Geochemical Evaluation and Biomarkers Applications in Source Rocks and Crude Oils, Kaikang Trough, Muglad Rift Basin, South West Central Sudan.

A thesis submitted to the University of Khartoum in fulfilment of the requirement for the degree of M.Sc. in (Geology)

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TABLE OF CONTENTS

Table of Contents........................................................................................................... I
List of Figures.................................................................................................................. VI
List of Tables.................................................................................................................. IX
ACKNOWLEDGEMENTS. ................................................................................................. X
Abstract. .......................................................................................................................... XI
الخلاصة.......................................................................................................................... XI
CHAPTER ONE .................................................................................................................... 1

1. INTRODUCTION

1.1 Location of the Study Area.................................................................................. 1
1.2 Topography.......................................................................................................... 1
1.3 Drainage system.................................................................................................... 4
1.4 Climate.................................................................................................................. 4
1.5 Soils....................................................................................................................... 5
1.6 Vegetation.............................................................................................................. 6
1.7 Population............................................................................................................. 6
1.8 Socio-Economic Development of the Area....................................................... 7
1.9 Statement of the problem.................................................................................... 7
1.9.1 Previous Related Work.................................................................................. 8
1.9.2 Objectives....................................................................................................... 10
1.9.3 Present Work: (Materials and Methods)..................................................... 10

CHAPTER TWO.................................................................................................................. 12

2. GEOLOGICAL EVOLUTION AND HISTORY OF OIL EXPLORATION
2.1 Geological Evolution...........................................................................12
2.2 History of Oil Exploration..................................................................16

CHAPTER THREE................................................................................18

3.GEOTECTONIC AND STRUCTURAL SETTING
3.1 Geotectonic Setting............................................................................18
3.2 Structural Setting................................................................................21
3.2.1 Pre-rifting Phase..............................................................................21
3.2.2 Rifting Phase...................................................................................21
3.2.3 Sag Phase.........................................................................................22

CHAPTER FOUR..................................................................................24

4. THE STRATIGRAPHY OF MUGLAD RIFT BASIN
4.1 Basement Complex (Precambrian).....................................................24
4.2 Cretaceous Sedimentary Units............................................................24
4.2.1 Abu Gabra Formation (Neocomian –Berremian)............................26
4.2.2 Bentiu Formation (Aptian-Cenomanian).........................................26
4.2.3 Darfur Group (Turonian –late Senonian)........................................27
4.2.3.1 Aradeiba Formation : (Turonian –Santonian)...............................27
4.2.3.2 Zaraga Formation (Campanian-Maastrichtian)............................27
4.2.3.3 Ghazal Formation (Campanian-Maastrichtian)............................28
4.2.3.4 Baraka Formation (Maastrichtian)................................................28
4.3 Tertiary Sedimentary Units................................................................28
4.3.1 Amal Formation (Paleocene)...........................................................28
4.3.2 Kordofan Group: (late Eocene Oligocene –to Middle Miocene)....29
4.3.2.1 Nayil Formation (Late Eocene-Early Oligocene).........................29
4.3.2.2 Tendi Formation (Late Oligocene-Early Miocene)......................29
4.3.2.3 Adok Formation (Late Miocene-Pliocene)...................................30
4. 3.2.4 Zeraf Formation (Quaternary).....................................................30
4.4 Petroleum System...............................................................................31
4.4.1 Source Rock.....................................................................................31
4.4.2 Maturity ......................................................................................... 32
4.4.3 Seals .......................................................................................... 32
4.4.4 Trapping Styles .......................................................................... 33
4.4.5 Reservoir Characteristics .......................................................... 34

CHAPTER FIVE ................................................................................... 36

5. METHODOLOGY

5.1 Introduction ................................................................................... 35
5.1.1 Sedimentary Organic Matter ...................................................... 35
5.1.2 Diagenesis Stage ....................................................................... 36
5.1.3 Catagenesis Stage ..................................................................... 36
5.1.3.1 The Oil Window .................................................................. 37
5.1.4 Metagenesis Stage .................................................................... 37
5.2 Geochemical Techniques ............................................................... 37
5.2.1 Rock-Eval Pyrolysis Technique ................................................ 38
5.2.1.1 Evaluating Source Rock Using Rock-Eval Parameters ......... 38
5.2.1.1.1 Quantity of Organic Matter .............................................. 38
5.2.1.1.2 Quality of Organic Matter (Kerogen Types) ................. 39
5.2.1.2 Maturation of Organic Matter ............................................. 41
5.2.1.2.1 Tmax from Rock-Eval Data ............................................. 41
5.2.3 Vitrinite Reflectance (VRo) ....................................................... 42
5.2.4 Palynofacies Analysis ................................................................. 43
5.2.5 Gas-Chromatography GC & Gas-Chromatography Mass
Spectrum ......................................................................................... 44
5.2.5 The Gas-Chromatography Mass Spectrum GCMS ............... 46

CHAPTER SIX .................................................................................... 48

6. BIOMARKERS

6.1 Introduction to Biological Markers ................................................ 48
6.2 Applications of selected biomarkers ............................................. 49
6.2.1 Paraffins........................................................................................................49
6.2.2 Acyclic isoprenoids......................................................................................50
6.2.3 Terpanes........................................................................................................50
6.2.3.1 Hopanes.....................................................................................................51
6.2.4 Steranes..........................................................................................................53
6.3 Biomarkers parameters for source and depositional environment.............56
6.3.1 Carbon Preference Index..............................................................................56
6.3.2 Terrigenous/Aquatic Ratio (TAR).................................................................56
6.3.3 Pristane/Phytane Ratio (Pr/Ph)....................................................................57
6.3.4 Tricyclic Terpanes.........................................................................................57
6.3.5 Gammacerane/C30 hopane (Gammacerane Index).................................58
6.4 Biomarker parameters for maturity assessment...........................................58
6.4.1 Terpanes.........................................................................................................58
6.4.1.1 Hopanes.....................................................................................................59
6.4.1.1.1 Ts/ (Ts+Tm) Ratio................................................................................59
6.4.1.1.2 22S/ (22S+22R) C31; Homohopane isomeration.................................59
6.4.2 Aromatic Hydrocarbons................................................................................60
6.4.2.1 Methylphenanthrene Indices: (MPI 1 and MPI 2)...................................60

CHAPTER SEVEN.....................................................................................................61

7. RESULTS AND DISCUSSION

7.1 Kaikang-3 well..................................................................................................61
7.1.1 Organic Richness “Quantity of Organic Matter”........................................61
7.1.2 Source Rock Quality from Rock-Eval..........................................................65
7.1.3 Quality of Organic Matter Using Palynofacies Analysis............................66
7.1.4 Maturity from Rock-Eval T_{max}..................................................................72
7.1.5 Maturity from Vitrinite Reflectance Measurement.....................................72
7.2 Kaikang West-1 Well.......................................................................................74
7.2.1 Organic Richness “Quantity of Organic Matter”........................................74
7.2.2 Source Rock Quality from Rock-Eval..........................................................78
7.2.3 Quality of Organic Matter Using Palynofacies Analysis.................80
7.2.4 Maturity from Rock-Eval $T_{\text{max}}$....................................................82
7.2.5 Maturity from Vitrinite Reflectance Measurement.................................82
7.4 Gas Chromatography Results.................................................................84
7.4.1 Oil Samples........................................................................................84
7.4.2 Source Rock Extracts........................................................................87
7.5 Biomarker Characteristics of the Crude Oils and Source Rocks............92
7.5.1 Oil Samples........................................................................................92
7.5.2 Source Rock Extracts.........................................................................99
7.6 Maturity..................................................................................................103
7.6.1 Oil samples.......................................................................................103
7.6.2 Source rock Extracts.......................................................................104
7.7 Steranes Biomarkers.............................................................................104

CHAPTER EIGHT......................................................................................113

8. CONCLUSION AND RECOMMENDATIONS

8.1 Conclusion..........................................................................................113
8.2 Recommendations...............................................................................117

REFERENCES..........................................................................................118

APPENDIX

Sample Preparation Procedure for Rock-Eval.........................................128
Procedure for Preparation of Polished Block...........................................130
Palynofacies Samples Preparation...........................................................131
Procedures for Extraction of Bitumen......................................................133
Procedures for Liquid Column Chromatography (LCC)..........................134
### LIST OF FIGURES AND TABLES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1. Location map of the study area in south west central Sudan</td>
<td>2</td>
</tr>
<tr>
<td>Figure 1.2. Location map of studied wells; Kaikang West-1 and Kaikang-3, Kaikang trough, Muglad Rift Basin, Sudan</td>
<td>3</td>
</tr>
<tr>
<td>Figure 3.1. Tectonic and Structural map of the Central African Shear Zone (CASZ)</td>
<td>23</td>
</tr>
<tr>
<td>Figure 5.1. Modified Van Krevelen diagram showing kerogen types</td>
<td>40</td>
</tr>
<tr>
<td>Figure 6.1. Chemical structures of various terpenoid classes present in saturated fraction of the petroleum</td>
<td>51</td>
</tr>
<tr>
<td>Figure 6.2. Origin of hopanes in petroleum from bacteriohopanetetrol</td>
<td>52</td>
</tr>
<tr>
<td>Figure 6.3. Origin of steranes in petroleum from sterols</td>
<td>55</td>
</tr>
<tr>
<td>Figure 7.1. Modified Van Krevelen diagram showing the Rock-Eval hydrogen and oxygen indices of Kaikang-3 samples</td>
<td>65</td>
</tr>
<tr>
<td>Figure 7.2. Showing Palynofacies components of the samples from Kaikang-3 and Kaikang west-1 wells</td>
<td>67</td>
</tr>
<tr>
<td>Figure 7.3. A comparison of maturity vs depth plots of Kaikang-3 well</td>
<td>73</td>
</tr>
<tr>
<td>Figure 7.4. Relationship between Total Organic Carbon (TOC) and potentiality of the source rock, Kaikang-3 well</td>
<td>77</td>
</tr>
<tr>
<td>Figure 7.5. Relationship between Total Organic Carbon (TOC) and potentiality of the source rock, Kaikang West-1 well</td>
<td>77</td>
</tr>
<tr>
<td>Figure 7.6. Modified Van Krevelen diagram showing the Rock-Eval hydrogen and oxygen indices of Kaikang west-samples</td>
<td>79</td>
</tr>
<tr>
<td>Figure 7.7. A comparison of maturity vs depth plots of Kaikang West-1 Well</td>
<td>83</td>
</tr>
</tbody>
</table>
Figure 7.8. Gas Chromatography (GC) trace of Kaikang-3 well DST oil sample.................................................................86

Figure 7.9. Gas Chromatography (GC) trace of Kaikang West-1 well DST oil sample..........................................................86

Figure 7.10. Gas Chromatography (GC) trace of Kiakang-3 well (1110m) rock extract sample..............................................89

Figure 7.11. Gas Chromatography (GC) trace of Kaikang west-1 well (2060m) rock extract sample...........................................89

Figure 7.12. Cross plot Pr/n-C17 versus Ph/n-C18 of two oil samples and two rock extract samples from Kaikang area................90

Figure 7.13. Cross plots of Pr/Ph ratio and dibenzothiophene/phenanthrene (DBT/Phen) ratio suggesting source rocks of oils and source extracts.................................................................................91

Figure 7.14. Gas Chromatography Mass Spectrum (GCMS) m/z (191) showing terpanes distribution of Kaikang-3 well DST oil sample. ........................................................................................................95

Figure 7.15. Gas Chromatography Mass Spectrum (GCMS) m/z (191) showing terpanes distribution in the saturate fractions of Kaikang-1 well DST oil sample.........................................................96

Figure 7.16. Gas Chromatography Mass Spectrum (GCMS) m/z (191) showing terpanes distribution in the saturate fraction of Kaikang-3 well (1110m) source rock extract sample..............101

Figure 7.17. Gas Chromatography Mass Spectrum (GCMS) m/z (191) showing terpanes distribution in the saturate fraction of Kaikang west-1 well (2060m) source rock extract sample 102

Figure 7.18. Gas Chromatography Mass Spectrum (GCMS) showing the C27- C29 steranes distribution in the saturate fraction of the Kaikang West-1 well rock extract (2060m)......................106

Figure 7.19. Gas Chromatography Mass Spectrum (GCMS)
chromatogram showing the C27- C29 steranes distribution the saturate fraction of the kaikang -1 well DST oil sample

Figure 7.20. Gas Chromatography Mass Spectrum (GCMS) (m/z 178,184, and 192) aromatic hydrocarbon of Kaikang-3 well oil sample. Peaks identification are given in Table (7-8). 109

Figure 7.21. Gas Chromatography Mass Spectrum (GCMS) (m/z 178,184, and 192) aromatic hydrocarbon of Kaikang-1 well oil sample. .................................................................110

Figure 7.22. Gas Chromatography Mass Spectrum (GCMS) (m/z 178,184, and 192) aromatic hydrocarbon of Kaikang West-1 well source extract sample.................................111

Figure 7.23. Gas Chromatography Mass Spectrum (GCMS) (m/z 178,184, and 192) aromatic hydrocarbon of Kaikang-3 well source extract sample.................................112
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1 Geological and Structural Evolution of the Muglad Rift Basin, south west central Sudan</td>
<td>15</td>
</tr>
<tr>
<td>Table 3.1 Generalized lithostratigraphical scheme of Muglad Rift Basin</td>
<td>25</td>
</tr>
<tr>
<td>Table 5.1 Geochemical parameters describing source rock generative potential (Quantity)</td>
<td>39</td>
</tr>
<tr>
<td>Table 5.2 Geochemical parameters describing type of hydrocarbon Generated (Quality)</td>
<td>39</td>
</tr>
<tr>
<td>Table 5.3 Rock-Eval geochemical and Ro parameters describing source rock thermal maturity</td>
<td>41</td>
</tr>
<tr>
<td>Table 7.1 Kaikang-3 well Rock-Eval Pyrolysis Result</td>
<td>63</td>
</tr>
<tr>
<td>Table 7.2 Palynofacies analysis results, Kaikang-3 well</td>
<td>71</td>
</tr>
<tr>
<td>Table 7.3 Kaikang West-1 well Rock-Eval pyrolysis results</td>
<td>75</td>
</tr>
<tr>
<td>Table 7-4 Palynofacies analysis results, Kaikang West-1 well</td>
<td>81</td>
</tr>
<tr>
<td>Table 7.5 Biomarkers oil and source extract parameters for Kaikang wells, Muglad Basin obtained from GC data</td>
<td>85</td>
</tr>
<tr>
<td>Table 7.6 Compounds identified in the m/z 191 mass fragmentograms shown in Figs (7.13,7.14,7.15 and7.16)</td>
<td>97</td>
</tr>
<tr>
<td>Table 7.7 Ratios calculated from GCMS data (m/z 191 and 217) saturated hydrocarbon and (m/z 178, 184, 192) aromatic hydrocarbon</td>
<td>98</td>
</tr>
<tr>
<td>Table 7.8 Compounds identified in the m/z 217mass fragmentograms shown in (Fig. 7.18) and (7.19)</td>
<td>108</td>
</tr>
<tr>
<td>Table 7.9 Compounds identified in (m/z 178,184 and 192) of aromatic hydrocarbon</td>
<td>108</td>
</tr>
</tbody>
</table>
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ABSTRACT

Cuttings samples were collected for Organic Geochemical studies from two selected wells namely, Kaikang-3 well (59 samples), and Kaikang West-1(40 samples), Muglad Basin, Sudan. It is aimed to evaluate source rocks potentiality for hydrocarbons generation in terms of their Total Organic Content (TOC) and quality of organic matter by Kerogen Type as well as the Maturity Level.

Rock-Eval data, Vitrinite Reflectance measurement and palynofacies analysis from Kaikang-3, revealed a very good-quality of thin oil source beds with excellent generating potential. These beds lie within Tendi Formation at depth interval (1070-1110m). They are characterized by kerogen type II and a mature source rock placed at the beginning of the oil generative window. Analysis for Kaikang West-1 well also indicated very good-quality of thin oil source beds with excellent generating potential within Tendi and Baraka Formations at various depth intervals of Tertiary age. Two crude oil Drill Stem Tests (DSTs) samples from Kaikang-3 well and Kaikang-1 well, as well as two source rock extracts samples from Kaikang-3 well and Kaikang West-1 well were selected for Gas Chromatography (GC) and Gas Chromatography Mass Spectrum (GCMS) analyses. The resulting biomarkers parameter distributions show that, the Kaikang’s oils are similar and derived from lacustrine shale source with relative contribution of bacterial/algal organic matter deposited under suboxic to anoxic conditions and they were derived at the early peak of oil generation window.

The two rock extracts showed that the oils were derived from lacustrine shale with high contribution of land plant organic matter deposited under suboxic to oxic conditions. Maturity assessment for these extracts reveal that the sources entered the main phase of oil generative window.
It is recommended to carry out Gas Chromatography Mass Spectrum/Mass Spectrum (GC MS/MS) technique to determine the geological age of the source rocks and oils in the Kaikang Trough
الخلاصة

إشتملت الدراسة على التحليل الجيوكيميائي للعينات كسرات صخرية من بنري كيكانق-3 وكيكانيق غرب-1 من حوض المجذب بغرض تقييم صخور المصدر من ناحية احتماليتها لتوليد النفط (الهيدروكربونات) خاصة ما يتعلق بالكلي للمادة العضوية ونوعيتها (أنماط الكيروجين) ومستوى نضج تلك المادة.

أشارت تحاليل تقييم الصخور وقياسات الانعكاس الزجاجي وتحاليل السحبات البالينولوجية لعينتين بنري كيكانق-3 إلى وجود طبقات رقيقة من صخور المصدر، ذات احتمالية جيدة لتوليد النفط. هذه الطبقات تقع داخل تكوين تندي في المدى العمقي من 1070-1110 متراً. وهي تتميز بالنمط الثاني من الكيروجين وبأنها ناضجة تقع في بداية النافذة الزيتية.

دلت تلك التحاليل أيضاً لعينتين من بنري كيكانق غرب-1 على وجود طبقات رقيقة بإمكانات توليد جيدة للنفط تقع داخل تندي وبركه وعلى مدى عمقي متفرقة في العمر الثلاثي، أيضاً تتميز بالنمط الثاني من الكيروجين وهي صخور مصدر ناضجة تقع في قمة النافذة الزيتية.

تم اختيار عينتين من النفط الخام من بنري كيكانق-3 وكيكانيق-1 وعينتين من النفط المستخلص من صخور المصدر من بنري كيكانيق-3 وكيكانيق غرب-1 لتحاليل كروماتوغرافيا الغاز وكرماتوغرافيا الغاز-مقياس الطيف الكتلي.

توقفت الدراسة البيولوجية أوضحت أن عينات نفط كيكانيق متشابه ذات منشأ ناتج من الطفل البحري بأشكال من البكتريا والطحالب كمادة عضوية كانت قد تبقيت في بيئة قليلة إلى معدومة الأكسجين. وقد تحولت عند بداية النافذة الزيتية وعينات النفط المستخلص من صخور المصدر أنهما من مصدر من الطفل البحري بأشكال من النباتات الأرضية كمادة عضوية كانت قد تبقيت في بيئة قليلة إلى كثيرة الأكسجين.

وتمت التوصيات بأجراء تحاليل باستخدام تقنية كروماتوغرافيا الغاز مقياس الطيف الكتلي-مقياس الطيف الكتلي وذلك لتحديد العمر الجيولوجي لصخور المصدر والنفط في منطقة منخفض كيكانيق.
CHAPTER ONE

1. INTRODUCTION

1.1 Location of the Study Area:
The NW-SE trending Abu Gabra Rift (Muglad Rift Basin) is the largest of the Central African Rift basins located in southwest central Sudan. It covers an area of 120,000 km² and is up to 200 km wide, and over 800 km long. Locally the basin contains up to 13 km of Cretaceous to Tertiary sediments. It extends from western Kordofan, southern Darfur States in the north and further to the south passing through the Sudanese Kenyan border. The Kaikang Trough (present study area) is located in the north west of Unity State, south central of Muglad Rift Basin. It is bounded approximately by Latitudes 09° 17′ 05″ and 9° 26′ N and Longitudes 29° 5′ and 29° 10′ E (Fig. 1.1). Two wells from the study area were selected for the present study, namely Kaikang-3 and Kaikang West-1 (Fig. 1.2).

1.2. Topography:
The topography of the study area is characterized by sand dunes which occupy more than 65% of the northern parts of Darfur and about 10 to 15% of southern Darfur. The region is characterized by gently undulating to nearly level uplands; however, it is interspersed with various hills and mountains. The mountainous and hilly trains occupy some areas of central Darfur and featured mainly by the massive Jebel Marra and other hills such as Meidoub and Tagabo. Clay and Gardud soils occupy the western and south western parts and some areas in the north.
Fig. 1.1 Location map of the study area in South West Central Sudan.
Fig.(1.2): Location Map of Studied Wells Kaikang West-1 & Kaikang-3, Kaikang Trough, Muglad Rift Basin, Sudan.
1.3 Drainage System:
The Muglad area is flat land drained by wadis, seasonal water courses raging from rivulets (khor) that flow only occasionally during the wet season to the large wadis that flow for most of the rainy season to the gentle slope is to the south. These wadis flow southward and southeastward from Jebel Marra and Nuba Mountains area respectively into Bahar Al Arab River which in turn drains into the White Nile River. Jebel Marra forms the water divide where seasonal streams and wadis flow east, west and south of the Jebel. Wadi Barei and Wadi Azoom flow to the west and south west. Wadi Al Ku, Wadi Taweela, Wadi Kutum and Wadi Al Kaj flow to the east and south east. Wadi Kass and Wadi Bulbul flow to the south and southeast. Although all these wadis are seasonal, some of them retain surface and subsurface waters where shallow wells are dug to grow some vegetables and horticultural crops. Examples of these are in Kabkabiya, Kuttum and Garsila. Deeper water aquifers are in Baggara, Sag Annam and Umbayada where good drinking water for both human and animals is always available.

1.4 Climate:
Sudan can be divided into three regions. The desert region north of latitude 19°, the typical tropical continental climate south of latitude 19°. The rainfall is in the range of less than 100mm in the desert to 1500mm in the high rain fall Savannah and mountain rain forests of the subtropics. The third region is the Red Sea coast. The study area lies within sub-Saharan region (Rodis, et. al. 1964).
The Muglad area is characterized by short and mild dry windy winters and long, hot rainy summers with adequate sunshine and great variations between day and night temperatures. The winter season begins in December and ends in February. The summer season practically
dominates the rest of the year. The annual minimum temperature is 20\(^\circ\)C and the maximum temperature is 36 \(^\circ\)C. Normal winter temperatures range between 8\(^\circ\) and 16\(^\circ\)C and the normal summer temperatures range between 30\(^\circ\) and 36 \(^\circ\)C. The humidity increases from north to south and ranges between 25% and 40%. High humidity values are observed in the hilly areas particularly in Jebel Marra area. The region includes a number climatic zones ranging from desert in the north to rich Savannah in the far south.

1.5 Soils:

The two main soils in the study area are the sandy soils and the dark clay soils. The sandy soils are mainly stabilized sand dunes known locally as Qoz lands. These are generally flat to undulating with various depths. They are very permeable, efficiently drained and have low water holding capacity. The clay soils are part of the central plains of the Sudan. These are vertisols with high clayey content. The clayey pediplain soils known locally as gardud prevail in many parts particularly in southern Darfur and the Naga’a soils which mainly exist in southern Darfur.

The general descriptions of the soils and the soil types in Darfur credit their origin to the information found at [http://aquella.pl/wiki/Geography_of_Sudan](http://aquella.pl/wiki/Geography_of_Sudan). Based on recent soil surveys it is evident that the soils vary from pure sands occupying the desert and semi-desert mainly confined to the northern half of the region, to clay and volcanic deposits which are dominant in the south and west. The sandy soils in the northern part of Darfur have potential for different types of agriculture particularly millet and other staple food in addition to groundnuts and sesame as cash crops. The vast alluvial clay plains in the south extending up to Bahr El Arab are constrained by marshy conditions near the river. The silt deposited around water courses such as Wadi
Azum represents fertile soils where vegetables, tobacco, fruits and cereals are grown.

1.6 Vegetation:
Monumental work on vegetation on the Sudan is regarded as the most genuine work for the whole country and information can be found at [http://aquella.pl/wiki/Geography_of_Sudan](http://aquella.pl/wiki/Geography_of_Sudan). Given the broad phytogeographical zonation, northern Darfur is sub-divided into the desert and the semi-desert region, and southern Darfur comprises the Low Rainfall Woodland Savannah and the associated areas such as the Hill Catena and Baggara repeating pattern. This categorizing is closely associated with plant species which favour specific climatic zones. It has been reported that the basic vegetation cover still exists in most areas and the complete disappearance and extinction of all species has not been reported. However, overuse and misuse activities such as heavy grazing and over cutting of trees in addition to droughts and over population of both man and animals have reduced the densities of plant species. However, the common types of vegetation are the dominant types of *Acacia* trees.

1.7 Population:
Kaikang area is located in the northwest of the Unity State. Unity is one of 26 wilayat or states of Sudan. It has an area of 35, 956 km\(^2\) and estimated population of approximately 175,000 (2000 census). Bentiu is the capital of the state. It has nine districts and is the location of some rich oil fields. Unity is inhabited by two southern Sudan tribal groups, the Nuer (majority) and the Dinka (minority). The nine districts which comprise the Unity State are; Mayom, Rubkona, Parieng, Leer, Koch, Abeimnom, Mayendit and Payinjiar.
1.8 Socio-Economic Development of the Area:

Community Development is a unique program and a part of oil companies’ code of ethics and social responsibilities to improve the living standards of the local communities living in oil concession areas or along and around the pipeline route.

Based on the comprehensive survey done to develop staff to the various local communities living near to the facilities, Oil Companies Community Development Program has been mainly designed to address the basic needs. The primary concern of those local communities is health, education, water, agriculture, capacity building and other socio-economic activities such as social and cultural clubs.

Oil companies so far have developed a number of health centres, schools, water wells, hand pumps and social clubs in many villages and towns in Unity, Western and Southern Kordofan States and the Red Sea State. Moreover, they constructed a number of gravelled roads which have facilitated the movement of inhabitants from one area to another, especially during the rainy season. These programs have contributed positively towards the settlement of the number of inhabitants living around oil companies facilities have significantly increased and doubled in the last few years.

1.9 Statement of the problem:

Muglad Basin represents part of the Central African Rift System (CARS) with a dextral movement 120o, generally trending NW-SE. Ditch cutting samples and oil samples from, Kaikng-3 and Kaikang West-1 wells have been analyzed to evaluate the source rock potentiality for hydrocarbon generation of the Early Cretaceous synrift lacustrine sediments of the deeper area of the Muglad Basin (Kaikang trough) using different geochemical techniques.
1.9.1 Previous Related Work:

Schull, (1988) summarized the geochemical data of Chevron Overseas Inc. including routine analyses of whole-rock pyrolysis and organic carbon content based on thousands of rock samples from 65 wells. The analytical data indicate that dark grey lacustrine claystones and shales of the early rift phase (Neocomian-Albian) are moderately rich oil prone source rocks. Total organic carbon content average 1.3% (range 1 to 5%). The primary source of kerogen are degraded algal and plant material. During thermal maturation, these hydrogen–rich kerogenes generate paraffinic, low sulfur, high pour point oils. The oils have 18°-45°API gravities and 80°-105° F (45°-59° C) pour points.

(Schull, op. cit.) drew a geochemical log in which the various columns indicate the oil–prone nature of the source rocks HI (Hydrogen Index), the source potential (S2) and the maturation level (Ro).

The geochemical log provided by Peters (1986) reflect the limited source potential of the younger claystone-shale interval. The temperature gradient ranges from 1.0° to 1.8°F/100 ft (18°-33°C/km) with a 1.4°F/100 ft (26°C/km) average. Earliest generation typically begins at approximately 10,000 ft (3,048 m).

Robertson Research International (RRI,1990) evaluated the previous work of Chevron Overseas Inc in the interior rift basins in Sudan and presented a volume en titled The Geology and Petroleum Potential of South, Central and Eastern Sudan. In their study they used various geochemical techniques to evaluate source rock potentiality for hydrocarbon generation.

Mustafa and Tyson, (2002) identified the lacustrine Aptian-Albian shales of Abu Gabra Formation as the main source rock in the Muglad Basin. With an overall mean TOC of 1.34% (n== 146), compared with those from in the NW part of the basin (Sharaf area) being approximately twice
as organic i.e. richer than those in the SE (Heglig area). The Abu Gabra Formation contains two distinct organic facies: a lower interval dominated by higher TOC values (1.5-2.3%), higher measured hydrogen indices (338-546), higher amorphous kerogen contents (>80%) and heavier $\delta^{13}$ C TOC values (> -27%); and an upper, less rich interval (mean TOC 1.4%, mean HI 83, $\delta^{13}$ C TOC approximately -28%). They used S2v. TOC plots and suggested a corrected true mean hydrogen indices of around 800 in the richer facies (corresponding to a Type I kerogen). Mean random vitrinite reflectance, pyrolysis, Tmax values, and visually determined fluorescence colours indicate that the source rock is immature, or at most in the earliest part of the oil window (<0.7% VRo). The biomarker data suggest that the vitrinite reflectance values may be suppressed by up to 20%.

Mohamed, et al., (2002), studied the source rock of the Abu Gabra and Sharaf Formations. They found that these formations have an average total organic carbon of 1.0% and hydrogen index (HI) of 280 and they modelled for hydrocarbon generation. However, their studied section was divided into four layers, namely Abu Gabra-1 (Albian), Abu Gabra-2 (Aptian), Sharaf-1 (Barremian) and Sharaf-2 (Neocomian). Also they found that the conditions for hydrocarbon generation were present through out the Sharaf Formation and also in Abu Gabra-2 layer.

Mahgoub, (2009) did a geochemical correlation and studied source rocks from Melut Basin. The work forms a good base as a scientific reference for further oil geochemical studies in Sudan Rift Basins. She selected about 31 crude oil samples and 65 rock samples to identify types of source, depositional environment and maturity assessments. Different analytical techniques were used such as Rock-Eval, Vitrinite Reflectance (VRo), Liquid Coulmn Chroamtography (LCC), Gas Chromatography (GC), and Gas Chromatography Mass Spectrum (GCMS) in order to
characterize the oil and rock samples. Hierarchical Cluster Analysis (HCA), Principal Component Analysis (PCA) and biomarker distributions were also used to establish oil-oil and oil-source correlation to describe the geochemical character of the oil, determine the number of genetically related crude oil families and to carry out genetic correlation of potential and effective source rocks.

1.9.2 Objectives
To evaluate source rock potentiality for hydrocarbon generation of the Early Cretaceous/Tertiary synrift lacustrine sediments of the deeper parts of the Muglad Rift Basin (Kaikang trough) using different geochemical techniques.

To identify biomarkers and use their parameters to indicate source organic matter input, depositional environment during burial, and thermal maturity.

1.9.3 Present Work: (Material and Method)
A total of about 99 cutting samples from two wells were selected for study. The cutting samples from Kaikang-3 and Kaikang west-1 from Muglad basin, south west central Sudan. Two extract source rock and DST oil samples were selected from Kaikang-3 and Kaikang west-1 wells.

For the geochemical evaluation:
Rock-eval pyrolysis was conducted on washed, hand picked cutting samples using Rock-Eval 6 equipment.
Vitrinite reflectance was measured on whole rock polished block sample. Reflectivity was measured using PMT-microscope photometer version 1.0.
Palynofacies analysis involved demineralizing the sediments by treating with hydrochloric acid (HCl) and hydrofluoric acid (HF). The concentrated kerogen is mounted on 26mm X 76mm glass slide and observed under transmitted light microscope (Leica DLMB model).

**For the biomarkers applications:**

Bitumen extraction was performed using soxhlet apparatus for 32 hours with dichloromethane (DCM).

The extracts and crude oils were fractionated by liquid column chromatography (LCC) using activated silica gel, alumina, petroleum spirit and dichloromethane (DCM), giving saturate and aromatic fractions. The saturate and aromatic fractions of source rocks and crude oils were analyzed by using gas chromatography (GC) VARIAN CP-3800 GAS CHROMATOGRAPH with flame ionization detector (FID). The capillary column was programmed from 40°C-300°C at 5°C/min.

Gas chromatography-mass spectrum (GC-MS) analyses were undertaken using quadrupole system to determine the distribution of the biomarkers in the extracts from the source rocks and the oils.

The GC-MS was performed using Aglient 6809N network system interfaced with 5973N network, mass selective detector. The GC-MS was fitted with a 60m Agilent fused silica capillary, HP-5MS 0.25 mm ID, 0.25µm films. Helium was used as a carrier gas, head pressure 4-5 bar, split ratio 15:1, injector temperature 300°C, EI source 230°C and SIM mode was cycled at 2 seconds.
CHAPTER TWO

2. GEOLOGICAL EVOLUTION AND HISTORY OF OIL EXPLORATION

2.1. Geological Evolution
Muglad Basin is one of a series of similar troughs which occur across North-Central Africa. The troughs were formed by regional rifting since the latest Jurassic through Cretaceous to early Tertiary periods (Schull, 1988) (Table 2.1). Tensional tectonics with normal syn-sedimentary faulting have been prevalent since the Cretaceous period with evidence from seismic data (Moniem, et al. 1984). The results of the rifting have provided a variety of sedimentary rocks, mainly continental in origin. The sources for the continental sediments have probably been the flanks of the basin (Moniem, et al. op. cit).

During geological time extending from Neocomain through Barremain to Aptian-Albian, a large system of lakes began to develop in the central depression formed by the rift basin. Lacustrine shales, clays, silts and occasionally fine-grained sandstone beds were deposited during Neocomain-Barremain (Moniem, et al. op. cit.). In Muglad Rift Basin the maximum penetration referred to as Lower Abu Gabra Formation, the thickness approximately 1,200 ft (366m, Schull, 1988).

The sediment deposition system continued through Neocomin-Barremian period forming the sediments of Abu Gabra Formation, in a slowly widening sedimentary basin. The lacustrine sediments interfingered laterally with delta–fan and alluvial–fan as well as with floodplain, silts and clays deposited in the large flat area surrounding the lakes.

Dark lacustrine shales of the Abu Gabra Formation form the principal source rocks in the Muglad Basin. Rapid deposition, anoxic condition in the lakes and covering by sediments prevented the organic material from
oxidizing. The organic material is derived from autochthonous organic production within the lakes as well as from the land plant material derived from the surrounding land and transported into the lacustrine environment by streams.

Continuous movements of syn-sedimentary faults gave rise to a stronger differentiation of the basin, with rather thick sedimentary sequences of Upper Abu Gabra sediments in the faster subsiding areas of the trough.

During the Aptian-Cenomanian period changing sedimentary conditions indicate a break in the basin development. This is characterized by supply of elatic material, and stronger uplift of the flanks of the basin, leading to partly higher energy environment than before, with subsequent distribution of coarser material. During this period the characteristic sediments of Aptian-Cenomanian sediments of Bentiu Formation were deposited mainly of fluvialitile sands with intercalations of some floodplain clays and silts of limited lateral continuity up to 5,000 ft (1,525m) thick, typically showing good reservoir quality (Schull, 1988).

The sediments of the Turonian-Maastrichtian Darfur Group lie unconformably over the Bentiu Formation. Generally the Darfur Group is characterized by sandstones succession intercalated with claystones. This group can be differentiated into Aradeiba Formation which, is dominated by claystone with some sandstone in between. The Aradeiba Formation then is overlain by Zerga and Ghazal Formations. The last two formations consist predominantly of sandstone interbedded with some claystone. The above mentioned formations overlain by Baraka Formation, which mainly consists of sandstone. According to (Schull, op.cit) the maximum thickness of Darfur Group is up to 6,000 ft (1,829m).

The Cretaceous period ended with deposition of coarser sediments reflected by the higher sand percentage of Ghazal and Baraka
Formations. These formations could be important reservoirs in Unity fields (Schull, op.cit). The continuous movements of the basin through syn sedimentray faulting with uplifts of parts of the trough, caused the partial erosion of Darfur Group in some areas of the basin. Stronger uplifts of the sediment supplying flanks have led to deposition of Amal Formation which is characterized by coarse, braided type fluvial sands. The thickness of the massive sandstone of the Amal Formation is up to (2,500 ft ) (762m, Schull, 1988).

The sediments of the Kordofan Group were deposited during the time from the late Eocene to Pliocene, with a thickness reaching approximately 16,000 ft in the deepest parts of the basin (Schull, op.cit). In the lower part of Kordofan Group (Nayil and Tendi Formations), the sediments are fine-grained.

Covering Amal formation these Formations, play an important role by offering an excellent potential seal. Upward, these units are overlain by Adok and Zeraf Formations which consist of interbedded sandstones and claystones with an increase in the sand from bottom to the top.

These Formations were deposited in fluvial-floodplain and limited lacustrine environment, and this may give way to the increasing alluvial input reflected in the sand-rich braided stream and fan deposits (Schull, op.cit).
(Table 2.1): Geological and Structural Evolution of the Muglad Rift Basin, South West Central Sudan (modified after Schull, 1988 and Awad, 1999).

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<thead>
<tr>
<th>Era</th>
<th>Period</th>
<th>Chorono Stratigraphy</th>
<th>Formation and Groups Nomenclature</th>
<th>Rifting Phases</th>
<th>Depositional Environments</th>
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<tr>
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<td>Quaternary</td>
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<td>Tendi Formation</td>
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<td>Nai1 Formation</td>
<td>Massive Sandstone Sequences</td>
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<td>Eocene</td>
<td>Amal Formation</td>
<td>Predominantly Sandstones with some Claystones interbeds</td>
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<td>Baraka Formation</td>
<td>Predominantly Sandstones with some Claystones interbeds</td>
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<td></td>
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<td>Albian</td>
<td>Lower Bentiu Formation</td>
<td>Predominantly Claystones/ Shales fine Sand/silts</td>
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<td>Aptian</td>
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<td>Lacustrine Deltaic</td>
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<td></td>
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<td>Barremian</td>
<td>AbuGabra Formation</td>
<td>Lacustrine Fluvial- Floodplain</td>
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<td></td>
<td></td>
<td>Neocomian</td>
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</table>

**Litho-Stratigraphy Description:**
- Interbeded Sandstone/ Alluvial Fans
- Predominantly Claystones/ Shales and Sandstones interbeds
- Massive Sandstone Sequences
- Predominantly Sandstones with some Claystones interbeds
- Predominantly Sandstones with increasing Sand content
- Predominantly Claystones/ Shales and Sandstones interbeds
- Predominantly Claystones/ Shales and Sandstones interbeds
- Massive Sandstone Sequences
- Predominantly Sandstones with some Claystones interbeds
- Predominantly Claystones/ Shales and Sandstones interbeds
- Predominantly Claystones/ Shales and Sandstones interbeds
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- Predominantly Sandstones with some Claystones interbeds
2.2 History of Oil Exploration:

In mid-late 1970s, oil companies showed an interest in the interior basins and commenced their own geological work. Consequently Chevron Overseas Petroleum Inc. had acreage in Sudan Interior Rift Basins, specifically Muglad, Melut and Blue Nile basins.

Total Oil Company made at least one trip to the southern areas of the concession in order to map any outcrops of sedimentary sequences including that of the Yirol beds.

In the mid 1980s Total made a field excursion to Gedaref and Kassala in order to evaluate the sedimentary pile in conjunction with their geophysical evaluation.

In early 1975, Chevron Overseas Petroleum Inc. commenced the first oil exploration in the Muglad, Melut, and Blue Nile sedimentary basins in Interior Sudan Rift Basins, which paved the way for the current exploration activities in the country.

In 1982, Phillips Petroleum Company undertook a brief field season in acreage north and west of Khartoum. The area was later relinquished and subsequently awarded to Sun Oil Company who conducted several field trips into this area during the mid 1980s.

The Exxon Texas, The Delta, The French Company Total and The Philippine companies conducted geological and geophysical surveys in areas and drilled 95 exploration wells of which 46 wells were productive in the Abu Gabra, Sharif, Unity, Talha, Greater Hehlig and Aderiel. Chevron made significant discoveries, but in 1990, it relinquished the whole concession to the Government of Sudan leaving these discoveries undeveloped.

In 1993, a small Canadian oil firm, State Petroleum Corporation (SPC), acquired Block 1, 2 and 4. These blocks are located in Muglad Rift Basin, which is about 1,000 km long, extending from the central part of Sudan
into the south. This basin is divided by the Ministry of Energy and Mining into 10 blocks, including Blocks 1, 2 and 4. State Petroleum made some additional discoveries.

In 1997, Greater Nile Petroleum Operating Co. Ltd (GNOPC), a consortium composed of China National Petroleum Corporation (CNPC), Petronas, Oil and Natural Gas Corporation (ONGC) and Sudapet; acquired Blocks 1, 2 and 4 from State Petroleum and launched an extensive exploration and development program. This led to discovery of 1.0 billion barrels of additional reserves. Shortly, GNPOC initiated numerous Field Development Plans (FDPs), constructed 1610 km export pipeline, and eventually, exported the first Sudanese oil in 1999.

The pipeline was built in order to transport the crude oil from the fields to the refinery in Khartoum, and then to Bashair in Eastern Sudan.
CHAPTER THREE

3. GEOTECTONIC AND STRUCTURAL SETTING

3.1. Geotectonic Setting

From geophysical investigations, palynological and well log data, it has been determined that the interior basins in the southern half of Sudan are broadly Mesozoic to Tertiary in age and have developed as a result of fault controlled subsidence (RRI, 1990). The largest basins being represented by NW-SE trending Muglad Rift Basin complex and the NNW-SSE trending Melut basin complex. A number of subsidiary basins are associated with these major basins trends; the Rakuba and Jonglie basins representing the extensions of the Muglad Rift Basin complex, whilst the Ruat and Pibor basin represent extension of the Melut basin complex. The Bagara, Nahud, Um Hani and Mahbuba basin are developed above a major WSW-ENE trending lineament across which the Melut and Muglad basin complexes do not continue northwest (RRI, 1999).

The extensional tectonism that formed these basins began in the Jurassic (?) –Early Cretaceous (Schull, 1988). Movement along major fault trends continued intermittently into the Miocene (Schull, op. cit). This deformation resulted in a complex structural history that led to the formation of several deep faults–bounded troughs, major interbasinal highs, and complex basin flanks. This tectonism has created a wide variety of structures many of which become effective hydrocarbon traps. The sedimentary basins of interior Sudan are characterized by thick non-marine clastic sequences of Jurassic (?)–Early Cretaceous and Tertiary age. Over 45,000 ft (1,716 m) of sediment were deposited in the deepest trough and extensive basinal areas are underlain by more than 20,000 ft (6,096 m) of sedimentary rocks. The depositional sequences include thick
lacustrine shales and claystones, floodplain claystones and lacustrine, fluvial, alluvial sandstone and conglomerate. The lacustrine claystones deposited in a suboxic environment provide good oil-prone source rocks. Reservoir sandstones have been found in a wide variety of non-marine sandstone facies (Schull, 1988).

The initiation of rifting in southern Sudan may have been directly related to Jurassic rifting in the Lamu embayment of Kenya (Reeves et al, 1987, Schull, op.cit). Anza trough of northern Kenya strikes in the same direction as the Muglad, Melut and Blue Nile basins.

This primary southern Sudan rifting phase continued into the Albian, corresponding with the initial opening of the south Atlantic and extension in the Benue trough (Wright, 1981).

During this period of regionally widespread rifting, thick sedimentary sequences were deposited in several developing African basins, e.g., Benue trough, East Niger basin, Doba basin, Ngaoundere Rift basin, and Anza trough. Some of these basins developed within and immediately adjacent to the Cretaceous shear zones and others formed near their endpoints at angles of 90°–120° to the shear movement.

Fairhead and Green (in Schull, op.cit) suggested that the movement along the Central African Shear Zone translated into the extensional basins of southern Sudan. This relationship is similar to that between the axial shear zone of the Benue trough and the East Niger rift basin. This mechanism could explain rift basin development contemporaneous with movement along the West and Central African shear zones.

The second southern Sudan rifting phase began in the Turonian and continued until near the end of the Cretaceous. This rifting was accompanied by the deposition of up to 6,000 ft (1,829 m) of sediments. Fairhead (in Schull, op.cit) has concluded that changes in the opening of south Atlantic account for a late Cretaceous period of shear movement on
the West and Central African rift system. This movement could explain Late Cretaceous Benue compression and dextral reactivation of the Central African Shear Zone. The second Sudan rifting phase may be related to this movement (Schull, 1988).

In the ENE- WSW trending Bagarra basin, a continuation of the Central African Shear Zone strike-slip movement occurred. This continuing strike-slip movement is not seen in the adjoining north western Muglad basin or further northeast. The eastnortheast-westsouthwest trend appears to have been terminated and replaced by the northwest-southeast trending basins interpreted to be extensional in their development, supporting the concept of translation of shear movement extension. Also during this period rifting and deposition continued in the northwest southeast-trending Anza trough.

The thick highly faulted lower Tertiary section of the southern Sudan basins indicates that the final rifting phase was a significant tectonic event. Regional data suggest the initiation of this phase was generally time equivalent to initial phases of the opening of the Red Sea (Lowell and Genik, 1972) and East African Rifting (Girdler, 1969). The Muglad, Melut and Blue Nile basins are subparallel to the Red Sea which rifted in response to the African Arabian extensional forces. A direct relation between the east African rifting and the development of the southern Sudan basins is not apparent.

Interestingly, a sharp contrast is seen between the Tertiary development of southern Sudan basins and the West African basins, which exhibited strong Cretaceous similarities. For example, the East Niger basin (Fig. 3) has only a thin relatively unfaulted Tertiary section (Avbovbo et al, 1986). This section indicates that the significant early Tertiary extension affecting southern Sudan and resulted in the accumulation of over 13,000 ft (3,962m) of sediment, was inoperative in West Africa basins. However,
the Anza trough, to the southeast, did experience rifting and thick accumulation. During late Tertiary, the regional stress regime changed resulting in the Middle Miocene termination of southern Sudan rifting. To the northeast, the Red Sea rift continued its development.

3.2 Structural Setting:
According to Schull (1988) the structure development of this area can be divided into a pre-rifting phase, three rifting phase and a sag phase.

3.2.1 Pre-rifting Phase:
By the end of the Pan-African orogeny (550+100 m.y.) this region had become a consolidated platform during the Paleozoic and early Mesozoic. This highland platform provided poorly sorted and various types of sediments to the adjacent subsiding areas, which is called the pre-rifting sediments.

3.2.2 Rifting Phases:
Three distinct periods of rifting occurred in response to crustal extension, which provided the isostatic mechanism for subsidence (Browne and Fairhead, 1983, Schull, 1988). Subsidence was accomplished by normal faulting parallel and sub-parallel to the basinal axes and margins. Based on widely spaced penetration, rifting is thought to have begun in the Jurassic (?)-Early Cretaceous (130-160 Ma). This initial and strongest rifting phase lasted until near the end of the Albian. The second rifting phase occurred during the Turonian to late Senonian. This phase resulted in the deposition of lacustrine and floodplain
claystones and siltstones which terminated the deposition of Bentiu Formation.
The rifting phase was accompanied by minor volcanism. The end of this phase is marked by deposition of an increasing sand-rich sequence that ended with a thick Paleocene sandstone of the Amal Formation. The final rifting phase began in the late Eocene-Oligocene. This final phase is reflected by a thick sequence of lacustrine and floodplain clayey sandstones and siltstones. After this period of rifting deposition became more sand rich throughout the late Oligocene-Miocene (Schull, 1988).

3.2.3 Sag Phase:
In the Middle Miocene the basinal areas entered an intracratonic sag phase of very gentle subsidence accompanied by little or no faulting. During this time extensive volcanism occurred in some adjoining areas to the north e.g., Jebel Marra, Meidoub Hills and in the East African Rift system to the east and southeast (Schull, op.cit).
Fig. 3.1 Tectonic and Structure Map of the Central African Shear Zone (CASZ), After Fairhead, (1988).
4. THE STRATIGRAPHY OF MUGLAD RIFT BASIN

The major stratigraphic units of the Muglad Rift Basin include the following units. Table 3.1 is a generalized lithostratigraphic scheme of the basin.

4.1 Basement Complex (Precambrian):
The basement is predominantly made up of Precambrian Cambrian metamorphic rocks with limited occurrences of foliated intrusive igneous rocks including granitic and granodioritic gneiss which has been penetrated only in two wells Baraka 1 and Adilla -1. In Adilla the basement consists of granite overlain by highly lithified sandstone on top while in Baraka the granodiorite gave an age of 540 Ma ± 40 m.y. (Moniem et al., 1984, Schull, 1988)

4.2 Cretaceous Sedimentary Units:
A few Nubian sandstone outcrops are encountered in the Muglad basin east and northeast of Muglad town. In this area, the rocks are water laid, non-marine, massively bedded, highly weathered, and medium- to coarse-grained sandstone. The depositional history and age was difficult to determine, because they from limited and scattered outcrops (Schull, 1988).

In the subsurface, a thick sequence of Cretaceous sediment has been penetrated. Based on seismic data and well control, an estimated 20,000 ft (6,096 m) of Cretaceous sediment has been deposited in the deepest troughs (Schull, op.cit).
<table>
<thead>
<tr>
<th>PERIOD</th>
<th>AGE</th>
<th>LITHOSTATICA T</th>
<th>LITHOLOGY</th>
<th>BIOSTRATIGRAPHY</th>
<th>MARKER TAXA</th>
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<td>Amal</td>
<td></td>
<td></td>
<td>Mauritiidites crassibaculatus Gemmamono. macrogemmaus Echimonocolpites rarispinosus</td>
<td>VIII</td>
</tr>
<tr>
<td>TERTIARY</td>
<td>Maastrichtian</td>
<td>Baraka</td>
<td></td>
<td></td>
<td>Proteacidites sigali Buttina andreevi Echidiporites barbetoensis</td>
<td>VII</td>
</tr>
<tr>
<td></td>
<td>Campanian</td>
<td>Ghazal</td>
<td></td>
<td></td>
<td>Syncolporites spp. Zlivisporis blanensis Scabratriporites simpliformis</td>
<td>VI</td>
</tr>
<tr>
<td></td>
<td>Santonian</td>
<td>Zarga</td>
<td></td>
<td></td>
<td>Mugladopollis sudanicus</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>Coniacian</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Turonian</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cenomanian</td>
<td>Upper Bentiu</td>
<td></td>
<td></td>
<td>Cretaceaiporites spp. Afropollis jardinus Gnetaceaepollenites spp. Crybelosporites pannuceus</td>
<td>III</td>
</tr>
<tr>
<td></td>
<td>Albian</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MESOZOIC</td>
<td>Aptian</td>
<td>Lower Bentiu</td>
<td></td>
<td></td>
<td>Afropollis zonatus Ephedripites jansonii Classopollis spp.</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td>Barremian</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>II/A</td>
</tr>
<tr>
<td></td>
<td>Neocomian</td>
<td>Abu Gabra</td>
<td></td>
<td></td>
<td>Aequitriradites spinulosus Pilosisporites trichopaplosus Exesipollenites sp. (Dyads) Dicheiropollis etruscus Appendicisporites spp.</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.2.1 Abu Gabra Formation (Neocomian-Berremian):
It consists of organic-rich fluvial lacustrine claystones and shales deposited with interbedded fine-grained sands and silts. The nature of this deposit was probably the result of the humid climate and lack of external drainage, indicating that the basins were tectonically silled. Thickness varies from 1000 to more than 6000 ft (1,829m, Schull, 1988). The basal contact to Lower Abu Gabra Formation is gradational, while the upper contact towards Bentiu Formation is well defined marking a clear break in a sedimentary pattern (Moniem, et al. 1984). Several wells have recovered oil from sand within this sequence. According to (Schull op.cit.) these sands were deposited in a lacustrine - deltaic environment.

4.2.2 Bentiu Formation (Aptian-Cenomanian):
The Bentiu Formation comprises a massive sandstone sequence with some thin claystone interbeds. The claystones grade downwards from reddish-brown to medium grey. They are medium- to coarse-grained and less consolidated than the overlying formation. The claystones appear to have limited lateral continuity, (Moniem, et al. op. cit.). The alluvial and fluvial-floodplain environment expanded probably due to a change from internal to external drainage. The regional basal level, which was created by the earlier rifting and subsidence, no longer existed. These thick sandstone sequences were deposited in braided and meandering streams. They are widely distributed throughout the Muglad basin. This unit, which is up to 5,000ft (1,524m) thick, typically shows good reservoir quality. Sandstones of Bentiu Formation are the primary reservoirs in Unity- and Heglig–fields(Schull, 1988).
4.2.3 Darfur Group (Turonian-Maastrichtian):
According to the RRI (1990) the Darfur group (DG) has been classified into two more subgroups, namely the Darfur Group Undifferentiated (DGU) with an age extending from the Turonian to Lower Campanian. The Darfur Group Undifferentiated (DGU) has been recognized in the NW of the Muglad Basin. Generally, the Darfur Group comprises the Aradeiba –Zarqa –Ghazal and Baraka Formations. Only in Unity and Heglig areas subdivision into four units can be made. In northwestern Muglad the Darfur Group is reduced to a thin sequence of mostly claystones which cannot be subdivided further; the tops and bottoms being recognized regionally as unconformities. (Moniem, et al. op. cit.). A brief description of the Darfur Group (DG) is given below:

4.2.3.1 Aradeiba Formation: (Turonian –Santonian):
This formation consists of interbedded the floodplain and lacustrine calystones, shales, and siltstones are fluvial /deltaic channel sands. The thickness varies from 700ft to over 2000ft. The Aradieba sands are important reservoirs in Unity and Heglig field (Schull, op.cit).

4.2.3.2 Zarga Formation (Campanian-Maastrichtian):
This consists of interbedded sandstones and claystones, the relative amount of the sands in this formation is higher than that in Aradeiba Formation. The sandstones are well defined in Unity field. The thickness ranges from 150ft to over 1000ft. (Moniem, et al. op. cit.).
4.2.3.3 Ghazal Formation (Campanian-Maastrichtian):
This formation consists of interbedded sandstones and claystones similar in composition to sediment assigned to the Zarga Formation. The thicker sands of Ghazal Formation indicate depositional environments of braided streams. The upper Ghazal sandstones indicate a return to the same depositional environment as that of Aradieba and Zarga Formations (Schull, 1988).

4.2.3.4 Baraka Formation (Maastrichtian):
This formation consists of sandstones within thin interbedded silty, claystones deposited in fluvial and alluvial fan environments which prograded from the basin margins (Schull, op.cit).

4.3 Tertiary Sedimentary Units:
The Tertiary is represented by cropping out sequences of unconsolidated sand, gravels silts and clays deposited in alluvial, fluvial, and shallow lacustrine environments (Vail, 1978).

An exposed thick sequence of medium- to coarse- grained sediments is associated with the final rifting phase.

4.3.1 Amal Formation (Paleocene):
This formation consists of massive sandstones composed dominantly of course -to medium- grained quartz arenites (Schull, op.cit).
4.3.2 Kordofan Group: (Late Eocene – Quaternary).
The sediments of this group are characterized by the coarsening upward sequences. The lower portion of this group is Nayil and Tendi Formations which are characterized by fine-grained sediments related to the final rifting phase. While the upper section is formed by Adok and Zeraf Formations which consist of sand and sandstones. The lake deposit of this interval appears to have only minor oil source potential (Shull, 1988). However, they offer an excellent potential as a seal overlying the massive sandstones of the Amal Formation.

4.3.2.1 Nayil Formation (Late Eocene-Early Oligocene).
This formation represents the lower part of Kordofan Group. It consists of hkclaystone, often silty, interbedded with sandstone. It is mainly distributed in the Kaikang trough. The upper boundary of this formation is taken at the change to the more radioactive clay stones of the Tendi Formation which is often darker in color (RRI, 1990).

4.3.2.2 Tendi Formation (Late Oligocene-Early Miocene).
This term was previously established by Chevron. Lithologically the formation consists of claystones which locally grade into sub-fissile and fissile shale, trace pyrite, kaolinites and some carbonaceous debris. The boundary is taken at the upward change from the claystone and shale sequence of the Tendi Formation, into the more arenaceous sequence of sand/sandstone and minor claystone of Adok Formation.
4.3.2.3 Adok Formation (Late Miocene-Pliocene).
The term Adok Formation was also introduced by Chevron. It consists of sand and sandstones in the variable colour. The formation is widely recognized throughout Muglad Rift Basin. The upper boundary is taken at the upward passage into a clear, more massive sequence of sands and sandstones of the Zeraf Formation.

4.3.2.4 Zeraf Formation (Quaternary).
The term Zeraf Formation was given previously by Chevron. It consists of massive sands with variable grain size, but predominantly coarse- to very coarse-grained. The upper boundary is difficult to be recognized, but generally the formation is widely known throughout Muglad Rift Basin.
4.4 Petroleum System:
Sudan contains many prospective basins for oil accumulations. There intracartonic basins contain numerous intrabasinal structures and highs. The most popular and known by size and structure are the Muglad, Melut, Blue Nile, White Nile and Atbara Basins. Oil discoveries and production were achieved in the two major Muglad and Melut Basins.

4.4.1 Source Rock:
The most significant source rock in the Muglad Rift Basin is the Abu Gabra Formation. It shows a wide range of present-day maturity levels for generation of oil. On the present-day, the deepest part of the source rock unit of the Abu Gabra Formation testing on small local highs, such as Sharaf –Abu Gabra Ridge, are actively generating hydrocarbon(RRI,1990). The other far less significant source rocks are present at least in the northwestern of Muglad Basin and in Kaikang trough. Of these the Tendi Formation is widespread, but immature in some places. The Aweil Formation which is equivalent to Nayil Formation, and Darfur Group, barely reach maturity, with only minor oil source potential in the northwest. Significant oil source potential is sometimes seen in the Argillaceous Members of the Aweil Formation in the Kaikang Trough, where sufficient burial depths for adequate maturation could be achieved (RRI, op.cit).
4.4.2 Maturity:
The temperature gradients in the Muglad basin is controlled by location in relation to structural elements is moderate being mainly between 20°C/km and 30°C/km. Only in a few specific areas changes in palaeotemperature gradients are linked to igneous activity. Maturity gradients show uniform increase with depth in most areas in Muglad basin (RRI, 1990). The rapid increase in maturity and temperature gradients are related to the thermal conductivity differences between the highly conductive, sand dominated Bentiu Formation and the underlying lower conductive shale dominating Abu Gabra Formation, which is excellent oil source rock and often mature.

4.4.3 Seals:
A number of shales and claystones interbedded with the potential reservoirs provide the necessary sealing potential throughout the Cretaceous-Tertiary rock sequence of Muglad basin. However, in some parts of the sequence a certain lack of sealing capacity seems to exist which might be responsible for the lack of hydrocarbon in some good reservoirs (Moniem, et al., 1984).

In Abu Gabra Formation interbedded shales provide excellent cap rocks for productive sands. In the lower and middle Bentiu Formation a number of thinner claystones exist but their sealing potential might be partly insufficient. The upper sand units of Bentiu Formation are apparently sufficiently sealed as seen by some productive horizons. Excellent cap rock potential is found in Darfur Group which is also shown by the significant number of productive horizons. The three lower formations of Darfur Group, Aradeiba, Zarga and Ghazal have an optimum ratio of reservoir sands and sealing clays. (Moniem, et al. op. cit.).
4.4.4 Trapping Styles:
The area was subjected to different tectonic episodes which resulted in a complicated system of faulting and folding, with antithetical as well as synthetically fault blocks together with horsts, grabens and domes, resulting in a large number of possible hydrocarbon traps. Rotated fault blocks are formed by simple block rotation along a normal fault plane. These structures are important producing traps, but entrapment depends upon a seal at or across faults for closure. This type of structure is common throughout the Muglad basin. Drape faults are formed in the sediments overlying the upthrown side of deeper normal faults. This type of closures have been found in areas where faults formed during the early rifting phase were not rejuvenated (Schull, 1988). Closures of this type have trapped oil in the Heglig field. In some locations, downthrown rollover anticlines have resulted from rotation into listric faults. These listric faults are often accompanied by antithetic faults sub parallel to the primary fault trend. Several anticline closures have trapped oil in the Unity area. Compression structure and strike slip movement is confined to the Bagarra block. In this area the structures associated with the major basin-bounding faults were formed by Cretaceous and Tertiary compressive forces related to strike-slip movements. These structures are generally folds associated with reverse faults. The basin in this area is narrow and has a trend similar to basinal areas in eastern Chad and Central African Republic, where dextral strike-slip movement is well documented (Browne and Fairhead, 1983).
4.4.5 Reservoir Characteristics:
According to Schull (1988) the reservoir rocks of Muglad basin range from quartz arenites and wackestones to arkosic arenites. The reservoir rocks were originally derived from the Precambrian and Cambrian basement gneisses. The primary reservoirs include sandstones deposited in fluvial-channel, lacustrine delta-plain-distributaries channel, and delta front environments. Typical Cretaceous reservoirs are very fine- to medium-grained, moderately sorted sandstones with subrounded to subangular sand grains (Schull, op.cit.). Coarser grained; more poorly sorted sandstones are common in alluvial intervals. Quartz and feldspar (both k-feldspar and plagioclase) are the dominant minerals. Rock fragments are generally rare and the heavy minerals content is low (0-5%). Clay minerals and mica predominate as matrix. Quartz and kaolinite, with less amounts of calcite and chlorite, are the predominant cement. Most of the Tertiary and Cretaceous sandstones are quartz wackestones and arkosic arenites and wackestones. The origin of these sandstones can be related to a period of lower relief and more intense weathering of the source terrain (Schull, op.cit.).
CHAPTER FIVE

5. METHODOLOGY

5.1 Introduction
A petroleum source rock is defined as any rock that has the capability to generate and expel enough hydrocarbons to form an accumulation of oil or gas. A potential source rock is the one that is too immature to generate petroleum in its natural setting but will form significant quantities of petroleum when heated in the laboratory or during deep burial. An effective source rock is one that has already formed and expelled petroleum to a reservoir. The relative ability of a source rock to generate petroleum is defined by its kerogen quantity total organic carbon (TOC) and quality (high or low in hydrogen). Whether or not it has generated petroleum it is defined by its state of maturation (immature, mature, or post mature with respect to oil) (Hunt, 1996).

5.1.1 Sedimentary Organic Matter:
After the death of organisms the component substances such as carbohydrates, proteins, lipids, lignin, etc. are subjected to decomposition to various degrees depending on the sedimentation medium (especially its redox properties). Part of the products of this decomposition recycled by other organism which use them as energy sources. Simple molecules such as CO₂, H₂O, CH₄, NH₃, N₂, SH₂, etc. are formed as the products of the metabolic processes. Another part is transformed into simple molecules (CO₂, H₂O, etc.) by physico-chemical processes (e.g. oxidation). The rest, which in most cases represents only a very small fraction of the initial quantity of living matter, escapes complete biological recycling or physico-chemical decomposition and is incorporated into the sediments.
This fraction is therefore the primary source of sedimentary organic matter OM (Durand, 1980).

Kerogen is the disseminated organic matter of sedimentary rocks that is insoluble in nonoxidizing acids, bases, and organic solvents (Hunt and Jamieson 1956). Kerogen in rocks has four principal sources: marine, lacustrine, terrestrial, and recycled.

5.1.2 Diagenesis Stage:
This stage corresponds to an immature kerogen, and little hydrocarbon generation has occurred in the source rocks. However, large quantities of carbon dioxide and water and also some heavy heteroatoms (N, S, and O) compounds may be produced in relation to oxygen elimination (Tissot & Welte, 1984). During this stage a whole series of low temperature reactions occur, such as decarboxylation, deamination, polymerization and reduction. Some free bitumen is released, which consists largely of biological markers such as n-paraffin, isoprenoids, steranes, triterpanes, and porphyrins. (Hunt, 1996).

5.1.3 Catagenesis Stage:
Organic matter is subjected to increasingly higher temperature with greater burial depth. Over time, these higher temperature cause thermal degradation of kerogen to yield petroleum range hydrocarbons under reducing conditions (Hunt, op.cit.). Catagenesis is the principal zone of oil formation, the zone of gas formation, where “wet gas” with increasing proportion of methane is generated in large amounts through cracking (Tissot & Welte, op cit).
5.1.3.1 The Oil Window:
The depth interval in which a petroleum source rock generates and expels most of its oil is called the Oil Window. Oil windows are formed mainly in the subsurface temperature range from 60° C to 160° C (Hunt, 1996).

5.1.4 Metagenesis Stage:
Metagenesis is last stage in the significant thermal alteration of organic matter. Metagenesis occurs in the temperature range of 200 to 250° C. In this stage some additional of generation hydrocarbons (mainly methane) from kerogen; liquid hydrocarbon previously generated are also cracked and converted to gas. Also it is a stage of structural rearrangement of the residual kerogen.

5.2 Geochemical Techniques:
The geochemical screening methods are simple modeling tools that satisfactorily assess the distribution of source rocks and their maturity throughout a basin, assuming that enough data is available. They also provide a good indication of the nature of the hydrocarbons generated. The parameters most commonly used in petroleum exploration are optical examination of kerogen, physicochemical analysis of kerogen, and chemical analysis of extractable bitumen. All of these techniques have been widely used during the first stage of surface petroleum geochemical survey (outcrop sample), or later on during exploration and development stages (Bordenave, 1993).
5.2.1 Rock-Eval Pyrolysis Technique:
The Rock-Eval pyrolysis instrument was developed by the Institute Francais du Petrole. It provides a rapid semi quantitative source rock analysis on small sample of rock by heating it, using special temperature program. It is an excellent screening technique for identifying possible source and reservoir intervals on which more detailed analysis should be performed.
Rock-Eval programmed pyrolysis analysis was performed on whole-rock samples using the equipment Rock-Eval 6 analyzer.
Two wells were selected for this method from Kaikang area. 59 cutting samples from kaikang-3 well and 40 from Kaikang West-1 well. The analytical results are shown in (Table 7.1) and (Table 7.2).

5.2.1.1 Evaluating Source Rock Using Rock-Eval Parameters:
Rocks are characterized according to the quantity of migrated or generated free hydrocarbons by cracking the OM in the rock. The quality of OM is defined in terms of kerogen types I through IV from HI/OI plots and the hydrocarbon type index (Hunt, 1979).

5.2.1.1.1 Quantity of Organic Matter:
The quantity of organic matter is usually expressed in as Total Organic Carbon (TOC) (Hunt, op. cit).
Table (5.1): Geochemical parameters describing source rock generative potential (Quantity) after (Peters & Moldowan, 1993).

<table>
<thead>
<tr>
<th>Quantity</th>
<th>TOC (Wt%)</th>
<th>S_2 (mg HC/g rock)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poor</td>
<td>&lt;0.5</td>
<td>&lt;2.5</td>
</tr>
<tr>
<td>Fair</td>
<td>0.5-1.0</td>
<td>2.5-5.0</td>
</tr>
<tr>
<td>Good</td>
<td>1.0-2.0</td>
<td>5.0-10.0</td>
</tr>
<tr>
<td>Very Good</td>
<td>&gt;2.0</td>
<td>&gt;10.0</td>
</tr>
</tbody>
</table>

5.2.1.1.2 Quality of Organic Matter: (Kerogen Types)

The most important factor controlling the generation of oil and gas is the hydrogen content of the Organic Matter (OM). (Hunt, 1996).

Table (5.2): Geochemical parameters describing type of hydrocarbon generated (Quality) after (Peters & Moldowan, 1993).

<table>
<thead>
<tr>
<th>Type</th>
<th>Hydrogen index (mg HC/g TOC)</th>
<th>Rock-Eval S_2/S_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>50-200</td>
<td>1-5</td>
</tr>
<tr>
<td>Gas and oil</td>
<td>200-300</td>
<td>5-10</td>
</tr>
<tr>
<td>oil</td>
<td>&gt;300</td>
<td>&gt;10</td>
</tr>
</tbody>
</table>

Classifying organic matter type using the atomic H/C versus O/C ratio Van Krevelen diagram. This diagram was originally developed to characterize coals (Van Krevelen, 1961; Stach et al., 1982) during their thermal maturity or “coalification”. Tissot et al. (1974) extended the use of Van Krevelen diagram from coals to include the kerogen dispersed in sedimentary rocks.

The four principal types of kerogen include Type I (highly oil prone), Type II (oil prone), Type III (gas prone), and Type IV (inert) (Fig. 5-1).
Type I kerogen has a high H/C ratio ($\geq 1.5$) and low O/C ratio (< 0.1). It is rich in lipids, especially the long-chain aliphatics and has high petroleum potential derived from algal and bacterial remains. Type I kerogen is oil prone. Type II kerogen has intermediate H/C (1.5) and O/C (< 0.2) ratios. It is derived primarily from planktonic and bacterial remains deposits. Its lipid content and oil potential are somewhat lower than type I kerogen. Type II is oil and gas prone. Type III kerogen has low H/C ratios (< 0.1) and O/C (> 0.3). It is rich in aromatic and poor in aliphatic structures. Its oil potential is poor, but can be a source of gas (particularly methane). A fourth kerogen type (IV) has low H/C ratio and low to high O/C which corresponds to the inertinite maceral group that generates little or no hydrocarbons during maturation. It has no petroleum potential (White, 1998).
5.2.1.2 Maturation of Organic Matter:
Organic matter can be described as immature, mature, or postmature, depending on its relation to the oil-generative window (Tissot & Welte, 1984). “Immature” organic matter has been affected only by diagenesis, including biological, physical, and chemical alteration. “Mature” organic matter has been affected by catagenesis, the thermal processes covering the temperature range between diagenesis and catagenesis. “Postmature” organic matter has been heated to such high temperature that it has been reduced to hydrogen-poor residue containing only small amounts of hydrocarbon gases.

5.2.1.2.1 $T_{\text{max}}$ from Rock-Eval Data:
Table (5.3) show how to use the $T_{\text{max}}$ from Rock-Eval pyrolysis to estimate thermal maturity. Rock-Eval $T_{\text{max}}$ less than 435°C indicate immature organic matter that has generated little or no petroleum. A $T_{\text{max}}$ greater than 470°C coincides with the wet-gas zone (Peters & Moldowan, 1993).

<table>
<thead>
<tr>
<th>Maturation Level</th>
<th>PI</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>Ro (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beginning of Oil window</td>
<td>0.1</td>
<td>435-445</td>
<td>0.6</td>
</tr>
<tr>
<td>Peak Oil Window</td>
<td>0.25</td>
<td>445-450</td>
<td>0.9</td>
</tr>
<tr>
<td>End Oil Window</td>
<td>0.4</td>
<td>470</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table (5.3): Rock-Eval geochemical and Ro parameters describing source rock thermal maturity (Peters & Moldowan, 1993).
5.2.3 Vitrinite Reflectance (VRo) Technique:

Vitrinite is an organic matter component derived mostly from lignin and cellulose of vascular plants. It increases in light reflectivity as organic matter during thermal maturity (e.g. lignite, bituminous, anthracite, and coal) and this property is used to determine sedimentary rock maturity. Precise vitrinite reflectance is measured with a microscope and calibrated to the oil and gas generation and preservation maturity zones.

A petrographic microscope is used to measure the amount of incident light, which is reflected from highly polished coal block or grains mounted on epoxy resins. Reflectance values are taken on a minimum of 50 vitrinite particles for one sample. The results are reported in a histogram form, with an accompanying statistical analysis of the histogram shape. Histograms showing the frequency distribution of reflectance are established. They usually show several groups of reflectance values corresponding to the various constituents, or macerals of the kerogen concentrate (Tissot & Welte, 1984).

From correlation of huminite vitrinite with other parameters of source rock maturation, and also with occurrence of oil and gas fields, the following stages can be distinguished (for which Ro is the mean reflectance in oil): (Tissot & Welte, 1984).

- Ro < 0.5 to 0.7%: diagenesis stage, source rock is immature,
- 0.5 to 0.7 %< Ro < ca. 1.3%: catagenesis stage, main zone of oil generation; also referred to as oil window,
- ca. 1.3 %< Ro< 2%: catagenesis, zone of wet gas and condensate,
- Ro> 2%: metagenesis stage; methane remains as the only hydrocarbon (dry gas zone). (See Table 5.3).

Seven samples from Kaikang-3 and six from Kaikang West-1 wells were selected for this analysis. The results are given in (Figure 7.2) and (Figure 7.7).
5.2.4 Palynofacies Analysis:

Petrographic classification of organic matter refers to the first detailed classification made by coal petrologists, who classified coal components according to their appearance under the microscope with reflected light. The three major maceral groups in coals are liptinite (also called exinite), vitrinite, and inertinite.

Van Bergen et al, 1990, presented a basic framework for classification of dispersed organic matter in palynological slides. The types of organic matter recognized were classified into three groups:

Palynomorph: This main group contains all dispersed organic material, which include pollen grains, spores, algae, fungal spores, and chitinizoa.

Structured palynodebris: this group includes all structured taxonomically unassignable particles; which include wood remains, cuticles, plant tissue, animal remains and fungal remains.

Structureless palynodebris: this group includes a blocky amorphous organic matter which was formed by the degradation of organic matter under aerobic and anaerobic conditions, as well as fluffy amorphous what are mostly derived from alga. Under transmitted light the color of these groups have a range from light yellow, brown, dark brown to black.

The cutting samples were selected for this technique are from Kaikang-3 well (24 cutting samples) and Kaikang West-1 (24 cutting samples).

The analytical result are given in (Table 7.3) and (Table 7.4) respectively.
5.2.5 Gas-Chromatography GC & Gas-Chromatography Mass Spectrum GCMS.

Gas chromatography is one of the separation techniques and is a type of chromatography which employs gas as the mobile phase. In gas chromatography, a sample is vaporized and swept through a tabular column by an inert carrier gas (H₂, He or N₂). The column contains a reactive, stationary liquid phase which is coated on the wall of the column. At specific temperature, usually 50°C to 300°C, the movement of the compounds through the column is retarded by their solubilities or partition coefficients and retained to differing extents and will become physically separated in the column. Thus, under appropriate condition of temparture, carrier gas flow and column chacteristics, the components in the mixtures will elute from the column at different times depending on their specific solubility in the stationary, liquid phase and detected.

Gas Chromatography GC is accomplished by means of a long capillary or eutectic column through which the vaporized hydrocarbons from the extract or oil are passed by means of a carring gas. As the rate of the travel of any compound through the capillary column depends on its molecular weight, fractionation results and the lighter compound arrive at the end of the column before the heavier ones. The arrival time of the various components and the amount of each component is measured by a flame ionization detector coupled to a recorder which plots a graph of the run.

The GC analysis of whole oil was carried out using VARIAN CP-3800 GAS CHROMATOGRAPH in central petroleum laborotaries (CPL).
Only two cutting samples were selected for advanced characterization of Extractable Organic Matter (EOM) from Kaikang-3 and Kaikang West-1 wells. Two oils Drill Stem Test (DSTs) samples were selected for GC characteristic ratios from Kaikang-3 and Kaikang-1 well. The analytical result are shown in (Table 7.5). All mentioned samples were analyzed by GCMS and the results in (Table 7.7)
5.2.6 The Gas-Chromatography-Mass Spectrum GCMS:

Computerized Gas Chromatography/Mass Spectrum GCMS (McFadden, 1973; Watson, 1985) is the principal method used to evaluate biomarkers. It can be used to detect and provisionally identify compounds using their relative GC retention times, elution patterns, and the mass spectral fragmentation patterns characteristic of their structures (Peter & Moldowan, 1993).

The GC-MS technique is best suited for identification of components of complex mixtures. To do this it is necessary to separate the component by GC and obtain a mass spectrum of each separated component for identification. This is accomplished by joining this directly to a mass spectrum (MS) through an interface which render the eluting GC peaks compatible with the sample introduction requirements of the MS. The mass spectrometer is designed to characterize and identify chemical compounds by breaking them up into electrically charged fragments (ions). Each compound’s fragmentation pattern, which is closely related to its chemical structure, provides a unique fingerprint for that compound. Compounds eluting from GC are ionized by hitting with a large amount of energy, thus knocking an electron out of the molecule. The fragment ions are then accelerated in an arc by the magnetic field within the evacuated MS chamber. The radius of the arc depends upon the mass/charge ratio (m/z) of the ion and the strength of the magnetic field. For any given field strength, only those ions with a particular m/z value pass through the centre of the chamber and strike the detector. As the field strength is varied rapidly during the analysis, ions the different m/z values are allowed to strike the detector. The detector responses over the range of field strength employed are summed to yield a mass spectrum. The height of each bar is proportional to the number of the ions with the particular m/z value.
In petroleum geochemistry, GC-MS is used to study the biomarker distribution in crude oil and source rocks extract (Idris et al, 2008). The most commonly used fragment ions are 191 and 217 which are relevant to terpanes and steranes, two of the most important abundant families of saturated polycyclic biomarkers within the C\textsubscript{27}-C\textsubscript{37} range. Measurement of peak areas are performed in order to obtain the related molecular parameters. Most of these parameters are related to terpanes (C\textsubscript{29}-C\textsubscript{35} hopanes, tricyclic, bisnorhopane, T\textsubscript{m}, T\textsubscript{s}, and gammacerane) and regular steranes (Peters & Moldowan, 1993).

The GCMS analyses were performed using VARIAN CP-3800 GAS CHROMATOGRAPH. VARIAN 4000 GC/MS in central petroleum laborotaries (CPL).
CHAPTER SIX

6. BIOMARKERS

6.1 Introduction to Biological Markers:

Biological markers or biomarkers (Eglinton et al., 1964; Eglinton and Calvin, 1967) are molecular fossils, meaning that these compounds are derived from formerly living organisms. Biomarkers are complex organic compound composed of carbon, hydrogen, and other elements. They are found in rocks and sediments and show little or no change in structure from their parent organic molecules in living organism. They are useful because their complex structures reveal more information about their origin than other compounds (Peters & Moldowan, 1993).

The organic compounds in sediments, rocks, and crude oils whose carbon structures, or skeleton, can be traced back to living organism are called biological markers or biomarkers. They are microfossils generally less 30 nm in diameter and are highly variable in their stereochemistry which is spatial arrangement of the atoms and groups in their molecules (Hunt, 1996). Biomarkers have increasingly been applied as diagnostic indicators for crude oils and ancient sediments (Summons et al., 1992; Moldowan et al., 1994).

Biomarkers are also useful because they can provide information on the organic matter in the source rock (source), environmental conditions during its deposition and burial (diagenesis), the thermal maturity experienced by a rock or oil (catagenesis), the degree of biodegradation, some aspects of source rock mineralogy (lithology), and age (Peters & Moldowan, 1993).

Biological markers are organic compounds present in the geosphere whose structure can be unambiguously linked to the structures of
precursor compounds occurring in original source material. Any alteration that may occur to the carbon skeleton of the biological marker during deposition and burial of the organic material in the sedimentary record should be minimal and wherever possible limited to stereochemical change (Philp, 1985).

Biomarkers are found both, free in the bitumen or bound to the kerogen in petroleum source rocks. They are also present in oils, which migrate from the fine-grained source rocks to the reservoir rocks. The most widely applied biomarkers in petroleum geochemistry are the triterpanes and steranes. These compounds are saturated hydrocarbons as indicated by the “ane” ending in each of the names.

Triterpanes and steranes themselves do not exist in living organic matter, but closely related precursor compounds (triterpenoids and steroids, including sterols) and are present in varying concentrations in many living organism. During diagenesis some of these precursor molecules are converted, through a complex series of chemical and biochemical changes, into the more stable saturated hydrocarbons biomarkers preserved in geological samples (Waples & Machihara, 1991).

6.2. Applications of Selected Biomarkers:

6.2.1. Paraffins:

The distribution of n-alkanes bears the imprint of their biochemical synthesis, i.e., the predominance of the n-alkanes with an odd number of carbon atoms in the high molecular weight range (nC25-nC33).

The distribution of the C_{15}^+ saturated hydrocarbons is dependent upon the type of organic matter (OM) originally deposited, the depositional environment and lithology of source rock, thermal maturity of source and
upon biodegradation and water washing (Cooper & Ower, 1980, Hunt, 1996).

Lacustrine shale gives n-paraffin maximum n-C_{17} whereas deltaic shale gives n-paraffin maximum at n-C_{31} suggesting different type of organic matter input (Carrol & Bohacs, 2001).

6.2.2 Acyclic Isoprenoids:

Acyclic isoprenoids are special type of isoalkanes in which one methyl group is attached to every 4th carbon atom in straight chains. A wide range of linear or acyclic compounds formally built up from several isoprene units, is known to occur in living plants, bacteria, sediments and petroleum, the most common isoprenoids are pristane and phytane (Pr & (Ph) (C_{19} & C_{20}). Chlorophyll, the green coloring matter is hydrolyzed to yield the long-chain alcohol phytol C_{20}H_{43}OH. Phytol is a major precursor to the pristane and phytane in petroleum (Peters & Moldowan, 1993). Phytol can be further reduced to form the hydrocarbon phytane (C_{20}) or oxidized and decarboxylated to form the hydrocarbon pristane (C_{19}) (Hunt, 1979).

6.2.3 Terpanes:

These are bicyclic to polycyclic hydrocarbons, comprises of condensed systems of 6-membered rings, although one 5-membered ring may also occur (Peters & Moldowan, 1993). Terpenoids can be classified based on structural types into diterpenoids and triterpenoids. Diterpenoids are categorized into bicyclic and tricyclic; triterpenoids are grouped into tetra & penta-cyclics. Pentacyclic triterpenoids-hopanes are the most studied (Fig 6-1).
Tricyclic and tetracyclic terpenoids: A series of C20-C26 tricyclic and tetracyclic alkanes is near ubiquitous in sediments and oils. Possible natural product precursors for all members of the series are not known, but may derive from incomplete biosynthetic cyclization of a regular hexaprenol.

![Chemical structures of various terpenoid classes present in saturated fraction of the petroleum. (Peters and Moldowan, 1993).](image)

6.2.3.1 Hopanes:
Hopanes are pentacyclic triterpenoid composed of four 6-membered and one 5-membered ring. Hopanes with more than 30 carbon atoms are called homohopanes which means that the compound has additional methylene groups on the parent molecule. Bacetrio-hopaneterol and related bacteriohopane is the major precursor for the hopanes in living organism. Hopanes are abundant in sediments and petroleum compared to other compounds whose structure are known, because their hopanoid precursor are important membrane
components in living cell, and are resistant to degradation during diagenesis. Dehydration and reduction of bacteriohopaneterol during diagenesis result in bacteriohopane which belong to the triterpanes class of biomarkers (Fig 6-2).

The hopanes are composed of three stereoisomeric series, namely 17α (H), 21β (H) and 17 β (H), 21 β (H) - hopanes and 17 β (H), 21 α (H) - hopanes. The compound in β α series are called moretanes. The C_{29} and C_{30} 17 α (H) hopanes have no chiral carbon atoms in their side chains. The C_{31}- C_{40} 17 α hopanes (often referred to homohopanes or extended hopanes) all have a single chiral carbon atom (C-22) in the side chain, and thus can exist as both the 22R and 22S epimers (Peters & Moldowan 1993).

Figure (6.2): Origin of hopanes in petroleum from bacteriohopanetetrol 1) found in the lipid membranes of prokaryotic organisms 2) by enzymes in the living organism is unstable during catagenesis and undergoes isomerization to geological configurations (3,4,5). The 17β,21α (H) hydrocarbons (3) are called moretanes while others are hopanes (2, 4, 5). (Peters & Moldowan, 1993).
6.2.4 Steranes:
Steranes are derived from sterols that are found in higher plants and algae but are rare in prokaryotic organisms (Volkman, 1986, 1988). Four principal sterols containing 27, 28, 29, and 30 carbon atoms have been identified in numerous photosynthetic organisms. These sterols give rise to four different regular steranes during diagenesis. These four steranes can be called “homologs” or members of “homologous series” because they only differ by the addition of a sequence of –CH₂- units to a certain place in the molecule. The term “regular” indicates that the carbon skeletons are the same as in biological precursors. The biological configuration [14α, 17α(H), 20R] imposed on the sterol precursor in its immediate saturate product by enzymes in living organisms is unstable during catagenesis and undergoes isomerization to geological configuration (Peters & Moldowan, 1993). Except for the loss of oxygen atoms and hydrogenation of the double bond, the detailed structures of the newly formed steranes and their precursor sterols have generally been assumed to be identical. In particular, newly formed steranes are believed to exist only as the 20R epimers, because only that form is produced biologically (Fig 6-3). The stereochemical changes can occur at C-14 and C-17 during diagenesis. The molecules that occur in sterol have hydrogen atoms in the alpha configurations at both positions. This form is designated variously as “(5α(H), 14α(H), 17α(H))” or “14α(H), 17α(H)” or more simply as “ααα” or “αα”. Although most diagenetically produced steranes is αα form, it has been suggested that “5α(H), 14β(H), 17β(H)” form (αββ or ββ) may also be produced during diagenesis, particularly in hypersaline environments (Peakman et al, 1989). In addition to regular steranes a family of rearranged steranes or diasteranes is commonly encountered. These compounds differ from the regular steranes by having methyl groups attached to C-5 and C-14.
instead of hydrogen atoms, and having hydrogen attached to C-10 and C-13 instead of methyl groups. The transformation from regular steranes to diasterane is believed to occur during diagenesis under certain conditions (Leeuw, et al, 1983). Beside the regular steranes, 4-methyl steranes (steranes with an additional methyl group attached to C-4), appear to form two distinct families. One family called dinosteranes is derived from dinoflagellates, the other family can be considered as the three regular steranes C_{27} to C_{29} containing an additional methyl group at C-4 (4-methylcholstanes) which are of uncertain origin (Goodwin et al 1988).
Figure (6.3): Origin of steranes in petroleum from sterols 1) found in the lipid membranes of eukaryotic organisms. Stereochemistry is indicated by open (α) and solid (β) dots. The biological configuration [14α, 17α (H), 20R] imposed on the sterol precursor and its immediate saturated product (2) by enzymes in living organism is unstable during catagenesis and undergoes isomerization to geological configurations (3, 4, 5) (Peters & Moldowan, 1993).
6.3 Biomarkers Parameters for Source and Depositional Environment:

6.3.1 Carbon Preference Index (CPI):
Carbon Preference Index CPI is a measure of the relative amounts of n-paraffins having odd numbers of carbon atoms to those having even numbers (Hsieh & Philip, 2001 and Hunt, 1996).

\[
\text{CPI} = \frac{[(C_{23} + C_{25} + C_{27} + C_{29}) + (C_{25} + C_{27} + C_{29} + C_{31})]/2}{(C_{24} + C_{26} + C_{28} + C_{30})}
\]

CPI > 1.0 odd carbon number preference
CPI = 1.0 no preference
CPI < even carbon number preference

Immature hydrocarbon from clay-rich source rocks have more odd numbered n-paraffins, immature from carbonate source rocks have more even numbered, while mature hydrocarbon (as always in the case of crude oil) have CPI values near 1.0 (Robinson, 1980).

6.3.2 Terrigenous/Aquatic Ratio (TAR):
This ratio between the long chain n-alkanes to the short chain n-alkanes has been used to evaluate the importance of terrigenous in put versus aquatic input. (Bourbonniere & Meyers 1996, Mille et al., 2007)

\[
\text{TAR} = \frac{C_{27} + C_{29} + C_{31}}{C_{15} + C_{17} + C}
\]
6.3.3 Pristane/Phytane Ratio (Pr/Ph):
Pr/Ph ratios are commonly applied because they are easily measured using simple gas chromatography. Pristane/phytane (Pr/Ph) ratio of oil or bitumens (source extract) have been used to indicate the redox potential of the source sediment. Didyk et al (1978) suggested that Pr/Ph ratios < 1 indicate anoxic environments; Pr/Ph ratios around 1 indicate alternating oxic, and Pr/Ph ratios >1 indicate oxic conditions. Oxic conditions indicated by Pr/Ph greater than one are also suggested by Peters et al., (1999). Haven et al., (1987) suggested that, the Pr/Ph ratio cannot be used as an indicator for oxygen levels. However, in hypersaline environments of deposition the low Pr/Ph ratio is understandable, and in these environments the application of the Pr/Ph ratio can be valid.

6.3.4 Tricyclic Terpanes:
The tricyclic terpanes (< C_{30}) appear to be derived from regular C_{30} isoprenoid such as tricyclohexaprenol (Aquino Neto et al, 1983), and could be a constituent in prokaryote membranes (Ourisson et al, 1982). Some tricyclic terpanes are terrigenous indicators (Noble, 1986). Tricyclic diterpanes (C_{19} to C_{20}) are believed to be derived from diterpenoids such as abietic acid, which are produced by vascular plants (Branes and Branes, 1983).
6.3.5 Gammacerane/C₃₀ hopane (Gammacerane) Index:

Gammacerane is a non-hopanoid triterpane which occurs only in a limited number of oisl and sediments. It has also been found in high concentration in oisl from hypersaline environments (Peters & Moldowan, 1993).

Gammacerane occurrence was originally reported in lacustrine sediments. High gammacerane concentrations were therefore originally considered to be markers for lacustrine facies (Poole & Claypool, 1984).

Gammacerane is thought to be the diagenetic product of tetrahymanol which occurs in protozoa, but it may have other origins (Abboud et al, 2005). Peters and Moldowan (1993) suggested that the use of gammacerane as an indicator for highly saline marine or nonmarine depositional environments.

6.4 Biomarker Parameters for Maturity Assessment:

These are ratios of certain saturated and aromatic biomarker compounds result from two types of reactions
- Cracking source rocks (including aromatisations)
- Isomerisations at certain asymmetric carbon atoms

6.4.1 Terpanes:

Tricyclics, tetracyclis, pentacyclis (hopanes) and other compounds contribute to the terpanes fingerprint (m/z 191).

With increasing thermal maturity tricyclic terpanes appear to be more resistant to thermal maturation compared to homohopanes (Peters & Moldovan, op.cit).
6.4.1.1 Hopanes

6.4.1.1.1 Ts/ (Ts+Tm) Ratio:

Often applied for immature to mature or postmature. With increasing maturity, the $17\alpha$ (H) - trisnorhopane (Tm) gradually disappears and the $18\alpha$ (H) - trisnorneohopane (Ts) increase in relative concentration (Peters & Moldowan, 1993). The increase in Ts concentration is not thought to be from conversion of Tm. In fact, both compounds were observed to increase in abundance due to generation, in which Tm is much greater than Ts. Ts increase significantly when the Tm starts to decrease in abundance as a result thermal degradation. The Ts/ (Ts+Tm) ratio being to decreases quite late during maturation, hence the ratio is very useful when evaluating oil or rocks from a common source consistent organic facies, as the ratio is not only affected by maturity, but also by source facies (Moldowan et al, 1986, Maccaffrey et al, 1996, and Holba et al, 1996).

6.4.1.1.2 22S/ (22S+22R) C$_{31}$; Homohopane Isomerization:

Transformation of the biologically produced 22R from the C$_{31}$-C$_{35}$ extended hopanes $17\alpha$ (H)-hopanes to the 22S epimer. Often applied, high specificity form immature to early oil generation, it can be calculated for any or all of the C$_{31}$-C$_{35}$ $17\alpha$ (H)-homohopanes. The 22S/ (22S+22R) C$_{31}$ ratio rises from 0 to about 0.6 during maturation (Seifert and Moldowan, 1986). Samples showing 22S/ (22S+22R) ratio in the range of 0.50 to 0.54 have barely entered oil generation, while ratios in the range of 0.57 to 0.62 indicate that the main phase of oil generation has been reached or surpassed (Peters & Moldowan, op.cit).
6.4.2 Aromatic Hydrocarbons:

6.4.2.1 Methylphenanthrene Indices: (MPI 1 and MPI 2)

It is based on the distribution of phenanthrene and three of four of its methyl homologs, which show a progressive change during maturation. Phenanthrenes are genetically related to steroids and triterpnoids found in biological source material.

\[
MPI(1) = 1.5\left(\frac{2 \text{ MethylPhenanthrene} + 3 \text{ MethylPhenanthrene}}{\text{Phenanthrene} + 1 \text{ MethylPhenanthrene} + 2 \text{MethylPhenanthrene}}\right)
\]

\[
MPI(2) = 3\left(\frac{2 \text{ MethylPhenanthrene}}{\text{Phenanthrene} + 1 \text{ MethylPhenanthrene} + 2 \text{MethylPhenanthrene}}\right)
\]

A strong correlation of the MPI 1 and vitrinite reflectance data within the 0.6- 1.3% VRo interval has been observed Radke et al, 1982, 1983 obtained a relationship between the chemical or calculated maturity parameter (Rc1) and geological maturity parameter Ro.

\[
Rc_1 = 0.6 \text{MPI} + 0.40 \text{ (for Ro < 1.35%)}
\]
\[
Rc_2 = 0.6 \text{MPI} + 2.30 \text{ (for Ro > 1.35%)}
\]

All the above ratios were calculated from the saturate and aromatic compound peak areas which were identified in the Kaikang oil and extract organic matter samples. The ratios are given in (Table 7.5) and (Table 7.7). The distribution of identified compounds in GC and GCMS traces for Kaikang-1 and Kaikang-3 oil and rock extract samples are given in figures (Fig.7.8 to Fig 7.11) (Fig.7.14 to Fig 7.23).
CHAPTER SEVEN

7. RESULTS AND DISCUSSION

Cutting samples were collected from two wells in Muglad basin. 59 samples from Kaikang-3 well and 40 samples from Kaikang West-1 well.

7.1 Kaikang-3 well:

Rock-Eval data is summarized in table (7.1).

7.1.1 Organic Richness “Quantity of Organic Matter”:

The (59) cutting samples were selected from Kordofan Group Adok, Tendi, and Nayil Formations. Adok Formation is characterized by having low total organic carbon content, TOC and S2 a values ranging between (0.1 to 0.2 wt% ) and (0.02 to 0.2 mgHC/g), respectively. Also the samples from Adok Formation have low hydrogen indices (17 to 70 mgHC/gTOC) and high oxygen indices (795 to 1915 mgCO2/gTOC) which indicate that they are poor source rocks(Table7.1).

Upper Tendi Formation is characterized by rich organic intervals. Five samples from the depth interval (1070m to 1110m) have TOC ranging from 2.36 to 3.89 wt% . The values of S2 (11.57 to 25.25mg HC/g) and high HI (354 to 649 mgHC/gTOC). These are very good source rocks, since are supported by excellent generation potential S2 yield. The rest of the samples from Tendi Formation range between poor to fair source rocks. TOC values range between 0.06 to 0.5 wt% and they also have low values of generation potential S2 yield range between 0.01 to 1.09 HC/g). Nayil Formation is characterized by poor to fair source rock. The TOC values range from 0.01 to 0.59 wt% except for one sample at depth
1755m which has 2.61 wt% TOC; \( S_2 \) is 8.42 mgHC/g and HI is 323 mgHC/gTOC. These parameters suggest a very good source rock with a good generation potential.
<table>
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<th>ample No</th>
<th>Depht (m)</th>
<th>Formation</th>
<th>S1 (mgHC/g)</th>
<th>S2 (mgHC/g)</th>
<th>S3 (mgCO2/g rock)</th>
<th>S1+S2 (mgHC/g)</th>
<th>Tmax (C0)</th>
<th>HI (mgHC/gTOC)</th>
<th>OI (mgCO2/gTOC)</th>
<th>TPI</th>
<th>S1/S1+S2</th>
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7.1.2 Source Rock Quality from Rock-Eval:
Plots of hydrogen index (HI) vs oxygen index (Van Krevelen diagram Fig 7.1) for Kaikang-3 well show the organic matter quality (kerogen types). Two samples have high HI and low OI and four other samples are mariganal to kerogen type I (oil prone). Seven samples have moderate HI and low OI representing kerogen type II (oil and gas prone). The rest of samples have high OI and low HI representing kerogen type III (gas prone kerogen).

Figure (7.1 ): Modified Van Krevelen diagram showing the Rock-Eval hydrogen and oxygen indices of Kaikang-3 samples.
7.1.3 Quality of Organic Matter Using Palynofacies Analysis:

Based on the optical analysis of cutting samples from Kaikang-3 two groups of organic facies were determined corresponding to Type II and III kerogen. Table (7.3) show these results.

The samples from Tendi Formation of Kaikang-3 well of the depth intervals (1070 to 1230m) represent kerogen type II which is dominated by yellow to brown Structureless Organic Matter (SLOM) and yellow to brown plant tissue and cuticles, with small amount of black wood remains and a few scattered spore and pollen grains (Fig.7.2).

The studied samples for kerogen typing from Nayil Formation are from the depth intervals (1510m to 2010m). The top of this formation at the depth interval (1510m to 1815m) is characterized by kerogen type II similar to that described above for the Tendi Formation. The depth intervals from (1830 m to 2010m) mainly represent kerogen type III which is dominated by more than 80% black wood remains and very small amount of plant tissue, cuticles and Structureless Organic Matter (SLOM) with a few scattered spore and pollen grains. The depth intervals 1840m, 1965m, and 2010m from the same formation represent kerogen Type II (Fig.7.2).
Figure. (7.2): Showing Palynofacies components of the samples from Kaikang-3 and Kaikang west-1 wells.

A  Structureless Organic Matter (SLOM).
B  Structure Organic Matter (SOM).
B-a Brown to black wood remains.
B-b Plant tissues.
B-c Cuticles
C  Palynomorph  Spore and Pollen grains
A  Structureless Organic Matter (SLOM).
B  Structure Organic Matter (SOM).
B-a  Brown to black wood remains.
B-b  Plant tissues.
B-c  Cuticles
C  Palynomorph  Spore and Pollen grains
A  Structureless Organic Matter (SLOM).
B  Structure Organic Matter (SOM).
B-a  Brown to black wood remains.
B-b  Plant tissues.
B-c  Cuticles
C  Palynomorph  Spore and Pollen grains
A  Structureless Organic Matter (SLOM).
B  Structure Organic Matter (SOM).
B-a  Brown to black wood remains.
B-b  Plant tissues.
B-c  Cuticles
C  Palynomorph  Spore and Pollen grains
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7.1.4 Maturity from Rock-Eval $T_{\text{max}}$:
The maturity determined by $T_{\text{max}}$ suggest that the samples from Adok Formation are immature samples $T_{\text{max}}$ range (264 to 346 °C). However, the samples from upper Tendi Formation from the depth interval (1070 to 1120m) are mature samples and lie within the zone of the beginning of oil window $T_{\text{max}}$ range (435 to 439°C). The rest of the samples from this formation are immature $T_{\text{max}}$ range (335 to 433°C). The samples from Nayil Formation vary between immature to mature samples. One sample from the depth 1730m is a mature sample and lies within the zone of oil window has $T_{\text{max}}$ (447°C). Two samples from the bottom of this formation from the depth 2100 and 2204m have $T_{\text{max}}$ (441 and 444°C) which indicate that these samples are also fall in the zone of oil window.

7.1.5 Maturity from Vitrinite reflectance measurement:
Seven samples were selected for the vitrinite reflectances. Figure (7.3) shows the plotting of $\text{VRo}$ readings vs. depth. The shallowest sample at the depth 665m from Adok formation has Ro 0.40 which indicate that it is immature source. Two samples from Tendi Formation 1070 and 1110m have Ro 0.48 and 0.50 respectively and this suggest that they are immature or marginally mature. They lie at the beginning of oil window. This is consistent with the result that obtained from $T_{\text{max}}$. The four remaining samples from Nayil Formation at the depths 1730, 1920, 2010 and 2100 have Ro (0.86, 0.87, 0.94 and 1.10 respectively) which indicate that these are mature source rocks and fall in the peak of oil generative window.

Sample at the depth 1730m show good correlation between vitrinite reflectance 0.89 VRo and $T_{\text{max}}$ 447 °C (according to Esitalie et al., 1985, Muhkhopadhyay, 1991).
Figure (7.3) A comparison of maturity vs depth plots Kaikang-3 well (after Mukhopadhyay et al., 1994)
7.2. Kaikang West-1 Well:

Rock-Eval data is summarized in table (7.3).

7.2.1 Organic Richness “Quantity of Organic Matter”:

40 samples were selected from the Cretaceous Darfur Group and Tertiary Kordofan Group.

Samples from Adok Formation are extremely lean of organic carbon content TOC (< 0.2%), they are poor source rock. They have low generation potential $S_2$ (0.02 and 0.04 mgHC/g) and hydrogen index HI (90 and 61 mgHC/gTOC).

Tendi Formation is characterized by poor, fair, and very good source rocks. The rocks which are very good source from the depths 980, 1189 and 1295m have TOC values of 4.5, 5.76, 6.85 wt% respectively. They have high generation potential (26.82, 39.48 and 49.78 mgHC/g), high hydrogen index HI (596, 685, and 726 mgHC/gTOC).

Amal Formation is characterized by poor source rocks TOC range from (0.05 to 0.06 wt%) low $S_2$ yield (0.04 to 0.08 mgHC/g) and low hydrogen index HI (58 to 136 mgHC/gTOC).

Baraka Formation is also characterized by poor, fair, and very good source rocks. The richest rocks are very good source are from the depths 2010 and 2060m. They have TOC 2.29 and 5.95wt%. respectively. $S_2$ (7.47 and 23.29 mgHC/g) and HI (327 and 393 mgHC/gTOC).

The samples from Ghazal, Zaraqa and Aradeiba Formations are poor source rocks with TOC values ranging from 0.06 to 0.59 wt%. They have generation potential $S_2$ ranging from 0.00 to 0.03 mgHC/g and have hydrogen index HI between 0 to 73 mgHC/gTOC.
Table. (7.3): Kaikang West-1 well Rock-Eval pyrolysis results.

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<th>Tmax (°C)</th>
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There is a relation between the total organic carbon (TOC) and the generation potential (S2) and from it the very good source can be determine from the others figure (7.6) show this relation.

Figure (7.4): Showing the relationship between Total Organic Carbon and potentiality of the source rock.

Figure (7.5): Showing the relationship between Total Organic Carbon and potentiality of the source rock.
7.2.2 Source Rock Quality from Rock-Eval:

Van Kervelen diagram (Fig 7.6) show plot of HI versus OI index for Kaikng West-1.

Two samples correspond to kerogen type I; an oil prone kerogen having high HI and low OI. Eight samples represent kerogen type II which is characterized by moderate HI and OI and it is an oil and gas prone. The rest of the samples have high OI and low HI and this distinguish kerogen type III it is a gas prone kerogen.
Figure (7.6): Modified Van Krevelen diagram showing the Rock-Eval hydrogen and oxygen indices of Kaikang west-1 samples.
7.2.3 Quality of Organic Matter Using Palynofacies Analysis:
The studied samples from Tendi Formation of Kaikang West-1 well table (7.4) represent kerogen type II, at the depth intervals from (980m to 1640m). Kerogen type II in this formation is dominated by more than 95% yellow to brown structureless organic matter, and 70% or more or less black wood remains and less amount of plant tissue and cuticles with few amount of spore and pollen grains (Fig.7.2).

Amal Formation at depth intervals (1720m to 1895) is represented by kerogen Type II. Baraka and Ghazal Formations are also characterized type II kerogen at the depth intervals (1990m to 1245m) and (2445m to 2705m), respectively.

The bottom part of Baraka (2800m) and Zarga Formations 2885m represent type III kerogen which is dominated by more than 95% black wood remains with very small amount of plant tissues and structureless organic matter.

Aradeiba Formation (2965m to 3270m) is characterized by type III kerogen, which contains 100% of black wood remains (Fig.7.2).
Table 7.4 Palynofacies analysis results, Kaikang West-1 well

<table>
<thead>
<tr>
<th>No of sample</th>
<th>Formation</th>
<th>Depth (m)</th>
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<th>Black wood remains %</th>
<th>Plant tissues</th>
<th>Cuticles</th>
<th>Structureless Organic Matter</th>
<th>Palynomorph Spore &amp; Pollen Grains</th>
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7.2.4 Maturity from Rock-Eval $T_{\text{max}}$:
The maturity determined $T_{\text{max}}$ suggest that the samples from Adok Formation are immature $T_{\text{max}}$ (394 and 374 °C).
Tendi Foramtion has immature samples $T_{\text{max}}$ range (427 to 434°C) but the majority of the samples from this formation are mature $T_{\text{max}}$ range (435 to 442°C) and they fall at the beginning of oil generative window.
Amal Formation has two immature samples $T_{\text{max}}$ (422 and 431°C) and two mature samples $T_{\text{max}}$ (439 and 436°C).
Baraka Formation has mature samples $T_{\text{max}}$ range (438, to 445°C) at the beginning of oil window, only one sample within peak of oil generative window $T_{\text{max}}$ (469°C).
The sample from Ghazal Formation are postmature $T_{\text{max}}$ (543 to 546°C).
Zarga and Aradieba Formations have immature samples $T_{\text{max}}$ range (377 to 429°C), only one mature sample and within the peak of oil window $T_{\text{max}}$ (450°C), the other one it is mature and in the end of oil generative window.

7.2.5 Maturity from Vitrinite Reflectance Measurement:
Six samples were selected for vitrinite reflectance measurement. They are from Baraka to Aradieba Formations.
Two samples from Baraka Formation have Ro (0.67 and 0.91) this express that these samples are mature one of them lie at the beginning of oil window and the other within peak of oil generative window. Fig (7-7) show plotting VRo vs. depth.
One sample from Ghazal Formation has Ro (1.02) indicates that this is sample mature and fall in the peak of generative oil window.
Three samples from Aradieba Formation have Ro (0.91, 1.02 and 1.28) which indicate that these sample are mature and at the peak of oil window.
The sample which have Ro (1.28) is overmature for oil generation, it may be a source of gaseous hydrocarbon (Michael et al., 1996), this is consistent with result obtained from $T_{\text{max}}$ (543°C).

Figure (7.7): A comparison of maturity vs depth plots of Kaikang west-1 well (after Mukhopadhyay et al., 1994).
7.4 Gas Chromatography (GC) Results:

Four samples were selected for advanced characterization for gas chromatography analysis, two of them DST oil samples, from Kaikang-3 and Kaikang-1 wells. The other two are extracts from cuttings samples (Extract Organic Matter EOM). They are from Kaikang-3 at the depth (1110m) and Kaikang West-1 at the depth (2060m). The result obtained from GC are summarized in (Table. 7.5).

7.4.1 Oil Samples:

These two oil samples are from a narrow intervals in the middle part of Tendi Formation.

The distribution of n-alkanes show little variation in the two oil samples (Kaikang-3 DST, (Fig.7.8) and Kaikang-1 DST (Fig. 7.9) ranging from C9 up to C33. They show a unimodal n-alkane distribution, maximizing at C17 which suggests that they are from lacustrine shale (Carrol & Bohacs, 2001). They are characterized by very low abundance of acyclic isoprenoids (Prisante and Phytane) relative to n-alkanes Pr/n-C17, Ph/n-C18 (0.19, 0.12) and (0.21, 0.19), respectively (Table 7.5). These ratios were plotted in a graphical form to infer oils source rock depositional environments (Hughes et al., 1995, Fig 7.13). The figure shows that the source rocks were probably deposited in less oxic to anoxic environments (Fig 7.12).

The pristane/phytane Pr/Ph ratios have been used as indicators of redox potential source rocks (Didyk et al., 1978). The relative high ratios of Pr/Ph (1.5 and 1.2) for Kaikang-3 and Kaikang-1 indicate that the source was deposited under oxic to suboxic conditions.

The Carbon Preference Index CPI (Bary and Evans, 1961) values for the two oil samples are slightly greater than one (1.02, 1.06) respectively.
Slight odd over even carbon preference suggest that, these oils were derived from non marine source.

Low molecular weight hydrocarbons (n-C_{13} to n-C_{19}) are present in high abundance. As indicted by Terrigenous /Aquatic Ratio (TAR) less than one (0.15) and (0.05) for Kaikang-3 and Kaikang-1 respectively this suggest a high contribution of aquatic environment to organic source input (Routh et al., 2006, Gomes & Azevedo, 2003).

Moderately high Pr/Ph ratios, low Pr/nC_{17} and Ph/nC_{18}, slight even over odd number carbon preference. All these parameters suggest that these oils were derived from nonmarine source deposited under oxic to suboxic conditions.

**Table (7.5): Biomarkers of oil and source extract parameters for Kaikang wells**

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample name</th>
<th>Depth (m)</th>
<th>Fm.</th>
<th>Pr/Ph</th>
<th>Pr/nC_{17}</th>
<th>Ph/nC_{18}</th>
<th>CPI</th>
<th>TAR</th>
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<tbody>
<tr>
<td>1.</td>
<td>Kaikang-3 DST</td>
<td>1247</td>
<td>Tendi</td>
<td>1.5</td>
<td>0.19</td>
<td>0.12</td>
<td>1.02</td>
<td>0.15</td>
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<tr>
<td>2.</td>
<td>Kaikang-1 DST</td>
<td>1249-1261</td>
<td>Tendi</td>
<td>1.2</td>
<td>0.21</td>
<td>0.19</td>
<td>1.06</td>
<td>0.05</td>
</tr>
<tr>
<td>3.</td>
<td>Kaikang-3 (EOM)</td>
<td>1110</td>
<td>Tendi</td>
<td>1.2</td>
<td>2.02</td>
<td>0.53</td>
<td>0.98</td>
<td>1.2</td>
</tr>
<tr>
<td>4.</td>
<td>KaikangWest-1 (EOM)</td>
<td>2060</td>
<td>Baraka</td>
<td>2.0</td>
<td>4.84</td>
<td>0.83</td>
<td>1.82</td>
<td>1.03</td>
</tr>
</tbody>
</table>
Figure (7.8): Gas Chromatography (GC) trace of Kaikang-3 well DST oil sample.

Figure (7.9): Gas Chromatography (GC) trace of Kaikang West-1 well DST oil sample.
7.4.2 Source Rock Extracts:

GC trace of Kaikang-3 (1110m) extract organic matter from Tendi Formation show unimodal n-alkane distribution ranging from n-C\textsubscript{12} up to n- C\textsubscript{42} maximizing n-C\textsubscript{25}. Figure (7.10)

Slightly high Pr/ph ratio (1.2) suggests that the source is deposited in suboxic conditions (Didyk et al., 1978). Carbon preference index (CPI) around one (0.98) indicating that the odd and even of n-alkane are present in equal amounts.

High molecular weight hydrocarbons n- C\textsubscript{27} to n-C\textsubscript{31} present in high abundance as indicated by terrigenous/aquatic ratio TAR being greater than one (1.2) suggests relative contribution of land plant source organic input.

This sample is characterize by relatively high abundance of acyclic isoprenoids pristane relative to n-alkanes Pr/n-C\textsubscript{17} (2.02) and low of Ph/n-C\textsubscript{18} ratios (0.53). The relative high amount of Pr/n-C\textsubscript{17} indicate that this source was derived from higher land plant (Peter & Moldowan, 1993, Abboud et al., 2005, Banerjee, 2002)

GC trace of Kaikang West-1 (2060m) extract organic matter show bimodal distribution of n-alkanes maximizing at n- C\textsubscript{15} and n-C\textsubscript{27} which is likely the result of a higher contribution from terrigenous organic matter (Isaksen, 1996) Figure (7.11).

The ratio Pr/nC\textsubscript{17} for this sample is believed to be high (4.84) and the ratio Ph/nC\textsubscript{18} is low (0.84) which indicate that this source was derived from land plant organic matter.

Highest Pr/Ph ratio is associated with fresh water deposition of terrestrial plant material, probably in sub-oxic condition (Huang & Pearson 1999). The ratio of Pr/Ph for this sample is relatively high 2.0 and is related to less anoxic conditions.
Mello and Maxwell (1990) suggested that high Pr/Ph ratios probably reflect the relationship between contributing organisms and the chemistry of the environment. In a fresh water environment photosynthetic organisms and methanogenic bacteria which contain the precursors of pristane are often dominant. In a fresh water environment photosynthetic organisms and methanogenic bacteria which contain the precursors of pristane are often dominant. With a marked increase in salinity, however the population of arechaebacteria which contain major source of phytane might be more abundant. This is consistent with the data obtained from GCMS m/z 191 fragmentogram. Gammacreane index for this sample is (0.001) which indicate low salinity condition.

This sample characterized by the predominance of n-alkane with odd carbon preference index CPI (1.82) suggest that the rock is a non-marine source.

Low molecular weight hydrocarbons present in relatively high abundance, as indicated by terrestrial/ aquatic ratio TAR greater than one (1.20) suggest relatively high contribution of terrestrial land plant to this source rock.
Figure (7.10): Gas Chromatography (GC) trace of Kaikang-3 well (1110m) rock extract sample.

Figure (7.11): Gas Chromatography (GC) trace of Kiakang West-1 well (2060m) rock extract sample.
Figure (7.12): Cross Plot Pr/n-c17 versus Ph/n-c18 of two oil samples and two rock extract samples from Kaikang area.
Figure (7.13): Cross Plots of Pr/Ph ratio and dibenzothiophene/phenanthrene (DBT/Phe) ratio suggesting source of oils and rock extracts.

Zone-1: Marine carbonate & marl
Zone-2: Lacustrine hypersaline
Zone-3: Marine shale & other lacustrine
Zone-4: Fluvio-deltaic shale & coal
7.5 Biomarker Characteristics of the Crude Oils and Source Rocks:

The mass fragmentograms show differences in the distributions of saturate and aromatic biomarkers in the two oil samples and two rock extracts from Kaikang wells. Figures present terpanes and steranes GC-MS fingerprints with peak identification in the m/z 191 fragmentogram shown in table (7.6) and peaks in the m/z 217 fragmentogram identified in table (7.8). The biomarkers source of organic matter, lithology, depositional environment, and maturity parameters are summarized in table (7.7). All molecular ratios were calculated using the peak areas.

7.5.1 Oil Samples:

In the oil samples chromatogram from Kaikang-3 DST 1249m (Fig 7.14) and Kaikang-1 DST 1247m (Fig 7.15). The terpanes (m/z 191) distributions, are dominated by the pentacyclic triterpanes hopane peaks. The terpanes present include tricyclics (C_{19} up to C_{26}), tetracyclic C_{24}, and pentacyclic triterpanes C_{27} up to C_{35} hopanes, diahopane, and gammacerane. The C_{21}, C_{23} and C_{24} tricyclic terpanes are the most abundant. The C_{19} and C_{20} tricyclic diterpane derived predominantly from higher plants with C_{19} as the dominant compound (Reed, 1977; Simoneit, 1977; Alberdi et al., 2001).

The C_{21}+ extended tricyclic terpanes derived from bacterial and/or algal sources (Ourisson et al., 1982; Moldowan et al., 1983; Aquino Neto et al., 1983; Zumberge, 1983).

The oils generated from algal organic matter show low C_{19}/C_{23} tricyclic terpane ratio, whereas oils generated from source rock containing appreciable amount of terrigenous organic matter show C_{19}/C_{23} tricyclic
terpane ratios of approximately one (1) or greater than one (1) (Ronald & Christopher, 2005).

The C19/C23 tricyclic ratio for two oil samples are low or less than one (0.86 and 0.66) (Table 7.7) indicating predominately mixed algal and bacterial organic matter.

The C26 tricyclic terpanes are more abundant than C25 tricyclic terpanes, the ratio C26/C25 for Kaikang-3 and Kiakang-1 oil samples are 1.4 and 1.2 are respectively characteristic, that is diagnostic for sourcing from lacustrine facies (Schiefelbein et al., 1999).

The pentacyclics terpane (hopanes) distributions of two oil samples are very similar to each other and characterized by a high abundance of C30 17\(\alpha\) (H) - hopane compared to homohopanes. Extended 17\(\alpha\), 21\(\beta\) (H) hopane concentrations decreased with increasing carbon number from C31 upward (Fig 7.14) (Fig 7.15).

The C30 diahopane is derived from bacteria input to the sediment containing clays and that deposited under oxic or suboxic conditions (Peters & Moldowan, 1993). The C30 diahopane/C30 hopane ratio of two oil samples (0.25 and 0.22) indicate clay rich source rocks deposited under oxic/suboxic conditions.

The C29/C30 hopane ratio has been used to differentiate shale- and carbonate-sourced oils (Zumberge, 1984; Conan et al., 1986; Clark and Phlip, 1987; Fan et al., 1987; Ten Haven et al., 1988; Peter and Moldowan, 1993). The C29/C30 hopane ratios are relatively high in carbonate- and evaporite-sourced oils (~ 0.7 or greater) and lower for shale-sourced oils (0.4-0.75) (Ronald and Christopher, 2005). The C29/C30 hopane ratios for Kaikang oils range between (0.27-0.71) indicating shale sources for Kaikang oils.

The 28, 30- bisnorhopane (BNH) is a bacterial marker associated with anoxic depositional environment (Waples and Machihara, 1991). High
BNH/C\textsubscript{30} ratio with low Pr/Ph ratio interpreted to indicate source-rock deposition under anoxic conditions (Curiale et al., 1985; Mello et al., 1990). The relatively low ratios of BNH/C\textsubscript{30} hopane indicate oxic to dysoxic conditions for the source that generated the two oil samples from Kiakang wells (0.09). This is consistent with the high ratios Pr/Ph for these samples see (Table 7-5).

Gammacerane was originally reported in lacustrine sediments. High gammacerane concentrations were therefore originally considered to be marker for lacustrine facies (Poole and Claypool, 1984). Also gammacerane is a biomarker indicative of hypersaline depositional environments (Moldowan et al., 1985; Fu et al., 1986). Gammacerane/C\textsubscript{30} hopane ratios are low (0.25, 0.31) for the two oil samples of Kaikang area indicating normal salinity conditions during source rock deposition.
Figure (7.14): Gas Chromatography Mass Spectrum (GCMS) m/z (191) showing terpanes distribution of Kaikang-3 well DST oil sample.
Figure (7.15): Gas Chromatography Mass Spectrum (GCMS) m/z (191) showing terpanes distribution in the saturate fractions of Kaikang-1 well DST oil sample.
Table (7.6): Compounds identified in the m/z 191 mass fragmentograms shown in Figs (7.14,7.15,7.16 and 7.17)

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<td>C_{27} 17\alpha(H)-22,29,30-trisnorhopane</td>
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<td>C_{28} 17\alpha(H),21\beta(H)-28,30-bisnorhopane</td>
</tr>
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<td>C_{29} 17\alpha(H),21\beta(H)-30-norhopane</td>
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<td>22</td>
<td>30\beta\alpha</td>
<td>C_{30} 17\alpha(H),21\beta(H)-hopane (Moretane)</td>
</tr>
<tr>
<td>23</td>
<td>31\alpha\betaS</td>
<td>C_{31} 17\alpha(H),21\beta(H),22(S)-homohopane</td>
</tr>
<tr>
<td>24</td>
<td>31\alpha\betaR</td>
<td>C_{31} 17\alpha(H),21\beta(H),22(R)-homohopane</td>
</tr>
<tr>
<td>25</td>
<td>30G</td>
<td>C_{30} Gammacerane</td>
</tr>
<tr>
<td>26</td>
<td>32\alpha\betaS</td>
<td>C_{32} 17\alpha(H),21\beta(H),22(S)-bishomohopane</td>
</tr>
<tr>
<td>27</td>
<td>32\alpha\betaR</td>
<td>C_{32} 17\alpha(H),21\beta(H),22(R)-bishomohopane</td>
</tr>
<tr>
<td>28</td>
<td>33\alpha\betaS</td>
<td>C_{33} 17\alpha(H),21\beta(H),22(S)-trishomohopane</td>
</tr>
<tr>
<td>30</td>
<td>33\alpha\betaR</td>
<td>C_{33} 17\alpha(H),21\beta(H),22(R)-trishomohopane</td>
</tr>
<tr>
<td>31</td>
<td>34\alpha\betaS</td>
<td>C_{34} 17\alpha(H),21\beta(H),22(S)-tetrakishhomohopane</td>
</tr>
<tr>
<td>32</td>
<td>34\alpha\betaR</td>
<td>C_{34} 17\alpha(H),21\beta(H),22(R)-tetrakishhomohopane</td>
</tr>
<tr>
<td>33</td>
<td>35\alpha\betaS</td>
<td>C_{35} 17\alpha(H),21\beta(H),22(S)-pentakishhomohopane</td>
</tr>
<tr>
<td>34</td>
<td>35\alpha\betaR</td>
<td>C_{35} 17\alpha(H),21\beta(H),22(R)-pentakishhomohopane</td>
</tr>
</tbody>
</table>
Table (7.7): Ratios calculated from GCMS data (m/z 191 and 217) saturated hydrocarbon and (m/z 178, 184, 192) aromatic hydrocarbon.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Kaikang-3 Oil</th>
<th>Kaikang-1 Oil</th>
<th>Kaikang-3 Extract</th>
<th>Kaikang West-1 Extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{19}T / C_{29}T</td>
<td>0.86</td>
<td>0.66</td>
<td>1.50</td>
<td>2.3</td>
</tr>
<tr>
<td>C_{26}T / C_{29}T</td>
<td>1.4</td>
<td>1.2</td>
<td>1.4</td>
<td>1.19</td>
</tr>
<tr>
<td>30G / C_{30} α β</td>
<td>0.25</td>
<td>0.31</td>
<td>0.05</td>
<td>0.001</td>
</tr>
<tr>
<td>30D / C_{30} α β</td>
<td>0.25</td>
<td>0.22</td>
<td>0.01</td>
<td>0.004</td>
</tr>
<tr>
<td>C_{29} α β / C_{30} α β</td>
<td>0.71</td>
<td>0.47</td>
<td>1.6</td>
<td>0.67</td>
</tr>
<tr>
<td>BNH / C_{30} α β</td>
<td>0.09</td>
<td>0.09</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>C_{30} α β hopane/ C_{29} sterane</td>
<td>Abs</td>
<td>4.6</td>
<td>Abs</td>
<td>25</td>
</tr>
<tr>
<td>DBT/ Phen</td>
<td>0.99</td>
<td>0.78</td>
<td>0.04</td>
<td>0.65</td>
</tr>
<tr>
<td>Ts / (Ts+Tm)</td>
<td>0.67</td>
<td>0.67</td>
<td>0.26</td>
<td>0.55</td>
</tr>
<tr>
<td>22S/22S+22R C_{31}</td>
<td>0.50</td>
<td>0.55</td>
<td>0.44</td>
<td>0.59</td>
</tr>
<tr>
<td>MPI1</td>
<td>0.46</td>
<td>0.52</td>
<td>0.67</td>
<td>0.76</td>
</tr>
<tr>
<td>MPI2</td>
<td>0.44</td>
<td>0.53</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>RC1</td>
<td>0.67</td>
<td>0.71</td>
<td>0.80</td>
<td>0.71</td>
</tr>
<tr>
<td>C_{27} sterane</td>
<td>Abs</td>
<td>26%</td>
<td>Abs</td>
<td>31%</td>
</tr>
<tr>
<td>C_{38} sterane</td>
<td>Abs</td>
<td>29%</td>
<td>Abs</td>
<td>29%</td>
</tr>
<tr>
<td>C_{29} sterane</td>
<td>Abs</td>
<td>45%</td>
<td>Abs</td>
<td>40%</td>
</tr>
</tbody>
</table>

Note: The Kaikang-3 well oil sample and also the extract rock samples of this well Kaikang-3 (1110m) are indistinguishable on the basis of steranes distribution.
7.5.2 Source Rock Extracts:

There are two rock extract samples from Kaikang-3 (1110m) and Kaikang West-1 (2060m). Figure (7.16) and (7.17).

The terpanes distributions (m/z 191) are dominated by the pentacyclic triterpanes hopane peaks. The terpanes present include tricyclics (C\textsubscript{19} up to C\textsubscript{26}), tetracyclic C\textsubscript{24}, and pentacyclic triterpanes C\textsubscript{27} up to C\textsubscript{35} hopanes, diahopane, and gammacerane. Tricyclics and tetracyclics present very small amounts compared with the pentacyclic hopanes.

The ratio C\textsubscript{19}/C\textsubscript{23} for the extract samples (1.5, 2.3) is greater than one which indicate high contribution from terrestrial higher plant to organic matter input to these source rocks.

The ratio C\textsubscript{26}/C\textsubscript{25} tricyclics terpanes for the extract samples (1.4, 1.19) indicate lacustrine facies for source rock (Table 7.7).

The pentacyclis terpane (hopanes) distribution is characterized by high abundance of C\textsubscript{30} 17\alpha(H) – hopane in Kaikang-3 rock extract (1110m), but in KaikangWest-1 rock extract the C\textsubscript{29} hopane present in more abundance than C\textsubscript{30} 17\alpha(H) – hopane. Petroleums from organic-rich evaporite-carbonate rocks generally show enhanced relative concentrations of the C\textsubscript{29} compared to the C\textsubscript{30} hopane (Zumberge, 1984; Conan et al., 1986; Clark and Philip, 1989). However, others have observed that high C\textsubscript{29} hopanes characterize many types of petroleum from source rocks rich in terrestrial organic matter (e.g., Brooks, 1986). The ratio of C\textsubscript{29}/C\textsubscript{30} hopane for the two Kaikang rock extracts (0.45 and 1.6) indicate shale facies but it relatively high (1.6) in Kaikang West-1 rock extract because of rich terrestrial organic input to this source rock.

The two extract source rock sample have very low amount of diahopane, the ratio of diahopane/C\textsubscript{30} hopane for these samples (0.05, 0.004), this consistent with the low contribution of bacterial organic matter to these source rock and clay poor source.
The bisnorhopane/hopane ratio which is used to evaluate redox condition during source-rocks deposition for the two extracts samples (0.07) indicate oxic deposition conditions for these source rocks. The ratio bisnorhopane/hopane sometimes is coupled with the ratio of pristane/phytane to evaluate redox conditions, while the ratio of pristane/phytane (> 1) and the ratio BNH/hopane (<<1) indicates oxic conditions, for these source rocks Pr/Ph (1.2, 2.0) and BNH/hopane ratios (0.07) for the two samples.

Salinity conditions that prevailed during source rock deposition were evaluated using the gammacerane/hopane ratio (Moldowan et al., 1985; Fu et al., 1986). Gammacerane has been interpreted to indicate a stratified water column sometimes resulting from hypersalinity at the depth (Sinninghe Damste et al., 1995) and large amount of gammacerane indicate highly reducing hypersaline conditions during source rock deposition (Moldowan et al., 1985; Fu et al., 1986). The ratio for the two extract samples (0.05, 0.001) indicating low salinity conditions during source rock deposition.
Figure (7.16): Gas Chromatography Mass Spectrum (GCMS) m/z (191) showing terpanes distribution in the saturate fraction of Kaikang-3 well (1110m) source rock extract sample.
Figure: (7.17): Gas Chromatography Mass Spectrum (GCMS) m/z (191) showing terpanes distribution in the saturate fraction of Kaikang west-1 well (1110m) source rock extract sample.
7.6 Maturity:

7.6.1 Oil Samples

Pentacyclic terpanes are also used to determine maturity level. Seifert and Moldowan (1986) described the hopane distributions and specifically discussed the two C\textsubscript{27} trisnorhopane, trisnorneohopane namely Ts and Tm, commenting on the used of the Ts/Tm ratio as maturity indicator based on the fact Tm was proposed to be more maturable than Ts. The Ts/(Ts+Tm) ratios for the two oil samples are the same (0.67) and indicate early oil window.

The 22S/22S+22R epimer ratio for C\textsubscript{31} hopane in the range (0.50 to 0.54) have barely entered oil generation, while ratios in the range (0.57 to 0.62) indicate that the main phase of oil generation has been reached or surpassed (Peters, et al., 1989). The ratio of 22S/22S+22R epimer for Kaikang oils from 0.50 to 0.55 indicating that these oils were derived at main phase of oil generative window.

The thermal maturity of oils was also assessed from the aromatic fraction. Phenanthrene and various methyl isomers of phenanthrene were used to calculate the methyl phenanthrene index MPI1 (Radke and Welte, 1983; Boreham et al., 1988) and equivalent vitrinite reflectance (R\textsubscript{c}) values were calculated from the MPI1 values using the relationship described by Boreham et al., (1988).

The methyphenanthrene index for Kaikang oils between 0.46 and 0.52 which gives an equivalent vitrinite reflectance (R\textsubscript{c1}) values between 0.67 and 0.71, suggest that these oils were derived at early peak of oil generative window.
7.6.2 Source Rocks Extract:
The $T_s/T_{s+T_m}$ ratio begins to decrease quite late during maturation; this ratio is not only affected by maturity, but also by source facies (Modowan et al., 1986, Maccaffrey et al., 1996 and Holba et al., 1996). The $T_s/T_{s+T_m}$ ratios for Kaikang-3 (1110m) and Kaikang west-1 (2060) rock extract are (0.26 and 0.55) respectively indicating that the oil derived from these sources at early of oil generative window.
The 22S/22S+22R ratio for the two extracts (0.44 and 0.59) also indicate that these at early phase of generation window.
The methyphenanthrene index for two Kaikang extacts (0.67 and 0.76 ) which give an equivalent vitrinite reflectance ($R_c$) values between (0.80 and 0.71) suggest that these sources are within peak of oil generative window.

7.7 Sterane Biomarkers:
The sterane and diasterane distribution of Kaikang-1 oil sample and Kaikang West-1 source rock extract sample are dominated by $C_{29}$ and $C_{27}$ respectively regular sterane. Fig. ( 7.18) and ( 7.19).
High concentration of $C_{29}$ steranes compared to $C_{27}$ and $C_{28}$-steranes may indicate a land plant source (Czochanska et al., 1988).
The steranes ($C_{27}$, $C_{28}$, $C_{29}$) distribution Table (7.7) show relatively high abundance of $C_{27}$% over $C_{28}$ and sterane $C_{29}$ (45% ) which suggest relatively high contribution algal organic matter input for Kaikang -3 oil sample.
The steranes ($C_{27}$, $C_{28}$, $C_{29}$) distribution Table (7-7) show relatively high abundance of $C_{29}$% over $C_{28}$ and $C_{27}$ sterane (40% ) which suggest relatively high contribution from land plant to organic matter input for Kaikang West-1 rock extract.
The hopane/ sterane ratio for source rocks containing marine organic matter is generally less than three 3, whereas source rocks containing terrigenous organic matter generally range between 5 and 30 (Moldowan, et al., 1985). Hopanes originate mainly from bacteria (prokaryotic organisms) and more abundant in non-marine environments. Steranes originate mainly from algae and higher plants (eukaryotic organism). The hopane/ sterane ratio for Kaikang-1 oil sample and Kaikang West-1 source rock extract between 4.6 and 25, offering further support for oil derived from land plant organic matter.

The Kaikang-3 oil and also rock extract sample of this well are indistinguishable on the basis of steranes distribution.
Figure (7.18): Gas Chromatography Mass Spectrum (GCMS) showing the C_{27}-C_{29} steranes distribution in the saturate fraction of the Kaikang West-1 well rock extract (2060m).
Figure (7.19): Gas Chromatography Mass Spectrum (GCMS) chromatogram showing the C_{27}-C_{29} steranes distribution in the saturate fraction of the kaikang -1 well DST oil sample.
Table (7.8): Compounds identified in the m/z 217 mass fragmentograms shown in (Fig. 7.18) and (7.19)

<table>
<thead>
<tr>
<th>Peak Label</th>
<th>Peak Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>27dbS</td>
<td>13 β(H), 17α(H), 20(S)-(C\textsubscript{27} diasterane)</td>
</tr>
<tr>
<td>27dbR</td>
<td>13 β(H), 17α(H), 20(R)-(C\textsubscript{27} diasterane)</td>
</tr>
<tr>
<td>27abR</td>
<td>5 α(H), 14 β(H), 17 β(H), 20(R)-(C\textsubscript{27} regular sterane)</td>
</tr>
<tr>
<td>27abS</td>
<td>5 α(H), 14 β(H), 17 β(H), 20(S)-(C\textsubscript{27} regular sterane)</td>
</tr>
<tr>
<td>28abR</td>
<td>24-methyl-5 α(H), 14 β(H), 17 β(H), 20(R) (C\textsubscript{28} regular sterane)</td>
</tr>
<tr>
<td>28abS</td>
<td>24-methyl-5 α(H), 14 β(H), 17 β(H), 20(S) (C\textsubscript{28} regular sterane)</td>
</tr>
<tr>
<td>29aaS</td>
<td>24-ethyl-5 α(H), 14 α(H), 17 α(H), 20(S) (C\textsubscript{29} regular sterane)</td>
</tr>
<tr>
<td>29abR</td>
<td>24-ethyl-5 α(H), 14 β(H), 17 β(H), 20(R) (C\textsubscript{29} regular sterane)</td>
</tr>
<tr>
<td>29abS</td>
<td>24-ethyl-5 α(H), 14 β(H), 17 β(H), 20(S) (C\textsubscript{29} regular sterane)</td>
</tr>
<tr>
<td>29aaR</td>
<td>24-ethyl-5 α(H), 14 α(H), 17 α(H), 20(R) (C\textsubscript{29} regular sterane)</td>
</tr>
</tbody>
</table>

Table (7.9): Compounds identified in (m/z 178, 184 and 192) of aromatic hydrocarbon.

<table>
<thead>
<tr>
<th>Peak No</th>
<th>Peak Label</th>
<th>Peak Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phen</td>
<td>Phenanthrene</td>
</tr>
<tr>
<td>2</td>
<td>DBT</td>
<td>Dibenzothiophene</td>
</tr>
<tr>
<td>3</td>
<td>1-MP</td>
<td>Methylphenanthrene</td>
</tr>
<tr>
<td>4</td>
<td>9-MP</td>
<td>Methylphenanthrene</td>
</tr>
<tr>
<td>5</td>
<td>2-MP</td>
<td>Methylphenanthrene</td>
</tr>
<tr>
<td>6</td>
<td>3-MP</td>
<td>Methylphenanthrene</td>
</tr>
</tbody>
</table>
Figure (7.20): Gas Chromatography Mass Spectrum (GCMS) (m/z 178, 184, and 192) aromatic hydrocarbon of Kaikang-3 well oil sample. Peaks identification are given in Table (7-8).
Figure (7.21): Gas Chromatography Mass Spectrum (GCMS) (m/z 178,184, and 192) aromatic hydrocarbon of Kaikang-1 well oil sample.
Figure (7.22): Gas Chromatography Mass Spectrum (GCMS) (m/z 178, 184, and 192) aromatic hydrocarbon of Kaikang West-1 well source extract sample.
Figure (7.23): Gas Chromatography Mass Spectrum (GCMS) (m/z 178, 184, and 192) aromatic hydrocarbon of Kaikang-3 well source extract sample.
CHAPTER EIGHT

8. Conclusion and Recommendations

8.1 Conclusion:

Two wells from Muglad Basin namely, Kaikang-3 and Kaikang West-1 were selected for geochemical studies in order to evaluate source rock potentiality for hydrocarbon generation and biological markers distributions in the oil and extract samples.

Kaikang-3 well represents poor, fair, and very good source intervals. The best interval from upper Tendi Formation (1070m to 1110m) representing very good source with organic richness or Total Organic Carbon TOC ranging from 2.96 to 3.89%wt and generative potential S2 yield ranging from 11.57 to 25.25 mg HC/g and a hydrogen index HI ranging from 354 to 649 mg HC/TOC.

Van Kervelen diagram represents kerogen type II for this interval; which an oil prone kerogen. Quality of kerogen based on palynofacies analysis also suggests that this interval has type II kerogen, dominated by yellow to brown Structureless Organic Matter (SLOM, more than 70%) and yellow to brown plant tissue and cuticles (15%) with a small amount of black wood remains and a few scattered spore and pollen grains.

Maturity assessment based on Tmax range from (435 to 439 °C) place the samples from this interval in the beginning of oil generative window. This result is consistent with the result obtained from vitrinite reflectance measurement Ro range from (0.48-0.5) for this interval.

The samples from Kaikang West-1 have high organic richness (TOC more than 2%) from the depths of 980, 1189, 1295, 2010, and 2060m in Tendi and Baraka Formations. In this interpretation we are dealing with them as one interval. They are very good source rocks with TOC ranging
from 2.29 to 6.86% wt, generation potential $S_2$ yield ranging from 7.47 to 49.78 mg HC/g and hydrogen index between 327 to 726 mg HC/TOC. Van Kervelen diagram represent kerogen type II which is an oil prone kerogen type.

Palynofacies analysis indicate that kerogen type II is dominated by more than 95% yellow to brown structureless organic matter with very small amount of brown to black wood remain. Baraka Formation is also dominated by structureless organic matter and brown to black wood remain at the 2010m depth.

Maturity of organic matter based on Tmax indicates that, the samples mentioned above are mature with Tmax range from (435 to 439°C) placing them in the beginning of oil generative window. One sample at the depth 2010m is placed within peak of oil generative window Tmax 446°C. This is consistent with result obtained from vitrinite reflectance measurement Ro range from (0.69 to 0.91).

Biomarkers distributions for oil characterizations has been applied only on two samples of DSTs oil from Kaikang-3 and Kaikang-1 and source rock extracts from Kaikang-3 and Kaikang West-1. Two oil samples have similar terpanes 191m/z distributions and dominated by $C_{30}\alpha\beta$ hopanes peaks indicating similar facies source. The relatively low abundance of $C_{19}/C_{23}$ (0.86 and 0.66) and relatively high abundance of $C_{26}/C_{25}$ sugges that oil is derived from lascutrine source rocks rich bacterial/algal organic matter. These oils were derived from these rocks under less oxic to anoxic conditions during deposition, this is shown in the slightly high abundance of Pr/Ph (1.5 and 1.2).

The $C_{30}$ diahopane is derived from bacteria input to the sediment containing clays and deposited under oxic to suboxic conditions. This is present in relatively low abundance of $C_{30}$ diahopane comparing to $C_{30}\alpha$.
The $C_{30}$ C/ $C_{30}$ α β hopane ratio of two oil samples (0.25 and 0.22) indicate clay rich source rocks deposited under oxic/ suboxic conditions. The $C_{29}$ α β /$C_{30}$ α β hopane ratio has been used to differentiate shale and carbonate- and evaporite sourced oils. The ratio $C_{29}/C_{30}$ hopane ratios are relatively high in carbonate- and evaporite–sourced oils (~0.7 or greater) and lower for shale-sourced oils (0.4- 0.75). The ratio $C_{29}/C_{30}$ hopane ratios for Kaikang oils are (0.27 and 0.71) indicating shale sources for Kaikang oils.

The 28, 30- bisnorhopane (BNH) is a bacterial marker associated with anoxic depositional environment. BNH/$C_{30}$ ratio low Pr/Ph ratio interpreted to indicate source-rock deposition under anoxic conditions. The relatively low ratios of BNH/$C_{30}$ hopane indicate oxic to dysoxic conditions for the source that generated the two oil samples from Kiakang wells (0.09).

Gammacerane which indicate salinity and lacustrine environment is present in relatively low abundance suggesting normal salinity conditions during source rock deposition.

The ratio of $C_{30}$ α β hopane/ $C_{29}$ sterane 4.6 and ratio of $C_{27}$ sterane to $C_{28}$ and $C_{29}$ (45%) for Kaikang-1 oil sample suggest further input from bacterial/algal organic matter to this source.

Maturity based on biomarkers distribution $Ts / (Ts + Tm)$ ratio (0.67), $22S/22S+22R$ C31 ratio (0.50 and 0.55), and values of RC1 which is equivalent to Ro (0.80 and 0.71) indicate that oils were derived at the peak of oil generative window.

GCMS 191m/z for Kaikang-3 rock extract sample characterized by the dominance of $C_{30}$ α β peak, the ratio of $C_{29}$ α β/ $C_{30}$ α β (0.67) suggest a terrestrial land plant organic matter input. This is consistent with relatively high abundance of C19 tricyclic terpane, ratio of $C_{19}/C_{23}$ (1.5) and high abundance of $C_{26}/C_{25}$ (1.4) indicating that this oil was derived
from lacustrine source rock. High abundance of C_{19}/C_{23} indicates terrestrial land plant organic input to this source. Gammacerane and diahopane are present in very low abundance. The ratio of 30G/C_{30}αβ and 30D/C_{30}αβ are (0.05) and (0.01) respectively indicating that this oil was derived from lacustrine shale deposited in suboxic to anoxic condition. Gammacerane/C_{30} hopane ratios are low (0.25, 0.31) for two oil samples of Kaikang area indicating normal salinity conditions during source rock deposition.

GCMS 191m/z for Kaikang West-1 rock extract sample show dominance of C_{29}αβ hopane peak. C_{19}/C_{23} (1.19), C_{26}/C_{25} (1.19), 30G/C_{30}αβ (0.001), 30D/C_{30}αβ (0.001) and C_{29}αβ/ C_{30}αβ (1.6) indicate that this oil was derived from terrestrial organic matter and from lacustrine shale source under oxic and low salinity conditions. Dominance of C_{29}αβ farther offering of more land plant organic input more than Kaikang-3 source.

Maturity based on biomarkers distribution for two extracts from Kaikang West-1 and Kaikang-3 Ts/(Ts + Tm) ratio (0.25 and 0.55), 22S/22S+22R C_{31} (0.44 and 0.59) respectively show that the first one was derived from more mature source than the second one.
8.2 Recommendations:
The main source rock of Muglad Rift Basin is believed to be Abu Gabra Formation of the Early Cretaceous (Neocomian-Barremian) age (Schull, 1988). The organic matter is mainly sourced from plant, algae and bacteria of continental origin. Kaikang-1 and Kaikang-3 wells were drilled in the area. Oil accumulations were found in these two wells. Drilling reached only Amal Formation of the Tertiary age (Paleocene).
A big question then arises whether this oil was sourced from the Tertiary and that there might be a Tertiary source rock in Kaikang area, since this area represents the deeper trough of the Muglad Rift Basin, or may be oil is migrated from Abu Gabra Formation and then trapped in the Tertiary of Kaikang Trough. More geochemical studies should be carried out to prove the age assignment of source rocks and oils accumulation in the area.
It is also recommended to carry out Gas Chromatography Mass Spectrum/ Mass Spectrum (GC MS/MS) technique to determine the age of the source rocks and oils in the Kaikang Trough. These source rocks and oils could be correlated with the identified main source rocks and oils from Early Cretaceous of Abu Gabra Formation.
REFERENCES


APPENDIX

Sample Preparation Procedure For Rock-Eval:

1- The condition of the samples was first checked.
2- The samples were then soaked overnight prior to washing.
3- Samples were then washed with distilled water to remove the drilling mud before drying in oven for overnight at 40°C.
4- Samples were then repacked in plastic bags.
5- Contaminants were then removed (such as well additives, cement etc...).
6- The correct lithology was picked (such as shale, coal) and crushed into powder form.

A small amount (100mg) of rock is heated under a helium atmosphere at 300 °C for three minutes, then temperature is increased by 25 °C/min up to 600 °C. As soon as generated. Pyrolysis products are swept along to the detectors by the helium flow, only primary cracking reactions do happen (open system). During heating, the following events are observed:

- Free hydrocarbons, oil and gas contained in the organic matter are vaporized at around 300 °C. This thermo-vaporization, for a period of three minutes gives a peak called the S1 peak, expressed in mg HC/g of rock.

- Between 300 and 600 °C, hydrocarbons and oxygen containing compounds are expelled from the rock during the cracking of both kerogen and heavy extractable compounds such as resins and asphaltenes. Hydrocarbons from the S2 peak correspond to the present potential of the rock sample; S2 is expressed in mg HC/g of rock. Oxygen compounds decomposed between 300 and 390 °C, and the resulting CO2 is measured as the S3 peak expressed in mg CO2/g of rock.
- The temperature which is recorded for the maximum of the S2 peak is called Tmax; it is expressed in °C and is used as an indication of the stage of maturation of the organic matter.

- The organic carbon remaining after the recording of the S2 peak (CR) is measured by oxidation under air oxygen atmosphere at 600 °C. The CO2 obtained is the S4 peak, expressed in mg CO2/g of rocks. The total organic carbon (TOC) which is expressed in weight % is automatically computed from peaks S1, S2 and S4

\[
\text{TOC} = \frac{0.82(S_1+S_2) + S_4}{10}
\]

S4: Total organic carbon in weight percent (TOC). TOC = pyrolysis carbon (PC) + residual carbon (RC). PC = 0.82(S1+S2)/10. RC = S4/10, where S4 = mg C/g rock.

The hydrogen index (HI): mg HC/g TOC is the ratio of S2/TOC×100 is called hydrogen Index (Esptalié et al. 1977).

The oxygen index (OI): mg CO2/g TOC is the ratio of S3/g ×100 TOC is called oxygen index (OI).

The Production Index (PI): (PI= S1/ [S1+S2]). PI used to characterize the evolution level of the organic matter.
Procedure for Preparation of Polished Block:

Sample Preparation:

1- Pick about 3 gram of washed sample and grind using Agate mortar and pestle.
2- Sieve the samples using 250 micron size.

Sample Mounting:

1- Wet a plastic mounting cup with release agent.
2- Place sample into the mounting cup.
3- Pour 60 ml resin into the mixing cup.
4- Add 10 ml of hardener into the resin and stir thoroughly by using spatula (N.B 6 part of resin needs 1 part of hardener).
5- Pour just enough of the resin mixture into plastic mounting cup to cover the samples. Stir to remove air bubbles that might be trapped between the sample fragments.
6- Top-up the plastic mounting cup with resin mixture.
7- Allow the mixture to harden overnight in fume cupboard.
8- Remove the mounted samples from mounting cup and vibro-engraver.

Grinding/Polishing:

1- Grind the mounted samples using grinding wheel with MD-Pino 220 and use water as lubricant. Grind the samples until considerable amount of sample particles are exposed and a flat surface is obtained.
2- Change the grinding wheel with MD-Allegro and grind until the bigger scratches from previous step disappear. Use DiaDuo grain size 9 micron as lubricant.
3- Change the grinding wheel with MD-Largo and grind until scratches from previous step disappear. Use DiaDuo grain size 3 micron as lubricant.

4- Now change the grinding wheel with SP-Policel 1 cloth and polish with OP-S suspension liquid until scratch disappear completely.

5- The block now is ready for measurement.

**Palynofacies Samples Preparation:**

1- 30-35 grams of each rock sample was crushed to 2-5mm particle size.

2- The samples were then washed three times with tap water, once with distilled water, and were then transferred into polythene beaker. This is to insure that the samples clean from any fibers or drill-mud additives.

3- To remove the calcareous material, the samples were left in concentrated hydrochloric acid for 24 hours, and then washed several times with distilled water till a sample becomes neutral. To check neutralization Litmus paper was used as indicator.

4- Then the samples were kept for 3-5 days in cold concentrated hydrofluoric acid (HF con. 40%), and were then put in hot water bath 15-30 minutes at 50°-70° C to remove the siliceous material, then washed several times in distilled water to remove HF. During this treatment the samples were stirred once to twice daily.

5- To dissolve the fluoride resulting from HF treatment the samples were stand in concentrated hydrochloric acid for 15-30 minutes.
6- Then the samples were washed several times in distilled water; samples that appear to contain high amount of fluorides were stand in mixture of 2:1 of HCl and HF respectively.

7- Heavy Liquid Separation was carried out for all the samples using Zinc Bromide (specific gravity 2.5) and centrifuged using 200 ml plastic centrifuge tubes.

8- The residue was then sieved through a 10µm mesh sieve using Ultrasonic disintegration and sieve holder.

9- The residue was then mounted onto glass slide by using Transparent Resin.

10- The slides were examined under a transmitted light microscope (Leica DLMB model).
**Procedures for Extraction of Bitumen:**

*(Soxhlet Extraction):*

1. All glassware had been cleaned with detergent (Decon 90) followed by rinsing with distilled water. Soxhlet extractors especially the draining tubes were rinsed with acetone before drying in the oven to ensure faster drying.

2. The granulated copper has been activated by treating them with 10% HCL acid to remove any copper oxide film forming at surface. Rinsed with distilled water and distilled acetone and allowed to dry in the oven.

3. The grined cutting sample was placed into a thimble which had been pre-extracted with Dichloromethane (DCM). A small plug of pre-extracted cotton wool was placed on top of the sample in the thimble.

4. The thimble was placed into the extractor body of the soxhlet extraction glassware by means of a pair of clean tweezers.

5. The round bottom flask (250ml) was filled to about half-full (150ml) with DCM.

6. Boiling chips and activated granulated copper into the round bottom flask by means of a clean spatula. (Before any heating begins).

7. Enough DCM was added so as to cover the thimble. Extractor body and condenser before switching on the heating mantle.

8. The rock samples were extracted for 23 hours.

9. After cooling down of all the contents, the DCM from extractor body was drained into the round bottom flask.

10. The solvent was removed by rotary vacuum evaporation and concentrated extracts were filtered through a plug of cotton wool into pre-weighted vial.
11. Finally solvent was removed under a stream of nitrogen and extracted weight was recorded as percentage yield of original sample.

**Procedures for Liquid Column Chromatography (LCC):**

Fractionation of rock extract (Bitumen) or crude oil into saturates and aromatics compounds:

1- All glassware were cleaned with detergent, soaked in chromic acid overnight and rinsed with distilled water and oven dried.

2- All silica gel 60 (70-230 mesh ASTM) and alumina (70-230 mesh ASTM) were pre-extracted with DCM for three hours, air dried and activated at 300° C.

3- The chromatographic column was clamped vertically and rinsed and filled to about ¾ full with petroleum spirit.

4- By means of long glass rod, a cotton wool plug was introduced into the lower part of the column.

5- Silica gel slurry was prepared by pouring some petroleum spirit into a beaker containing some silica and stirred to remove any air bubbles.

6- Silica gel slurry was introduced slowly into the chromatographic column to ensure even packing (packed up to ¾ of the length of the column.

7- Alumina was introduced up to 1 ½ inches on top of the silica gel.

8- In the meantime the sample (oil or extractable organic matter) was dissolved in DCM and adsorbed onto a small quantity of activated alumina.

9- The solvent was removed using nitrogen. After alumina was free flowing, it was placed on top of the alumina in the column prepared after running down the solvent level to about 1 cm of the adsorbent.

10- Petroleum spirit was added by means of pipette and continued
elution until about 50 ml was collected in 100 ml round bottom flask (saturate fraction).

11- As the last petroleum sprit was running through, the column was topped up with DCM (50 ml) and continued elution to get aromatic fraction.

12- The solvent was evaporated from the three elutes on a rotary vacuum evaporator till the volume was low enough. The sample was then transferred to weighted vial and the trace solvent was removed by blowing with nitrogen.