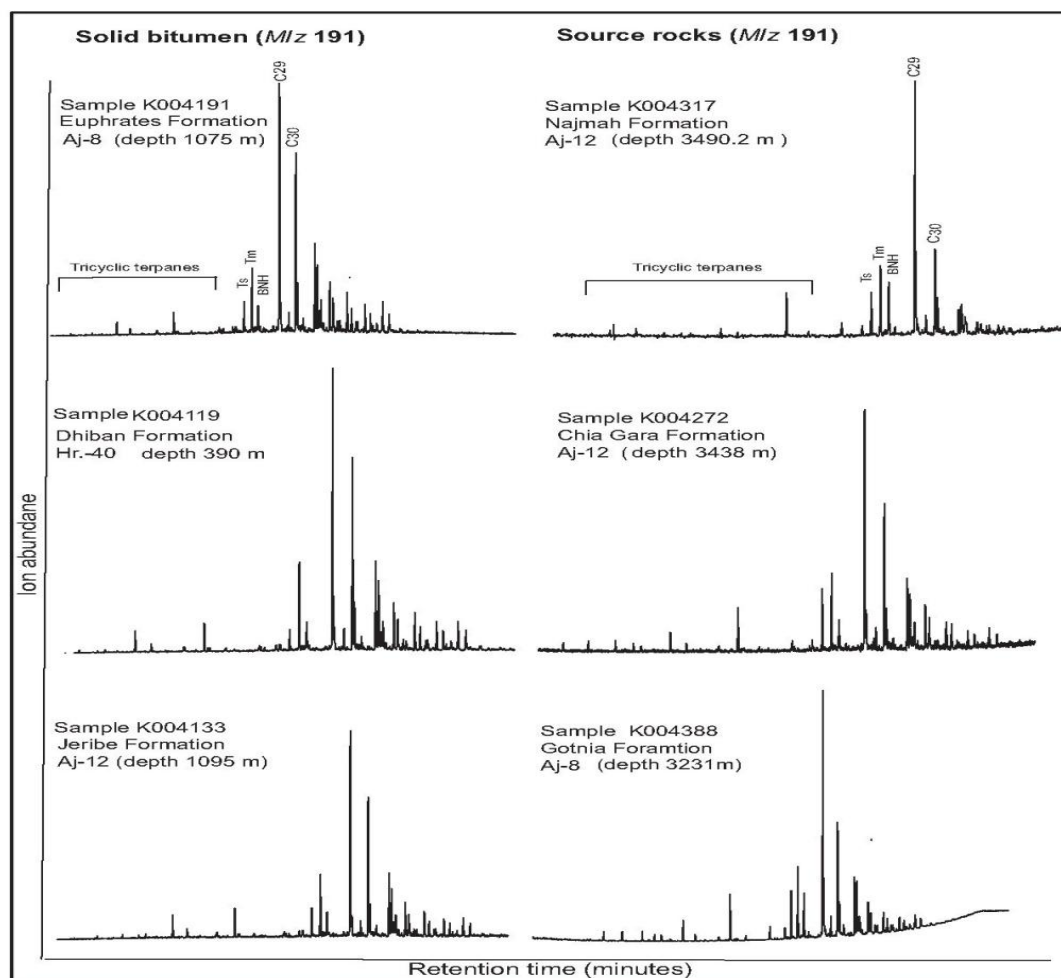


Fig. 4.17. The m/z 191 mass fragmentograms of saturated hydrocarbon fractions of the solid bitumen and the source rock extracts.

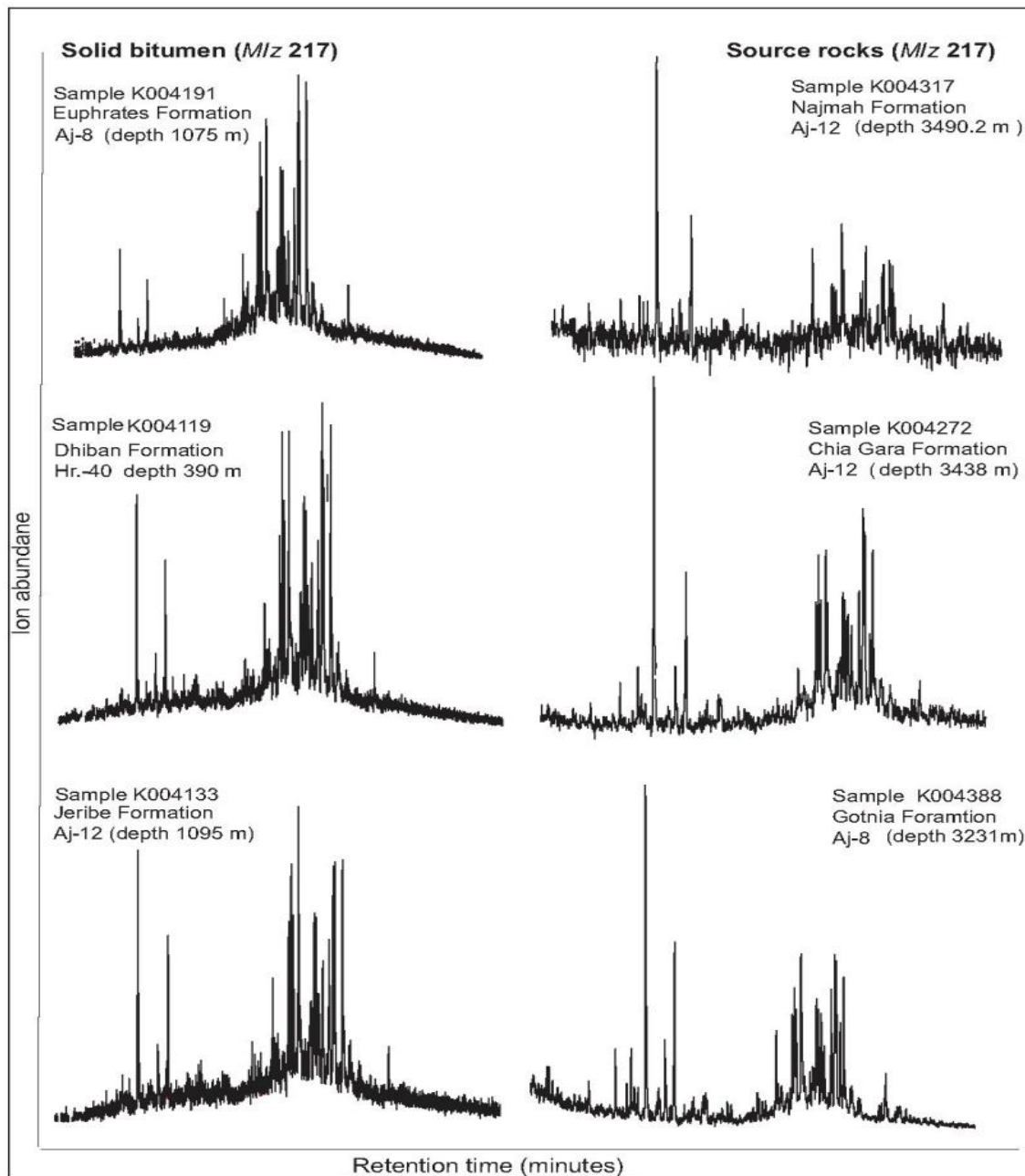


Fig. 4.18. The m/z 217 mass fragmentograms of saturated hydrocarbon fractions of the solid bitumen and the source rock extracts.

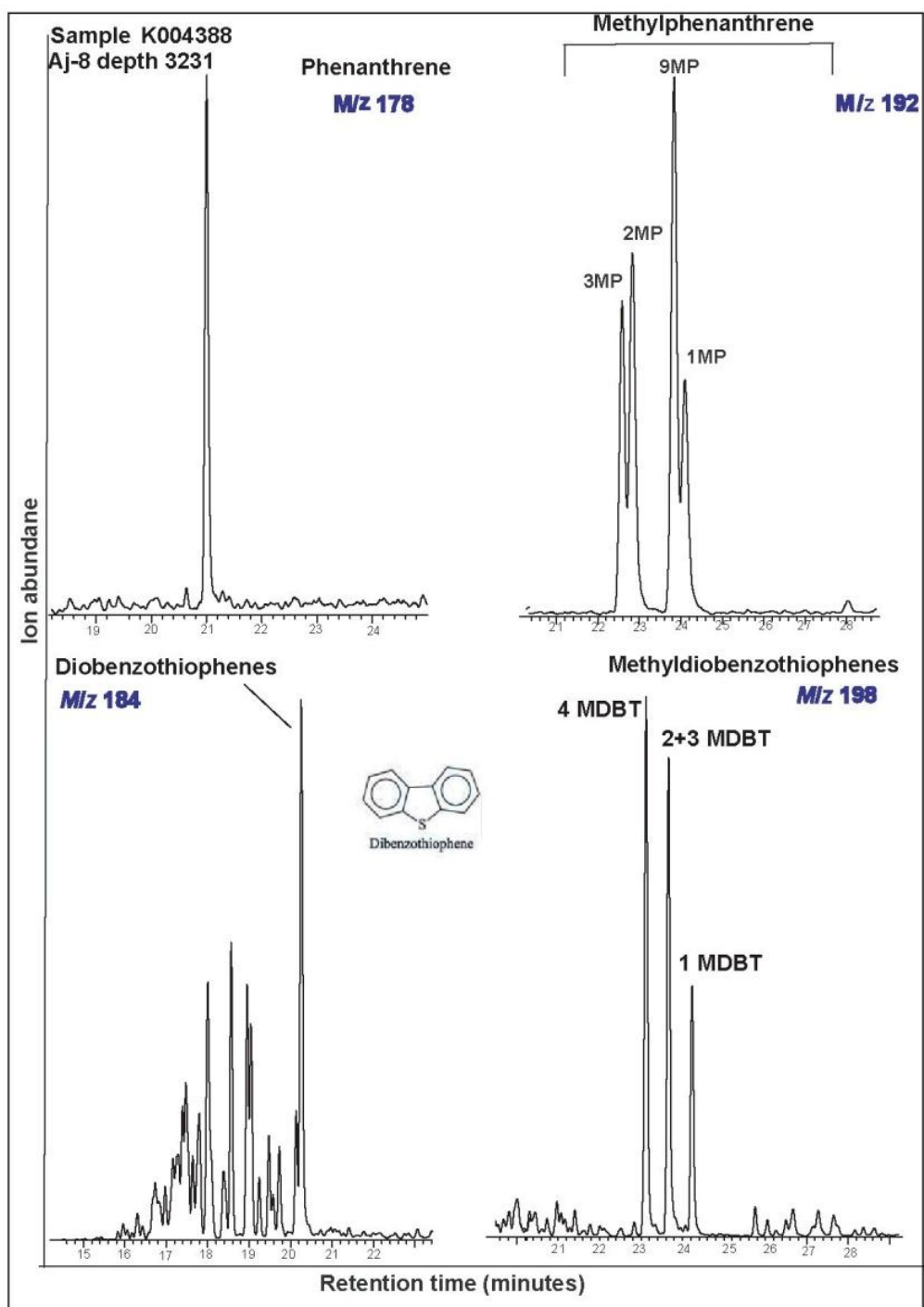


Fig.4.19. Mass chromatograms of phenanthrene, methylphenanthrenes and dibenzothiophenes and methylthiophenes for source rock select extract sample from Gotnia Formation.

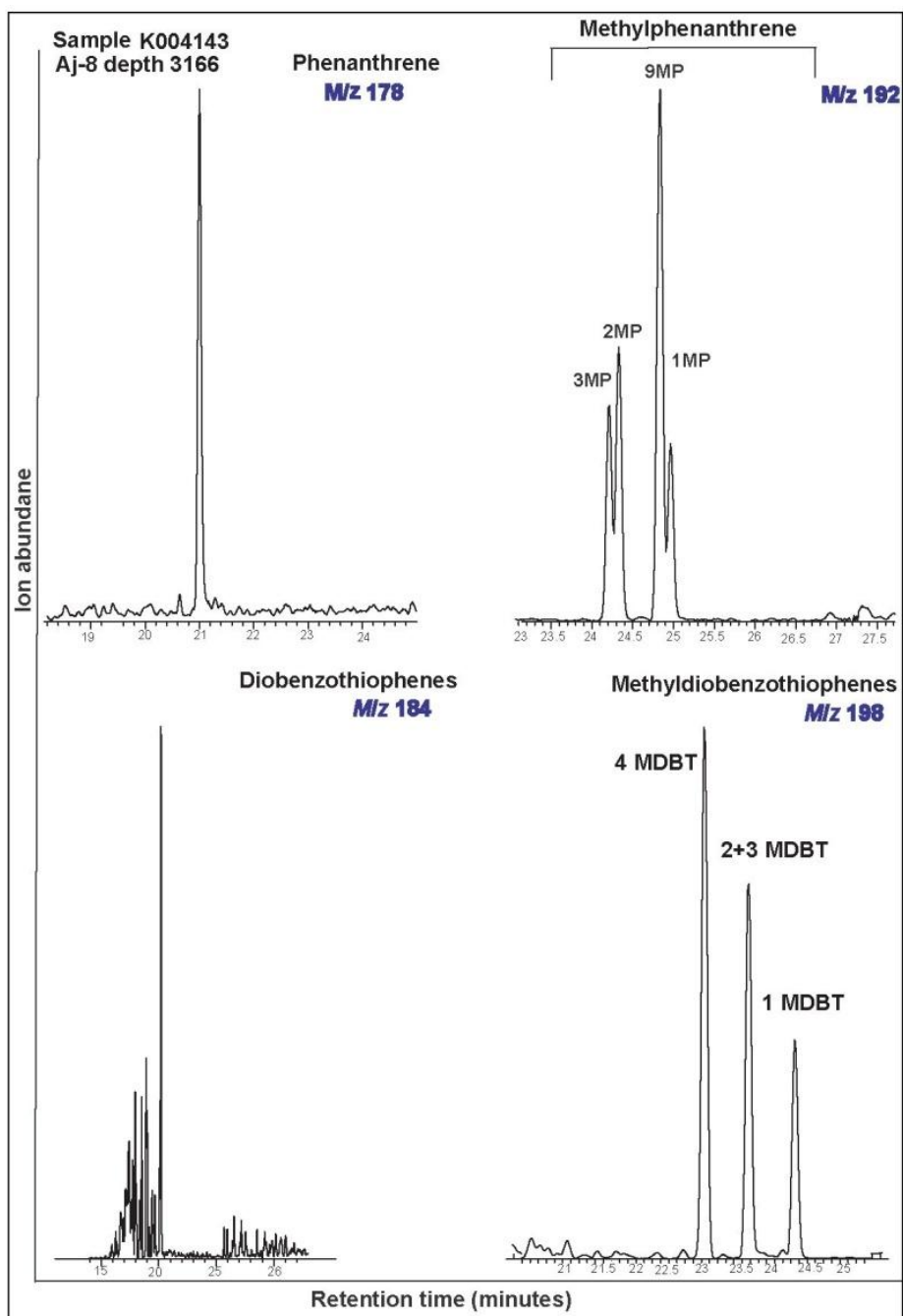


Fig.4.20. Mass chromatograms of phenanthrene, methylphenanthrenes and dibenzothiophenes and methyldibenzothiophenes for source rock select extract sample from Najmah Formation.

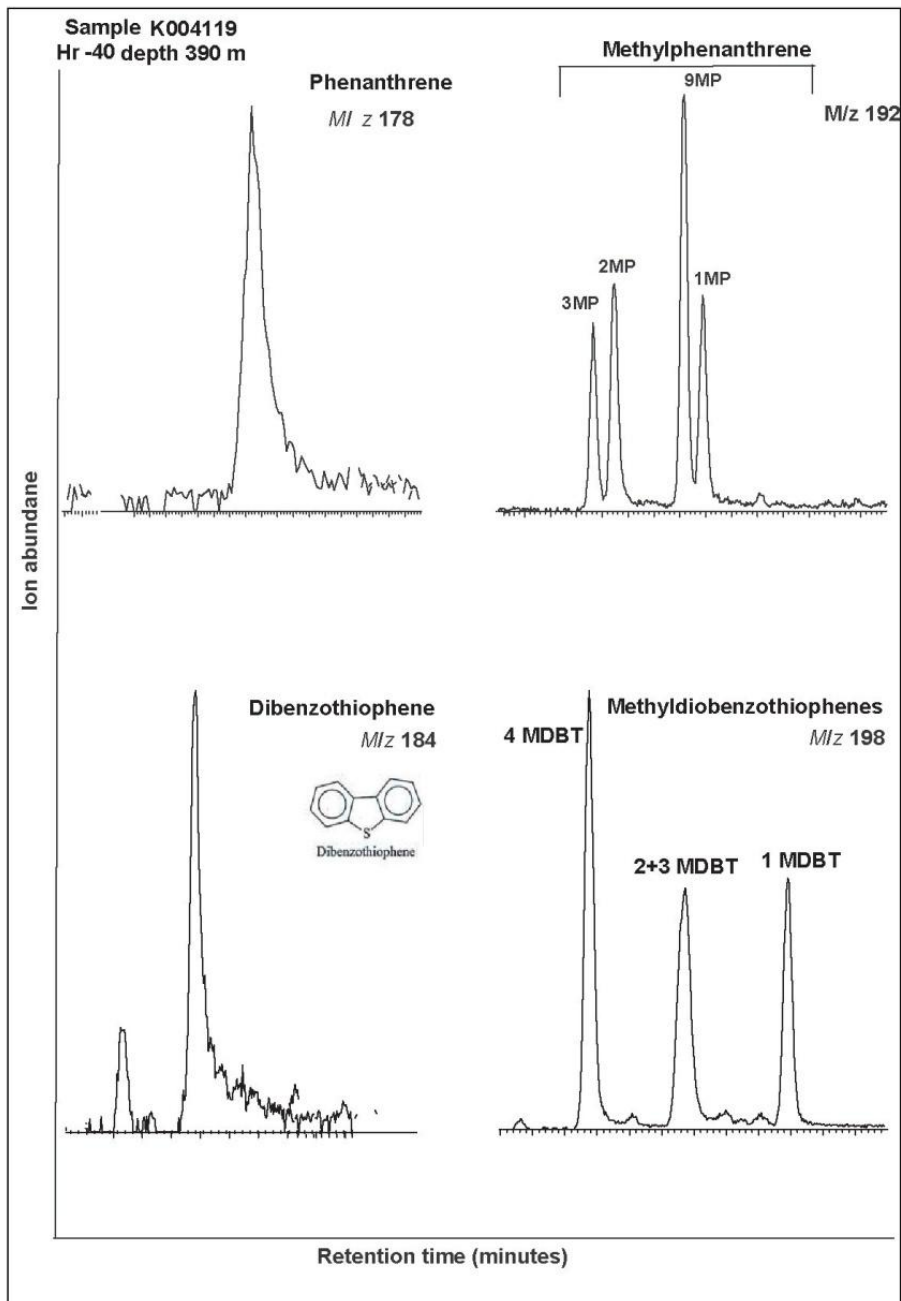


Fig.4.21. Mass chromatograms of phenanthrene, methylphenanthrenes and dibenzothiophenes and methylthiobenzothiophenes for solid bitumen select extract sample from Dhiban Formation Harmin oil field

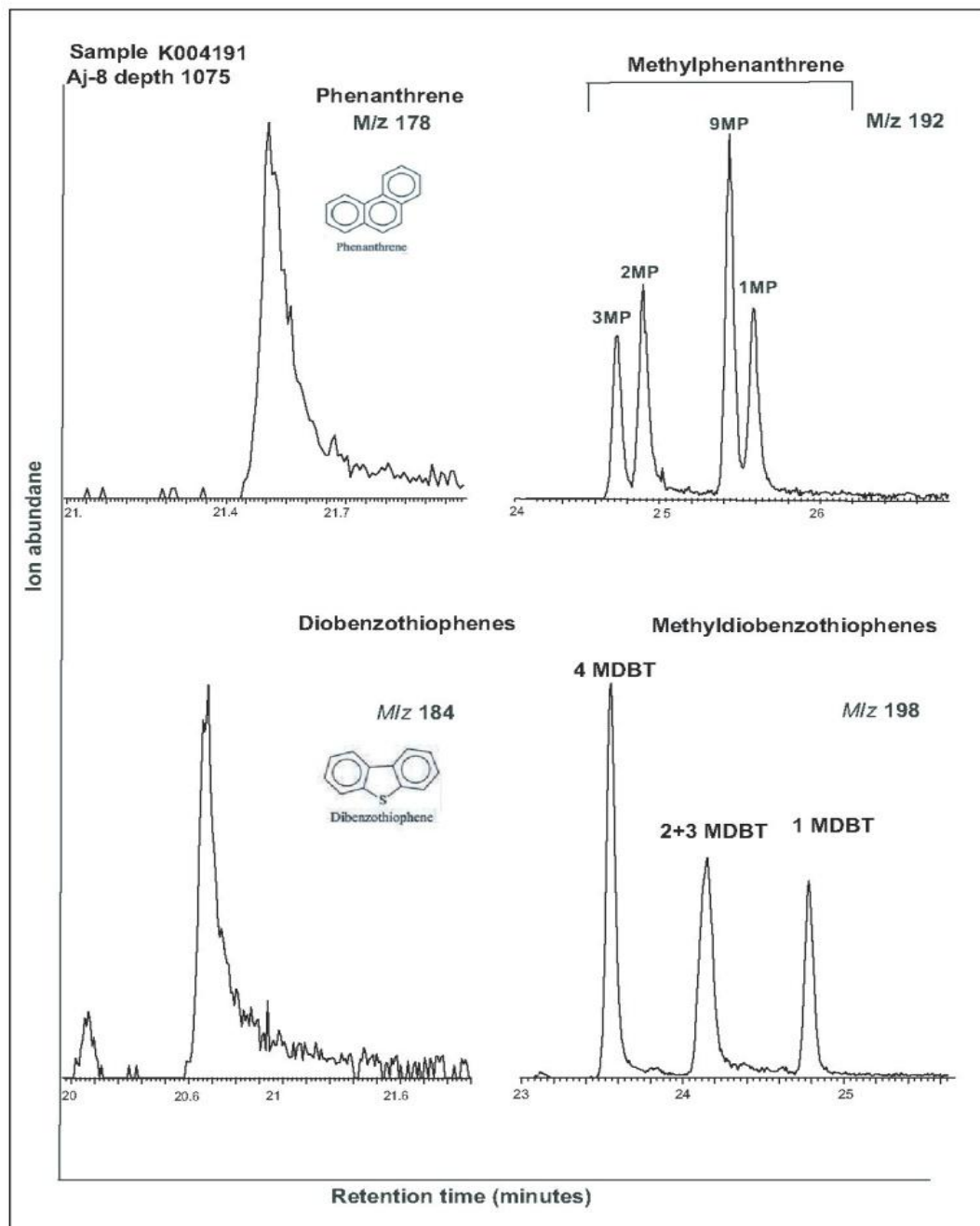


Fig.4.22. Mass chromatograms of phenanthrene, methylphenanthrenes and dibenzothiophenes and methyl dibenzothiophenes for solid bitumen select extract sample from Euphrates Formation Ajeel oil field.

Sterane Ternary diagram: Ternary plots of sterane carbon number are often used to facilitate oil-oil and oil-source rock correlation, and to provide a general comparison of depositional environments (Bowden et al., 2006) and can be to indicate depositional environment (Philp, 1985). The calculated ratio of the (C27%, C28%, C29%) regular steranes for extract solid bitumen from reservoir rocks and extract source rocks from Formations studied are plotted on the ternary diagram. The distribution of regular sterane are very similar and show the same rocks and environment (Carbonate rocks and marine environments, respectively) for both extract bitumen (Fig.3.22). The plots show that the bitumen in Jeribe reservoir Hamrin oil field is providing with high ratio from the Sargelu Formation, while the bitumen in this reservoir in Ajeel oil field is providing with high ratio from the Chia Gara Formation. The bitumen in Euphrates reservoir in Ajeel oil field plot near to the Gotnia Formation which mean the Gotnai Formation is providing the high ratio from this bitumen , while in Hamrin oil field is plot between the Gotnia and Chia Gara Formation which mean different ratio from these source rocks providing this bitumen.

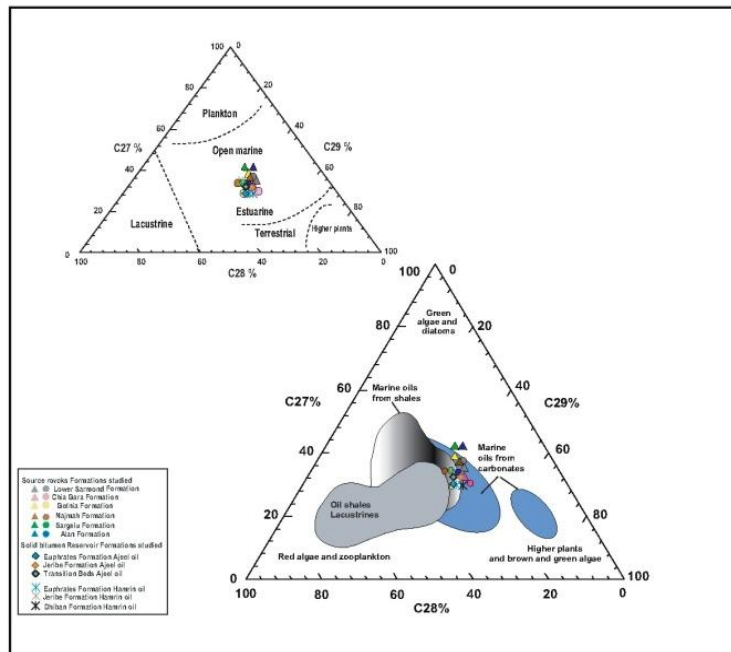
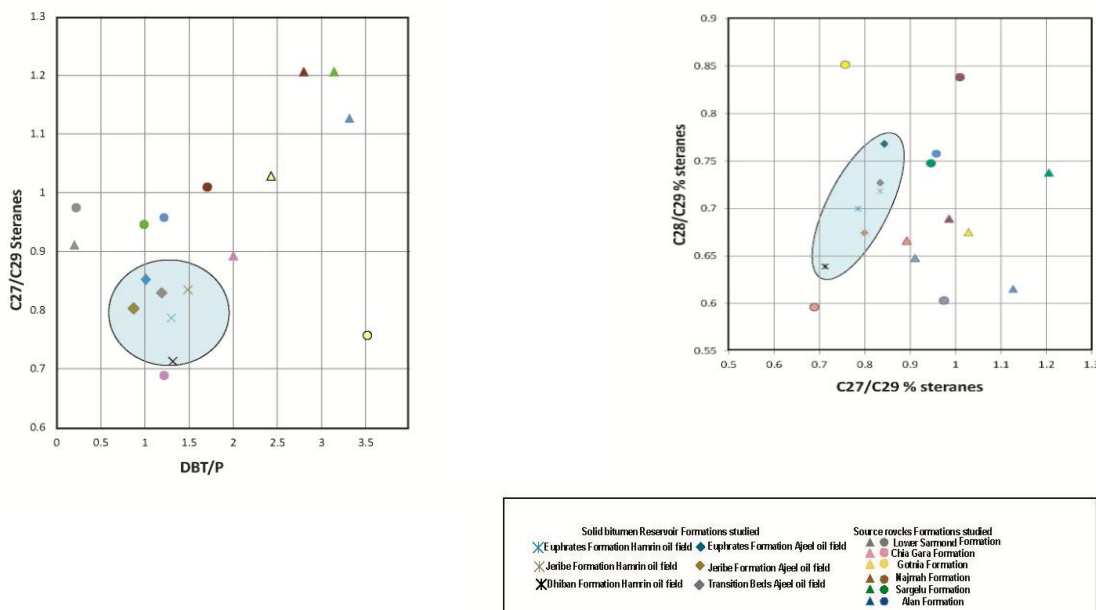


Fig.4.23. Triplot providing the composition of the C27-C29 regular steranes of the source rock and bitumen from the reservoir Formations showing the strong relationship between them

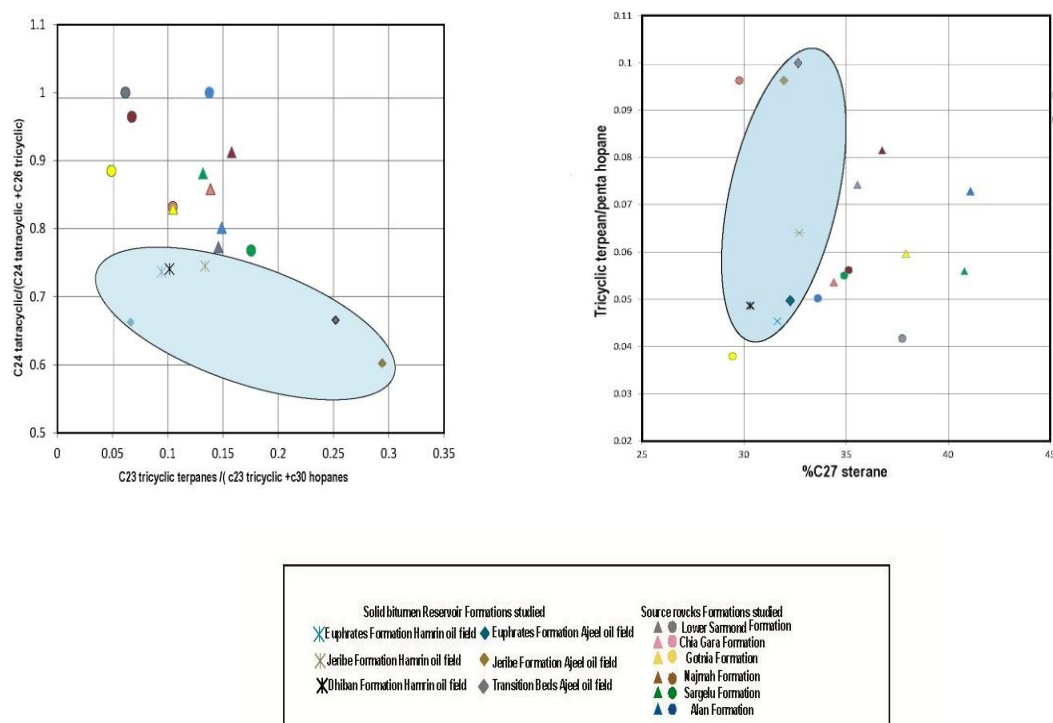
The **C27/C29 regular sterane ratio versus C28/C29 regular sterane ratio** are used and show that plots from these ratio for the solid bitumen and source rocks have strong relation between them. The same above result could see strong relation between the bitumen in the Euphrates reservoir Formation from Ajeel oil field and the extract from the Gotnia source rock, while this bitumen in this reservoir Formation in Hamrin oil field show strong relation with extract from source Chia Gara Formation then Gotnia Formation (from well Aj-8) which is mean the high ratio from Chia Gara Formation providing this solid bitumen then the other Formations providing the complete ratios and may be this explained the different in maturity and extract and the distribution of the biomarker for the bitumen in the Euphrates Formation in the two oil fields studied. The solid bitumen extract from Dhiban Formation in Harmin oil field and extract form the Chia Gara Formation in well Ajeel-12 have strong relation as show in the most plots diagram.

The **DBT/P ratio versus C27/C29 regular sterane ratio** is used and show relation between extract solid bitumen in generally and extract from source rocks studied. The plots in general show that the Sargelu Formation is provide the high ratio from the bitumen in the Jeribe reservoir Formation in the Hamrin oil field, while the Chai Gara Formation provided the high ratio to this reservoir Formation in Ajeel oil field.



Fig(4.24). Plots of different calculate ratios for correlation between the source rock extract and bitumen studied. The (left) DBT/P ratio versus the C27/C29 sterane and the (right) C27/C29 sterane versus the C28/C29 sterane . The plots in both figures show strong relationship between them.

The ratio of the tetracyclic terpane (C24)/ (C24+C26 tricyclic terpane) versus the ratio of the (C23) tricyclic / (C23 tricyclic+C30 hopane) and the ratio of the %C27 sterane versus the ratio of the Tricyclic terpane/penta hopane for the bitumen studied and source rocks extract show the same result above. The Jeribe Formation in Ajeel oil field had high ratio from tricyclic which make it plot far the source rocks extract in the plot of the (C23)tricyclic / (C23tricyclic+C30 hopane) as show in the Fig(3.23).



Fig(4.25). Plots of different calculate ratios for correlation between the source rock extract and bitumen studied. The (left) C24 tetracyclic/(C24 tetracyclic+C26 tricyclic) ratio versus the C23 tricyclic terpane/(C23 tricyclic+C30 hopane) and the (right) %C27 sterane versus the tricyclic terpane/penta hopane.

10. Conclusions remarks:

Solid bitumen complicate correlation studies because of their highly variable, sometimes refractory character. They consist of a wide variety of organic materials (Peters et al., 1993). Curiale (1986) divides solid bitumen into pre-oil and post-oil products using biomarkers and supporting data. Most pre-oil bitumen is intimately associated with their source rocks, while post-oil bitumen has undergone extensive migration prior to alteration. In this study extract from

solid bitumen samples studied are associated with their source rocks which indicate that they are **pre-oil bitumen**.

Correlations that are based on both molecular ratios and bulk parameters are better because molecular ratios are usually more resistant to secondary alteration processes (Peters and Moldowan, 1993; Peters et al., 2005). For the solid bitumen studied the plots for the bulk parameters such as maximum temperature (T_{max}) **versus production index (PI)** show that the solid bitumen is less mature than the extract from the source rocks. In addition, the maturity parameters from the biomarkers such as some **sterane ratios and aromatic ratios** show that the solid bitumen for the samples studied less in maturity from the source rock but at same time there is relationship between both of them.

The different ratios for correlation in general show that **the solid bitumen extract indicate that is Mixing from multiple source rocks and multiple maturity levels** and different reservoirs Formations (Mohammed et al., 2013) it is show that chia Gara Formation had the higher ratio in general for providing the solid bitumen, especially, the bitumen in Jeribe Formation in Ajeel oil field and at the same time there is strong relation between the extract from Chia Gara Formation and solid bitumen in Dhiban Formation in Hamrin Oil field and with the bitumen in Jeribe Formation in Ajeel oil field. The Gotnia Formation show good relation with the extract from the solid bitumen studied, especially with the bitumen in the Euphrates Formation reservoir with Najmah Formation. The solid bitumen in the Jeribe Formation reservoir in Hamrin oil field show strong relation with the source extract from the Sargelu Formation.

Mixing between the solid between studied in Ajeel and Hamrin oil fields related to the structure reasons which is improved by north oil company report about thrust fault separate these oil fields.

11. Characterization, maturity, origin and correlation of selected crude oils from Ajeel and Hamrin oil fields.

Seven crude oil samples from the Miocene reservoirs in the north of Iraq from the Ajeel and Hamrin oil fields were analyzed using molecular methods to determine their maturity and biomarker characteristics, as well as to obtain information on their respective source rocks.

The molecular composition for the crude oils studied characterized by low pristane/phytane ratios which range from (0.84 to 0.96) for the samples collected from the north of Ajeel oil field and relatively higher from Pr/Ph ratio range from (1 to 1.2) for the selected samples from the south Ajeel oil field and the samples studied from the Hamrin oil field which is DST samples and low values of Pr/n-C17 and Ph/n-C18 < than 1 for all samples the $T_s/(T_s+T_m)$ range from

(0.21 to 0.35). The steranes ratios of the C 29 Sterane $20S / (20S + 20R)$ rang form (0.42 to 0.48) and the C29 $\alpha \beta \beta$ ($\alpha\beta\beta + \alpha\alpha\alpha$) ratio rang form (0.51 to 0.53). Aromatic compound were analyzed for and show high from DBT/P ratio rang from (1.81 to 2.48) . From above the results which can be discussed are as a follow: The low values of Pr/n-C17 and Ph/n-C18 for all samples indicate that the samples are deposit under anoxic condition and non- biodegraded (Volkman et al., 1983) and also indicate that marine algae input is the origin for the crude oils selected from Ajeel oil field and mixing organic matter is the origin for the crude oils selected from the Hamrin oil field. The distribution of regular steranes (%C27, %C28, %C29) for the crude oils studied indicate that the Carbonate rocks is the type of the source rocks for this oil. Furthermore, the low Pr/Ph ratio and high sulfur content are indicators that the oils are derived from marine carbonate source rocks. For all acyclic ratio one crude oil sample from the Hamrin oil field show different result from the other crude oil samples. The two steranes maturity parameters plots show different in maturity for the oil studied samples which indicate as well as high maturity in general for all samples studied. The high DBT/P ratio for samples studied indicate that this oil is high sulfur content and derived from Kerogen content high sulfur and deposited under hypersalinity environment. the from the other crude sample from above canceled this oils are used as indicators of maturity and can be used in source. The figure () show different plots from different calculated ratios to study the characters for the selected crude oil samples.

The conclusion from that: the crude oil samples studied are derived from marine Carbonate rocks which deposit under anoxic ,hypersalinity, condition and the algae input is the origin for the organic matter with high sulfur content. Different in maturity for this oil indicate that is derived from different maturity level source rocks. The two crude oil samples from the Hamrin oil field show relatively different in biomarker distribution from the crude oil samples from the Ajeel oil field which could be relate to they are DST samples and could be relate to they are derived from different source rocks.

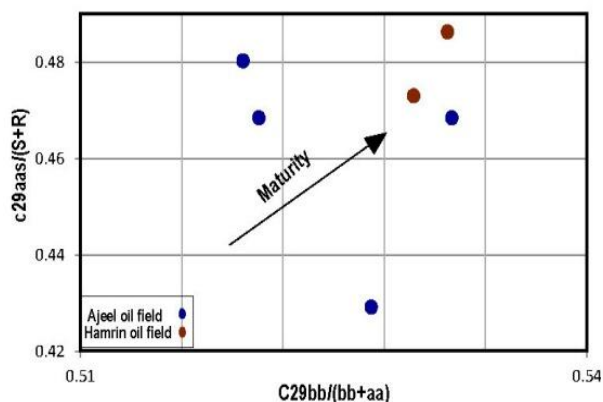


Fig. 4.26 plots for two steranes parameters comparing the maturity of the crude oils studied and extract from the core reservoir samples. The plots show high maturity for the crude oil samples in general which is higher than the bitumen samples studied.

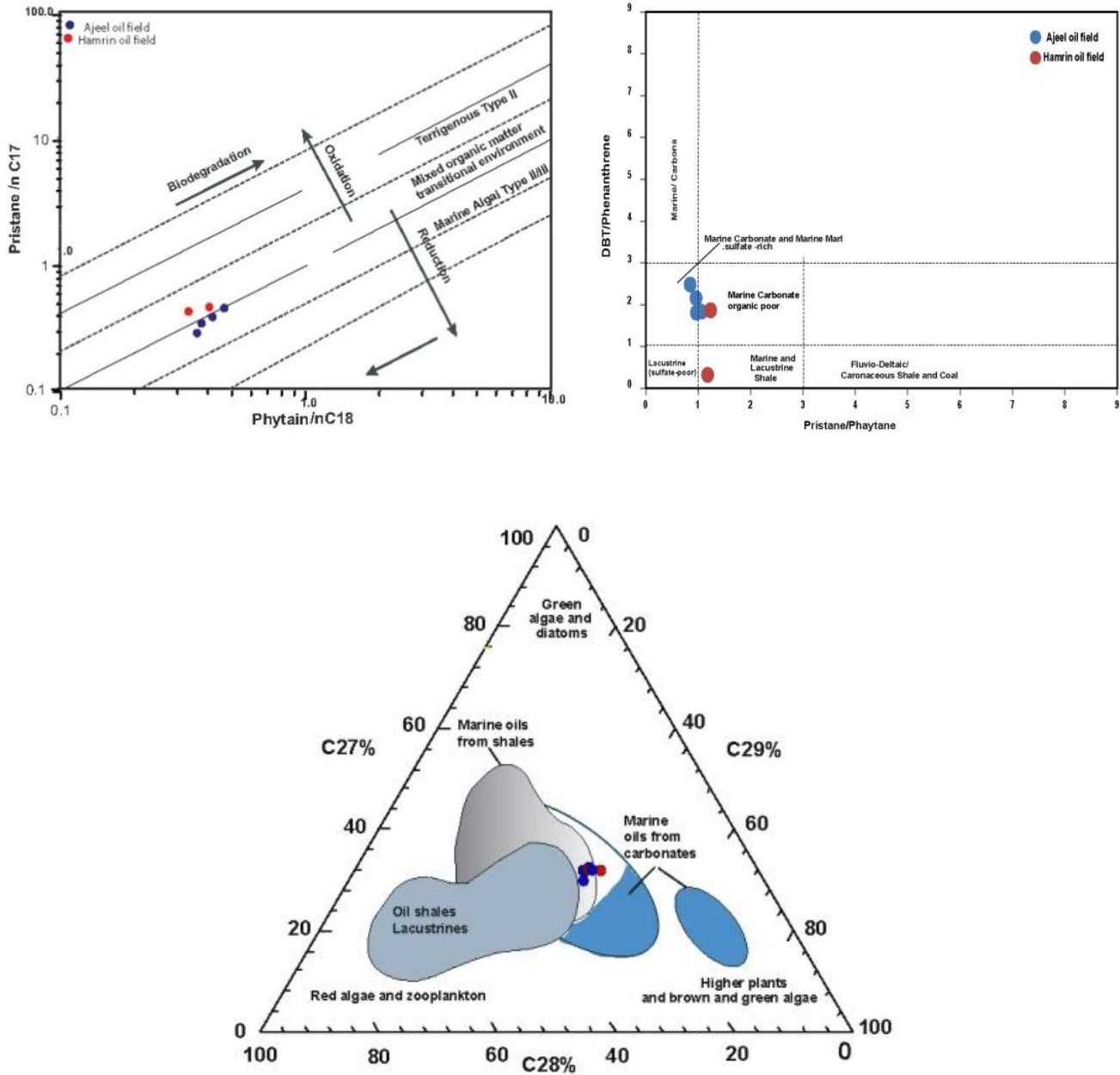


Fig.4.27 plots of different ratios to study the crude oils Characterization, maturity,and origin.

11.1 Oil-oil correlation

Correlation of oils to each other and to their source rocks is an essential in defining a basin petroleum system (Walter et al., 1998). Oil-Oil correlation seeks to determine whether oils were generated and expelled from the same source facies. Correlation studies endeavor to establish the original genetic relationship of geologic samples rather than a mere matching of bulk properties or chemical compositions. For oil-oil correlation different ratios are use as showing in Fig(). The BNH/(BNH+C29 hopane) ratio versus the pr/ph and versus Ts/(Ts+Tm) ratio; Pr/Ph ratio versus the DBT/P ratio and versus the %C27/C29 ratio. The penta hopane/regular sterane ratio versus the %C27/C29 ratio and the(C24)/ (C24+C26 tricyclic trepane) versus the (C23) tricyclic /(C23 tricyclic+C30 hopane). The plots from these ratios in general are separate the crude oils studied to the three groups which are in general : the south of Ajeel oil field group ; Hamrin oil field group and the north of Ajeel oil field group some plot ratio include some of Ajeel oil field crude oil with the Hamrin oil field group and as mention before there are mixing between the oil in reservoir Formation in these two oil fields (Ajeel and Hamrin oil fields) which is relate to structure reason.

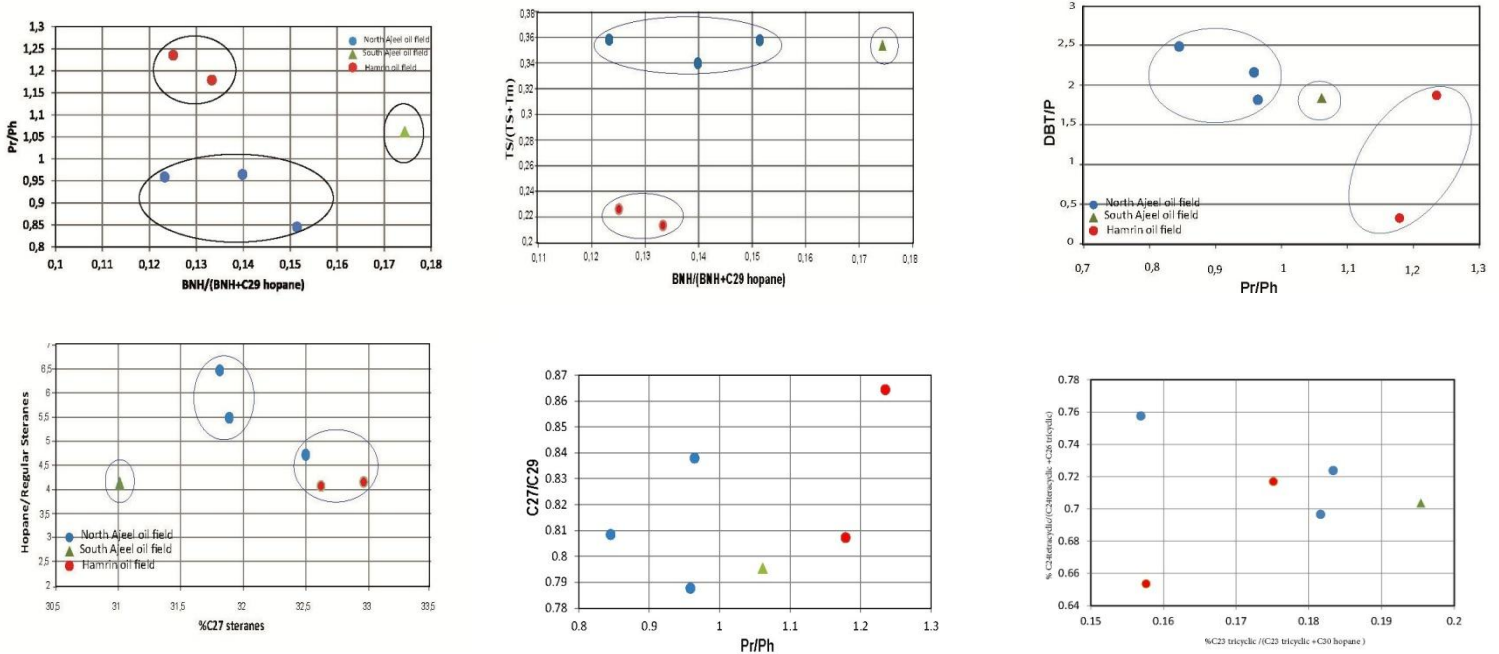


Fig.4.28. Plots for different calculate ratios for oil-oil correlation Pr/Ph ratio versus DBT/P, %C27/C29 and BNH/(BNH+C29 hopane) ratios . %C27 sterane ratio versus hopane/ sterane ratio and BNH/(BNH+C29 hopane) ratio and (C24)/ (C24+C26 tricyclic trepane) versus the (C23) tricyclic /(C23 tricyclic+C30 hopane) ratio. The plots in general show three subfamily for the crude oils in the study area

The conclusion from above : Three different oil families in the study area The Middel Juraasic represent by Sargelu Formation, Upper Jurassic oil families represent by Najamh and Gotnia Formations and the basal Lower Cretaceous represent by Chia Gara Formations . The source rocks providing the south of Ajeel oil field is different from the source rock which provide the north area from this oil field and different in biomarker distribution for the crude oil from Hamrin oil field and Ajeel oil field with mixing between them in some. The oils studied is derived from mixing source rocks with different ratios from them.

11.2 Crude Oil - Solid bitumen correlatio

There are two different oil phases exist in reservoir and carrier rocks, the production oil and residual oil. In this study reservoir core extract studied were compared with oils produced from the same Miocene reservoir age. For this correlation samples from different wells were select : four crude oil samples from four wells from the north and the south of the Ajeel oil fields and two crude oil samples from two wells from Hamrin oil field were studied. The crude oil samples were analysis to study their biomarkers distribution and compared with bitumen studied. The maturity for the crude oils studied were compared with the maturity of the solid bitumen studied by using two sterane maturity parameters C 29 Sterane $20S / (20S + 20R)$ and $\alpha \beta\beta (\alpha\beta\beta + \alpha\alpha\alpha)$ and the plots show that the crude oils studied is higher in maturity from the solid bitumen studied and also show that the crude oil sample from the well Aj-84 is relatively less in maturity than the other oil samples studied and like mentioned before the low maturity for the bitumen in Euphrates Formation reservoir in Ajeel oil field (Fig.4.29).

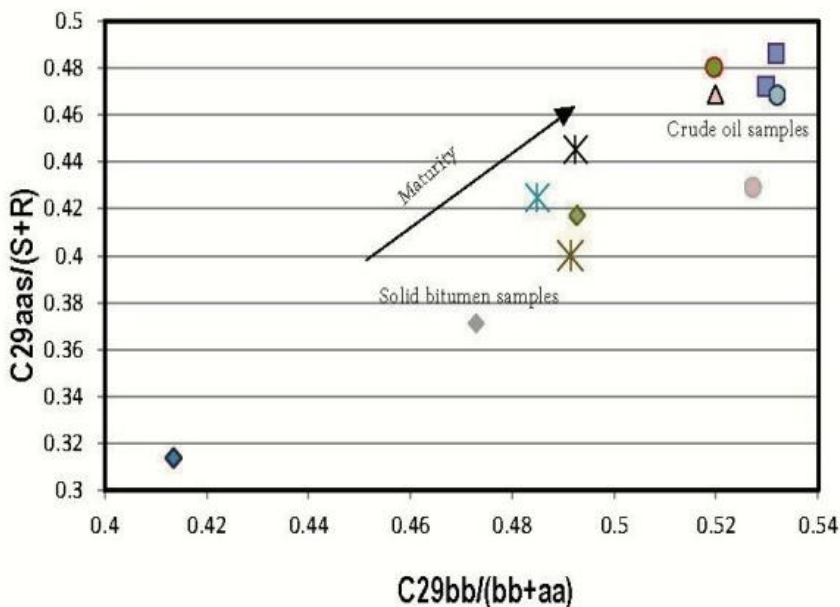
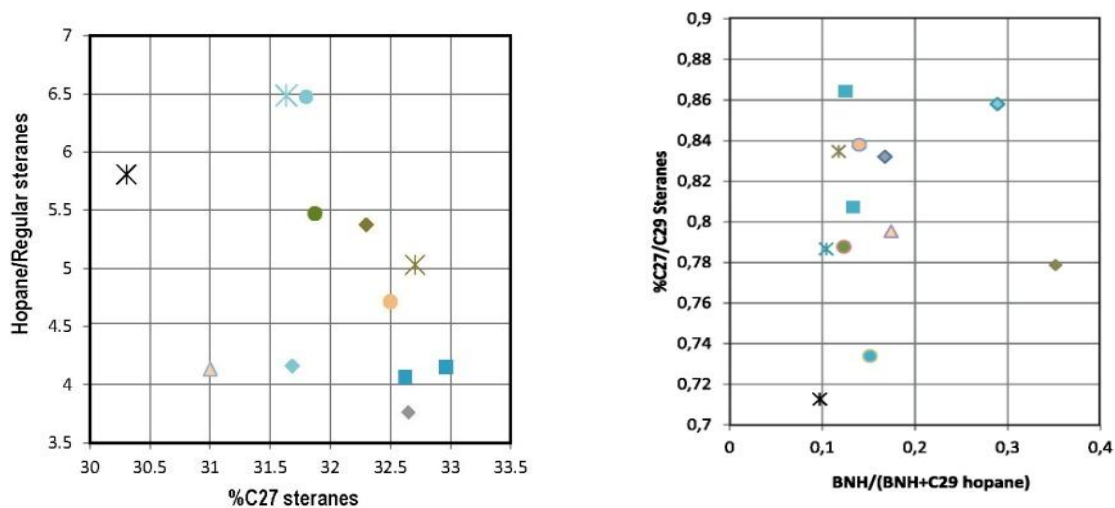


Fig.4.29. plots for two steranes parameters comparing the maturity of the crude oils studied and extract from the core reservoir samples. The plots show high maturity for the crude oil samples in general which is higher than the bitumen samples studied.

To investigate the genetic link between crude oils and bitumen extracts, the biomarkers parameters from the (saturated hydrocarbon and aromatic ratios) were used and supported by plots the BNH/ (BNH+C₂₉ hopane) ratio versus the %C₂₇/C₂₉ steranes ratio and the %C₂₇ sterane versus penta hopane /regular steranes ratio and the DBT/P ratio versus the %C₂₇/C₂₉ steranes ratio Fig (3.26). These ratios strongly reflect a close genetic relationship between the solid bitumen in the Miocene reservoirs and the crude oils in the same age reservoirs in general. The crude oil the well Aj-84 show strong relationship with the bitumen in the Jeribe Formation reservoir from the Harmin oil field and with the bitumen in the Euphrates Formation from the Ajeel oil field. From the crude oils maturity plot parameters as show in Fig (3.25) the crude oil in the well Aj-84 is plot in the trend of the plots with the Jeribe bitumen in the Harmin oil fields and the Euphrates bitumen in the Ajeel oil field. The Less in Maturity for the crude oil in the well Aj-84 comparing with the other crude oil samples which could give some reason for the mention before about the low maturity for the bitumen studied in the Euphrates Formation in the Ajeel oil field . The DST crude oil samples from Hamrin oil field show relationship with the bitumen from the reservoir Formations in this oil field , additionally, the bitumen from Ajeel oil field. near to the bitumen in the Jeribe and Euphrates reservoir Formations from the same oil field. The crude oil from the south Ajeel oil field show relation with the bitumen in the Jeribe Formation in the Ajeel oil field and bitumen in the Euphrates Formation in the same oil field. The crude oils from the wells (Aj-66 and Aj-26) which show high maturity depending on the sterane maturity parameter show strong relation with the bitumen in the Euphrates Formation in the Hamrin oil field and bitumen in the Jeribe Formation in the Ajeel oil field and both bitumen's studied are mature as well Fig(4.30) show correlation plots deeding on the some correlation ratios.



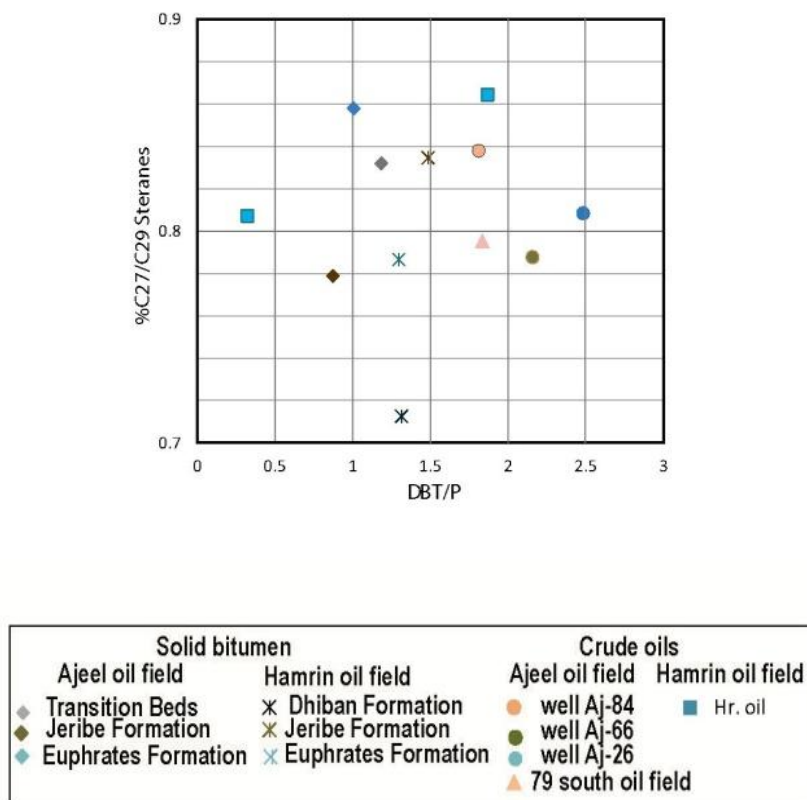


Fig.4.30. Different calculate correlation ratios comparing the crude oils studied and extract from the core reservoir samples.

11.3 Crude Oil -Source rocks Correlation

Correlation of a crude oil to one or more source rocks is a common industrial application of petroleum geochemistry. Confirmation that oil has been generated in the target sedimentary basin is the most critical piece of knowledge a petroleum explorations can derive; second in importance is the determination of the source of that oil (curiale, 2008). For the successful oil-source correlation must include three attributes:(requirement of causality, comparable chemical data for all samples, and geological support). The correlation in this study covered these attributes in general. Oil-source rock correlations can be obtained by using biomarker proportionalities because of their resistance to biodegradation (Peters and Moldowan, 1993; Hunt, 1996). A geochemical comparison was carried out between the crude oils studied and the source rock extracts studied s in order to explain the similarity and difference in biomarkers content as well as to show lateral distribution of them. The saturated and aromatic hydrocarbons

are more suitable for oil-source rock correlation than heterocompounds(Tissot and Welte, 1984). the crude oils from the six wells studied in an attempt to establish oil-source rock correlation. For this study oil-source rocks were correlated by using the biomarker ratios : penta hopane/regular sterane ratio versus %C27 regular sterane; BNH/(BNH+C29 hopane) ratio versus % C27/C29 regular steranes ratio; DBT/P ratio versus% C27/C29 regular steranes; DBT/P versus BNH/(BNH+C29 hopane ratio and the tetracyclic trepane (C24)/ (C24+C26 tricyclic trepane) versus the ratio of the (C23) tricyclic /(C23 tricyclic+C30 hopane). The first observed from the plotting for these ratios is the strongly relationship between the crude oils studied and the extract from the source rocks studied and Chia Gara Formation is assumed to have the major fraction of the crude oils studied, especially, the crude oils from the north of Ajeel oil field (the wells Aj-66 and Aj-26) in addition one of the crude oils from Hamrin oil field, while the Sargelu Formation is provide the highest ratio to the second sample from Hamrin oil field and the well Aj-84. The crude oil from the south of the Ajeel oil field is received most of it is oil from the Gotnia and Najmah Formations . The Fig() show the plots for the different correlation ratios(the crude oils studied refer to the north of Ajeel oil field show by circle symbol and triangle symbol for the south form this field) The square symbol refer to the crude oil from Hamrin oil field and for more clarification the Fig() show the number of the wells in different colors for each wells.

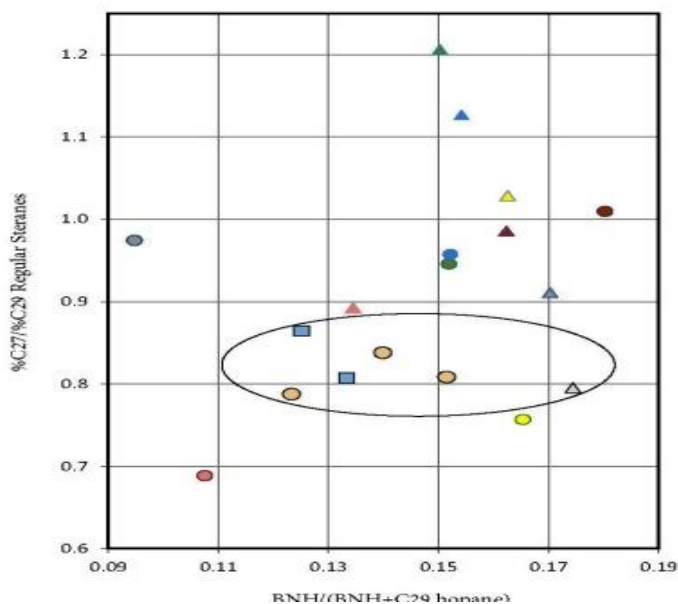


Fig.4.31. Plots of the BNH/(BNH+C29 hopane) ratio versus the %C27/C29 sterane ratio for correlation the crude with the extract source rocks studied . The plots show strong relation

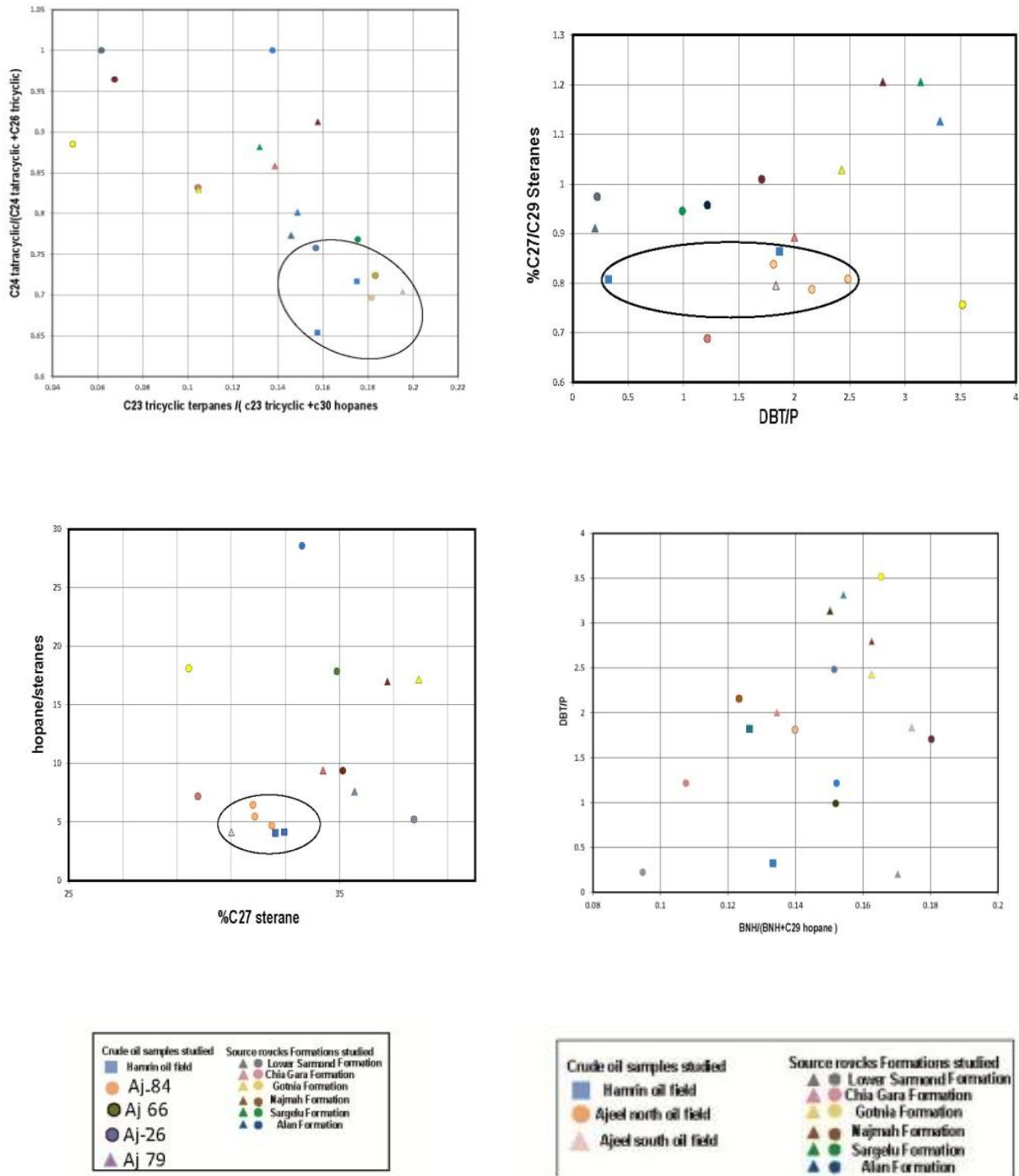


Fig.4.32. Correlation ratios plot for oil samples studied and extract from the source rocks studied. the maturity of the crude oils studied and extract from the core reservoir samples. The plots show high maturity.

11.4 Crude Oil - Solid bitumen - Source rocks Correlation

Several published, successful oil-source correlations have appeared since the first was presented by John Hunt and colleagues over 50 years ago (Curial, 2008). Hunt et al. (1954) provided clear chemical and geological evidence in a causal framework for the source of oils and solid bitumen's of the Uinta Basin (USA). In this study the source and oils and solid bitumen were

correlate. Different ratios used for correlation the crude oil -solid bitumen- source rock such as regular steranes (%C27, %C28, %C29) triplot, the BNH/(BNH+C29 hopane) ratio versus the %C27/C29 sterane ratio, DBT/P ratio versus % C27/C29 regular sterane ratio, the %C₂₇ sterane versus penta hopan. The correlation plots show that strong relation between the crude oils, bitumen, and extract from the source rocks in general (Fig 4.32). The crude oil from the south of Ajeel oil field show strong relation with the bitumen in the Euphrates Formation reservoir in the Ajeel and Hamrin oil field and with the extraction from the Gotnia and Najmah Formations source rocks. , while the other crude oil sample from this oil field is show relation with the bitumen in the Jeribe Formation reservoir and with the extract from the Chia Gara Formation Sargelu Formation is provide the highest ratio to the second sample from Hamrin oil field and the well Aj-84.

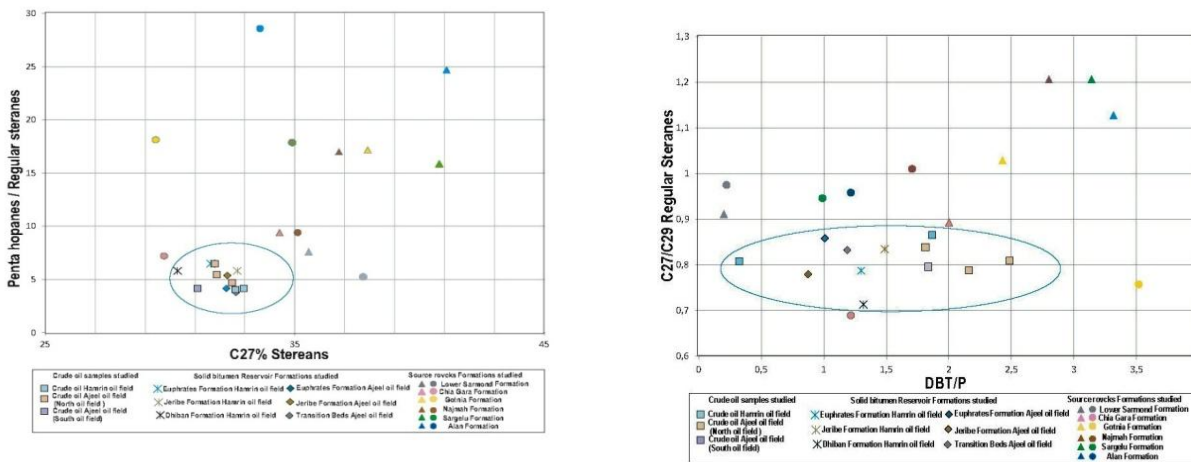


Fig .4.33. Plots of the DBT/P ratio versus %C27/C29 steranes ratio and %C27 sterane versus penta hopane/regular sterane show the strong relation between the crude oils, solid bitumen and extract from the source rocks studied.

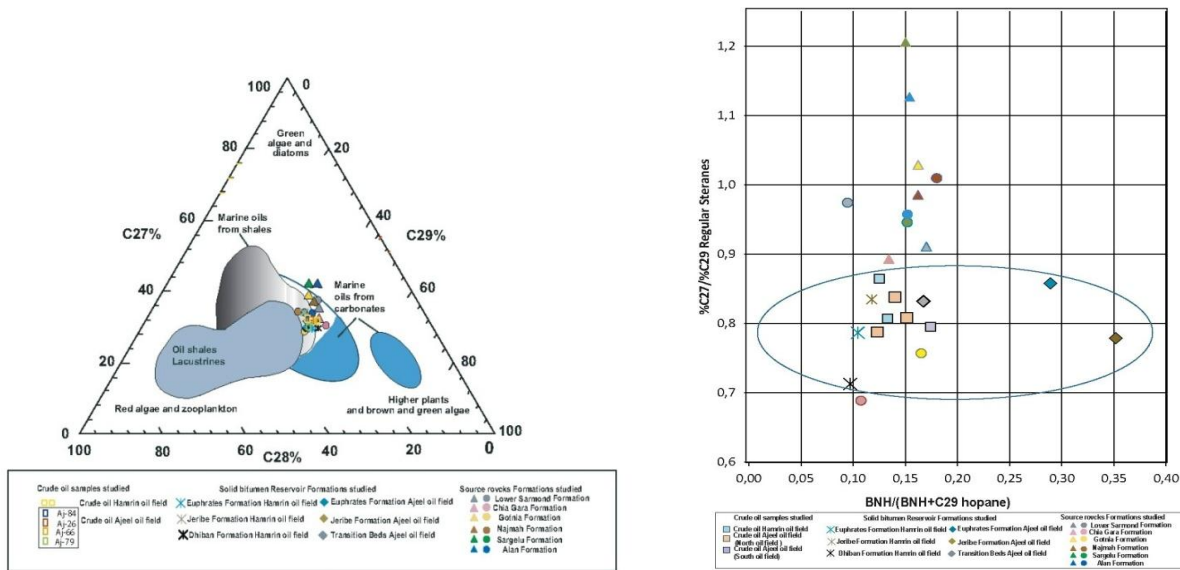


Fig. 4.33. Plots of the DBT/P ratio versus %C27/C29 steranes ratio and %C27 sterane versus penta hopane/regular sterane show the strong relation between the crude oils, solid bitumen and extract from the source rocks studied.

12. Conclusions remarks:

Three different oil families in the study area the Middel Juraasic repersent by Sargelu Formation, Upper Jurassic oil families represent by Najamh and Gotnia Formations and the basal Lower Creataceous repersent by Chia Gara Formations . The source rocks providing the south of Ajeel oil field is different from the source rock which provide the north area from this oil field and different in biomarker distribution for the crude oil from Hamrin oil field and Ajeel oil field with mixing between them in some place. Strong relation between the solid bitumen in the reservoir Formations studied and the crude oils studied in general. Mixing between the solid between studied in Ajeel and Hamrin oil fields related to the structure reasons. The crude oils studied and the solid bitumen extract are driven from mixing source rocks with different ratios from these source rocks and different maturity levels .

Chapter 5

Conclusions

Conclusions

This study reports an extensive characterization of the petroleum system in the Ajeel and Hamrin oil fields of northern Iraq, covering the time interval from the Lower Jurassic (Aalenian) to the Early Cretaceous (Barremian). The investigation primarily aims at a detailed investigation of source rock intervals by describing their oil/gas potential based on the kerogen quality and quantity in relation to their respective thermal maturity. An evaluation of the organic facies and the environment of deposition over the studied sediment sequence is based on a multidisciplinary approach including paleofacies maps, geophysical well logs, bulk geochemistry, and in particular on the distribution of biomarker and non-biomarker hydrocarbons. To facilitate a reliable oil/source rock correlation, samples from the overlying Lower Miocene (Euphrates and Jeribe Fm.) reservoir intervals were studied for both the residual oil composition of the reservoir rocks and for production oils from both fields that were characterized by molecular geochemistry of aliphatic and aromatic hydrocarbons.

1. - The Gotnia Formation acts as both as source rock as well as a cap rock. The character of being a regional seal in the study area and beyond on the Arabian Platform is well established for the Gotnia Formation. This study is the first to report carbonatic, organic-rich sedimentary layers sandwiched between the gypsum/anhydrite beds of the sabkha-like Gotnia Formation to contain substantial indigenous petroleum source potential. Oil generated from the Gotnia Formation was shown to contribute to the petroleum system of the Ajeel and Hamrin Fields of the study area and can be assumed to have done so in other reservoir of Northern Iraq.

2. - The Chia Gara Formation comprising a thickness of app. 220 m in the study area has previously been identified as the main source rock in the Berriasian/Tithonian Petroleum system of Northern Iraq. This work demonstrates that only the basal 30 m of the entire Chia Gara Formation has an excellent source rock potential, whereas the major middle and upper part is organic lean, thus not contributing to the source potential of the Chia Gara Formation. Determination of oil generation volumetrics and basin modelling studies have to account for this

source variability and have to be adjusted when calculating total oil in place. Presently, the volume of oil generated from the Chia Gara Fm. is overestimated by a factor of 5 to 10.

3. - The Najmah/Naokelekan Formation with an average thickness of around 30 m and the Sargelu Fm. With an average thickness of 80 m in the study area are excellent source rocks with kerogen quality identical to that of the Chia Gara Formation. The overestimation of oils generated from the Chia Gara Formation may in part be substituted by oils generated from the Naokelikan and additionally from the Sargelu Formation. The depositional environment of these three formations, all deposited in a restricted setting on the Arabian Platform was similar, which led to the accumulation of quasi-invariant kerogen types.

4. - Sargelu/Najmah/Chia Gara Formations are excellent source rocks for oil in the Ajeel and Hamrin oil fields, which received an additional input from carbonate intervals intercalated into the Gotnia Formation. High TOC values of up to 18% and high HI values in type II and II-S kerogens at a thermal maturity (T_{max}) increasing from the Upper Cretaceous to Lower Jurassic age, generated the large volumes of oil accumulated in the area around the Ajeel and Hamrin fields. Source rocks within Ajeel field (wells Ajeel 12 and Ajeel 8) presently are within the oil window but have not yet reached the main generation phase. In adjacent, deeper buried sections, the source rocks will have attained higher maturity to generate larger volumes of oil.

5. - Terpane biomarker and aromatic geomarker signatures reveal an origin of reservoir oils from similar source and facies regimes concordant with carbonate/evaporite cycles. The maturity parameters determined from the saturated and aromatic hydrocarbon fractions in the Ajeel and Hamrin fields show high and regular thermal maturity for the Jurassic Formations. The basal Cretaceous Chia Gara Formation, its organic lean upper part and the Lower Sarmond Formation show low maturity compared to the Jurassic strata. The Formations studied were deposited in a marine, carbonate rich, anoxic environment with more oxygenated conditions during deposition of the upper Chia Gara and Lower Sarmond Formations, thus reducing kerogen quantity and quality. The organic matter of the kerogens is predominantly derived from cyanobacterial and algal sources, whereby the cyanobacterial contributions increase

with sediments deposited under higher salinity (anhydrite in Gotnia and Alan Formations). This dependency of molecular composition of sediment extracts on facies is corroborated for carbonate/anhydrite sequences by a high ratio of dibenzothiophene (DBT) versus phenanthrene (P) that is also evident in their alkylated analogues, respectively.

6. – High resolution biomarker composition reflects local organofacies variation between deeper basinal and shallow marginal sections of the depocentre. Local facies variations, expressed in salinity and sulfurization gradients are reflected in samples on field scale and relate to a more basinal character at site Aj-8 compared to the more marginal facies detected in Aj-12 or between samples in the Ajeel versus the Hamrin field. A highly source and environment-specific biomarker was found in 29,30-bisnorhopane (BNH), which rarely occurs in other source rocks and the relative proportion of DBT/P. The source rock samples studied from the marginal Aj-12 and basinal Aj-8 site show inverse trends in molecular marker distributions via a low BNH/(BNH+C₂₉ hopane) and a high DBT/P ratio in basinal and the reverse in marginal settings. Diminished early diagenetic preservation of cyanobacterial structures in the shallower site Aj-12 (type II kerogen) versus excellent preservation of cyanobacterial biomass and high sulfurization of kerogen (type II-S) in the basinal setting of Aj-8 can be differentiated.

7. - Reservoir cores containing abundant residual oil in a solid bitumen phase indicate that the solid bitumen was derived from a source rocks that was deposited under anoxic conditions and contained marine organic matter. The molecular composition of aliphatic terpane biomarkers and aromatic hydrocarbons in reservoir bitumen is equivalent to that found in the Ajeel and Hamrin production oils. Reservoir bitumens generally show high amounts of extract in the Hamrin compared to the Ajeel oil field. Organofacies characteristics reveal a high DBT/P ratio accompanied by a low BNH/(BNH+C₂₉hopane) ratio in the Hamrin compared to the Ajeel oil field. This indicates a source rock kerogen with higher sulfur content and thus more restricted, deeper basinal conditions charging the Hamrin oil field. The relative abundance of tricyclic vs. pentacyclic terpenoids in oils of the Ajeel oil field is high, whereas it is low in the Hamrin oil field, potentially due to a better ventilation of source rocks feeding the Ajeel field. The subtle facies variations within the local kitchen areas charging into the Ajeel and Hamrin oil fields control the final composition of the reservoir oils, which are derived from of mixing of source rocks in highly variable depositional environments.

8. - Reservoir Bitumen in the Euphrates Formation shows high maturity and high amounts of extract in the Hamrin oil field while this formation shows low maturity bitumen and low bitumen extract yields in the Ajeel oil field. This indicates different source rocks have charged the Euphrates Formation in both fields.

9. - Mixing between the solid between studied in Ajeel and Hamrin oil fields is related to structural control. The bitumen in the Euphrates Formation of the Ajeel oil field equals the bitumen in the Jeribe Formation of the Hamrin oil field. In contrast, the bitumen in the Euphrates Formation of the Hamrin oil field equals the bitumen in the Ajeel oil due to migration conduits along faults allowing infiltration of oil in these two oil fields.

10. - The relation between the bitumen and source rocks studied shows that the bitumen derived from **mixing of charges from multiple source rocks at variable maturity levels**. The Chia Gara Formation is assumed to have contributed the major fraction of the reservoir bitumen, particularly to the Jeribe Formation in Ajeel oil field. A strong relation between the extract composition from Chia Gara Formation and the reservoir bitumen in Dhiban Formation of the Hamrin Oil field and with the bitumen located in the Jeribe Formation of the Ajeel oil field was established. Extracts from the Gotnia Formation also matched with the extract from the reservoir bitumen, especially with that in the Euphrates Formation reservoir, which further shows good agreement with oils generated from the Najmah/Naokelikan Formation. Reservoir bitumen in the Jeribe Formation of the Hamrin oil field revealed a strong relation with the source extract from the Sargelu Formation.

11. - Oils generated from the Sargelu, Naokelikan/Najmah and Chia Gara Fm. are sulfur-enriched and compositionally match residual oils as well as production oils from the Ajeel and Hamrin field. Triterpane distributions corroborate these three source units to have charged the Ajeel and Hamrin oils, which show low abundance of tri- vs. pentacyclic terpanes, a predominance of the regular C₂₉-hopanes and the presence of highly source specific 29,30-bisnorhopanes. A reliable oil-source-correlation could be established based on molecular aliphatic and aromatic tracers. The identification of the four most important source units and significantly improved knowledge of their volumetrics facilitates a re-evaluation of the overall

petroleum potential of the study area by basin modelling exercises to replace existing models, which are based on incorrect assumptions.

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Erklärung

Hiermit erkläre ich, Luma jassim Mohammed, Ich versichere an Eides statt durch meine eigenhändige Unterschrift, dass ich die vorgelegte Dissertation mit dem Thema: “Petroleum system analysis of the Lower Jurassic-Upper Cretaceous source and Miocene reservoirs in the NE of Iraq” selbstständig und ohne nicht offengelegte Hilfe Dritter verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel genutzt habe. Alle Stellen, die wörtlich oder dem Sinne nach auf Publikationen oder Vorträgen anderer Autoren beruhen, sind als solche in korrekter Zitierung kenntlich gemacht. Die Dissertation in der vorgelegten oder einer ähnlichen Fassung noch nicht zu einem früheren Zeitpunkt an der Christian-Albrechts-Universität zu Kiel oder einer anderen in- oder ausländischen Hochschule als Dissertation eingereicht worden ist. Ich versichere zudem, dass die Arbeit unter Einhaltung der Regeln guter wissenschaftlicher Praxis der Deutschen Forschungsgemeinschaft entstanden ist.

Kiel, den 26-7-2016

Luma Jassim Mohammed