GEOCHEMICAL APPLICATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS IN CRUDE OILS AND SEDIMENTS FROM PAKISTAN

Submitted By:

MUHAMMAD ASIF
05-Ph.D-Chemistry-02

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ENGINEERING AND TECHNOLOGY
LAHORE – PAKISTAN
2010
GEOCHEMICAL APPLICATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS IN CRUDE OILS AND SEDIMENTS FROM PAKISTAN

A Thesis Submitted
To
The University of Engineering & Technology Lahore In
Partial fulfillment of the Requirements for the Degree of

Doctorate of Philosophy
In
Chemistry
By
MUHAMMAD ASIF
2005-Ph.D-Chemistry-02

Supervisor
Prof. Dr. Fazeelat Tahira

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ENGINEERING AND TECHNOLOGY
LAHORE – PAKISTAN
2010
GEOCHEMICAL APPLICATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS IN CRUDE OILS AND SEDIMENTS FROM PAKISTAN

Research Thesis submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy in Chemistry

Approved on: _____________

Signature: __________________
Prof. Dr. Fazeelat Tahira
Internal Examiner

Signature: __________________
Prof. Dr. M. Akram Kashmiri
External Examiner

Signature: __________________
Prof. Dr. Saeed Ahmad
Chairman of the Department

Signature: __________________
Prof. Dr. Fazeelat Tahira
Dean Faculty of Natural Sciences, Humanities and Islamic Studies

DEPARTMENT OF CHEMISTRY
University of Engineering and Technology, Lahore-Pakistan,
This thesis has been evaluated by the following examiners

**External examiners:**

a) **From Abroad**

i) **Dr. R. Paul Philp**  
   Professor  
   Petroleum and Environmental Geochemistry  
   The University of Oklahoma  
   School of Earth and Energy  
   100 East Boyd street suite 810,  
   Sarkeys Energy Center  
   Norman, OK 73019 USA

ii) **Dr. Paul Greenwood**  
    Senior Research Fellow, Biogeochemistry  
    The University of Western Australia  
    35 Stirling Highway  
    Crawley WA 6009  
    Australia

b) **From within the country**

    **Dr. M. Akram Kashmiri**  
    Professor of Organic Chemistry  
    Chairman,  
    Board of Intermediate and Secondary Education, Lahore.

**Internal Examiner**

**Prof. Dr. Fazeelat Tahira,**  
Professor of Organic Chemistry  
Dean of natural sciences, humanities  
and Islamic studies,  
UET Lahore
Declaration

I “MUHAMMAD ASIF” declare that the Thesis entitled: “GEOCHEMICAL APPLICATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS IN CRUDE OILS AND SEDIMENTS FROM PAKISTAN” is my own research work. This thesis is being submitted for partial fulfillment of the requirements for the degree of Ph.D. in Chemistry. This thesis contains no material that has been accepted and published previously for the award of any degree.

_____________________
Signature
ACKNOWLEDGEMENTS

I express my heartiest and sincere thanks to my respected and honorable Research Supervisor, Prof. Dr. Fazeelat Tahira, Dean, Faculty of Natural Sciences, Humanities and Islamic Studies, University of Engineering and Technology, Lahore, who’s keen interest, guidance and encouragement has been a source of great help throughout this research work. Special and heartiest thanks to Prof. Dr. Kliti Grice, Director, WA-IOGC group, Curtin university of Technology, Perth, Australia for providing me an opportunity to work with an excellent group. Her unforgettable cooperation, guidance, source of knowledge and kind behavior towards me will be ever remembered. I would like to give respectful thanks to Prof. Dr. Robert Alexander for his guidelines for understanding of kerogen chemistry of sedimentary organic matter.

I thankful to Prof. Dr. Saeed Ahmad, Chairman, Department of Chemistry, University of Engineering and Technology, Lahore for providing me an opportunity to complete my degree.

I would like to acknowledge and thank to my friends Abdus Saleem, Saleem Aboglila, Umair Akram, Amy Bowater, Birgit Nabbefeld, Svenja Tulipani, Dawn White, Ercin Maslen, Christiane Eiserbeck, Christiane VVE, Pierre Le Metayer, Ken Williford, Hina Saleem, Muhammad Irfan Jalees, Shagufta Nasir, Shahid Nadeem, Arif Nazir and Imran Kaleem and many more for their friendly discussions and chat during this research thesis. I also thank to Geoff Chidlow, Sue Wang, Kieran Pierce, Tanya Chambers, Zia-ul-Hassan and Anwar Nadeem for technical support through out my research.

I am happy to acknowledge the love and prayers of my parents, brothers and sisters. Their moral support is a great source of strength for me in every field of life. Without their prayers, sacrifices and encouragements, the present work would have been a merry dream.

Muhammad Asif
Crude oils and sediments extracted from Kohat-Potwar Basin (Upper Indus Basin) were examined for polycyclic aromatic hydrocarbons (PAHs), heterocyclic aromatic hydrocarbons, biomarkers and stable isotope compositions. The first four chapters provide background to the research. Chapter 5 discusses the petroleum geochemistry of Potwar Basin where three groups of oils were recognized on the basis of diagnostic biomarkers, distribution of PAHs and stable bulk carbon and hydrogen isotopes. In chapter 6, PAHs distributions and compound specific stable hydrogen isotope compositions have been used to assess minor biodegradation in Potwar Basin oils. The final chapter of this thesis (chapter 7) describes the formation of heterocyclic aromatic hydrocarbons and fluorenes in sedimentary organic matter through carbon catalysis reactions.

Diagnostic biomarker parameters along with stable bulk $\delta^{13}$C and $\delta$D isotope abundance reveal three groups of oils in Potwar Basin. Group A contains terrestrial source of OM deposited in highly oxic/fluvi-o-deltaic clastic depositional environment shown by high Pr/Ph, high diahopane/hopane, high diasterane/sterane, low DBT/P ratios and higher relative abundance of C$_{19}$ tricyclic and C$_{24}$ tetracyclic terpanes. Aliphatic biomarkers for rest of the oils indicate marine origin however two ranges of values for parameters differentiate them into two sub-groups (B and C). Group B oils are generated from clastic rich source rocks deposited in marine suboxic depositional environment than group C oils which are generated from source rocks deposited in marine oxic depositional environment. Group C oils show higher marine OM (algal input) indicated by extended tricyclic terpanes (upto C$_{41}$ or higher) and higher steranes/hopanes ratios. Distribution of PAHs classified Potwar Basin oils into similar three groups based on depositional environments and source OM variations. Abundant biphenyls (BPs) and fluorenes (Fs) are observed in group A oils while group B oils showed higher abundance of dibenzothiophenes (DBTs) and negligible presence of dibenzofurans (DBFs) and Fs and group C oils showed equal abundance of DBTs and Fs. This relative abundance of heterocyclic aromatic hydrocarbons in Potwar Basin oils broadly indicate that the distribution of these compounds is controlled by depositional environment of OM where
sulfur compounds (i.e. DBTs) are higher in marine source oils while oxygen compounds (DBFs) and Fs are higher in oxic/deltaic depositional environment oils. Higher abundance of aromatic biomarkers the 1,2,5-trimethylnaphthalene (1,2,5-TMN), 1-methylphenanthrene (1-MP) and 1,7-dimethylphenanthrene (1,7-DMP) indicate major source of OM for group A oil is higher plant supported by abundance of conifer plants biomarker retene. Variations in distribution of triaromatic steroids (TAS) in Potwar Basin oils clearly indicate source dependent of these compounds rather than thermal maturity. Higher abundance of C_{20} and C_{21} TAS and substantial difference in distribution of long chain TAS (C_{26}, C_{27}, C_{28}) between the groups indicate different source origin of these compounds. Group A shows only C_{27} and C_{28} TAS while group B shows C_{25} to C_{28} TAS and absence of these compounds in group C oils revealed that the sterol precursors for these compounds are most probably different. Aliphatic and aromatic hydrocarbon maturation parameters indicate higher (late oil generation) thermal maturity for all oils from the Potwar Basin. The crude oils of group A and C are typically non-biodegraded mature crude oils whereas some of the oils from group B showed minor biodegradation indicated by higher Pr/n-C_{17}, Ph/n-C_{18} and low API gravity.

Distribution of PAHs and stable hydrogen isotopic composition (δD) of n-alkanes and isoprenoids has been used to assess the minor biodegradation in a suite of eight crude oils from Potwar Basin, Pakistan (group B). The low level of biodegradation under natural reservoir conditions was established on the basis of biomarker distributions. Bulk stable hydrogen isotope of saturated fractions of crude oils show an enrichment in D with increase in biodegradation and show a straight relationship with biodegradation indicators i.e. Pr/n-C_{17}, API gravity. For the same oils, δD values for the n-alkanes relative to the isoprenoids are enriched in deuterium (D). The data are consistent with the removal of D-depleted low-molecular-weight (LMW) n-alkanes (C_{14}-C_{22}) from the oils. The δD values of isoprenoids do not change during the minor biodegradation and are similar for all the samples. The average D enrichment for n-alkanes with respect to the isoprenoids is found to be as much as 35‰ for the most biodegraded sample. The relative susceptibility of alkylphenanthrenes at low levels of biodegradation was discussed. Alkynaphthalenes are more susceptible to biodegradation
than alkylphenanthrenes while extent of biodegradation decreases with increase in alkyl substitution on both naphthalene and phenanthrenes. A range of biodegradation ratios (BR) are purposed from dimethylnaphthalene (DNBR), trimethylnaphthalenes (TNBR) and tetramethylnaphthalene (TeNBR) that show significant differences in values with increasing biodegradation and are suggested as good indicators for assessment of low level of biodegradation.

Laboratory experiments have shown that activated carbon catalyses the reactions of biphenyls (BPs) with surface adsorbed reactants that incorporate S, O, N or methylene forming some common constituents of sedimentary organic matter namely, dibenzothiophene (DBT), dibenzofuran (DBF), carbazole (C) and fluorene (F). A relationship between the % abundance of the hetero element in kerogen and the abundance of the related heterocyclic compound in the associated soluble organic matter supports the hypothesis that these reactions occur in nature. More specific supporting evidence is reported from the good correlation observed between methyl and dimethyl isomers of the reactant BPs and the methyl and dimethyl isomers of the proposed product heterocyclics compounds i.e. DBTs, DBFs, Cs and Fs. It is suggested that these distributions reported for sediments and crude oils from the Kohat Basin are the result of a catalytic reactions of compounds with BP ring systems and surface adsorbed species of the hetero element on the surface of carbonaceous material. Similar distributions of heterocyclic aromatic hydrocarbon from Carnarvon Basin (Australia) were illustrated to show the global phenomenon of this hypothesis. Furthermore, the abundances of these compounds (DBT, DBF and BP) show similar concentration profiles throughout the Kohat Basin sediments suggesting that share a common source. These compounds also correlate well with changes in the paleoredox conditions. These data tends to point towards a common precursor perhaps lignin phenols of land plants. Coupling of phenols leads to BP, which has been demonstrated in laboratory experiments to be the source of C, DBT, DBF, and F.


Asif, M., Fazeelat, T., Grice, K., Petroleum Geochemistry of Potwar Basin, Pakistan: oil-oil correlation by bulk stable isotopes and aromatic hydrocarbons distributions (In preparations for Organic Geochemistry).
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter #</th>
<th>Description</th>
<th>Page#</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ACKNOWLEDGMENTS</td>
<td>i</td>
</tr>
<tr>
<td></td>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td></td>
<td>PUBLICATIONS AND CONFERENCE PRESENTATION</td>
<td>v</td>
</tr>
<tr>
<td></td>
<td>TABLE OF CONTENTS</td>
<td>vi</td>
</tr>
<tr>
<td></td>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
</tbody>
</table>

### Chapter–1 INTRODUCTION

1.1 Petroleum Geochemistry 1
1.2 Polycyclic Aromatic Hydrocarbons (PAHs) 1
1.3 Hetercyclic Aromatic Hydrocarbons and Fluorenes in Crude Oils and Sediments
   1.3.1 Incorporation of N, S, O Elements into Sedimentary OM 9
   1.3.2 S Compounds from Laboratory Simulations 11
1.4 Carbon Catalysis 12
   1.4.1 Kerogen 12
   1.4.2 Coal 13
   1.4.3 Activated Carbon 13
1.5 Scope and Framework of the Thesis 13

### Chapter–2 GEOLOGICAL SETTINGS AND DESCRIPTION OF SAMPLES

2.1 Geology Settings of Kohat-Potwar Geological Province 16
   2.1.1 Depositional Settings of Kohat-Potwar Basin 18
2.2 Descriptions of Crude Oils and Sediments
   2.2.1 Potwar Basin 21
   2.2.2 Kohat Basin 24
   2.2.3 Geochemical Description of Sediments 25

### Chapter–3 EXPERIMENTAL
3.1 Materials and Reagents

3.2 Geochemical Techniques

3.2.1 Sample Preparation

3.2.2 Liquid Chromatography of Crude Oils and SOM

3.2.3 Isolation of Branched and Cyclic Alkanes

3.3 Laboratory Experiments

3.3.1 Reference Compounds and Glass Tubes Preparation

3.3.2 Laboratory Heating Experiments

3.4 Analytical Methods and Instrumentation

3.4.1 Elemental Analysis of Sediments

3.4.2 $\delta^{34}$S of Pyrite from Sediments

3.4.3 Gas Chromatography-Mass Spectrometry (GC-MS)

3.4.4 Gas Chromatography-Isotope Ratio Mass Spectrometry

3.4.5 Elemental Analysis-Isotope Ratio Mass Spectrometry (Bulk Isotope Analysis)

Chapter 4 IDENTIFICATION OF BIOMARKERS AND AROMATIC HYDROCARBONS

4.1 Saturated Hydrocarbons

4.1.1 $n$-Alkanes and Isoprenoids

4.1.2 Tricyclic and Tetracyclic terpanes

4.1.3 Pentacyclic Terpanes

4.1.4 Steranes and Diasteranes

4.1.5 Diamondoid Hydrocarbons

4.2 Polycyclic Aromatic Hydrocarbons

4.2.1 Biphenyl and Alkylbipheneys

4.2.2 Naphthalene and Alkynaphthalenes

4.2.3 Phenanthrene and Alkylphenanthrenes

4.2.4 Dibenzofuran and Alkylbenzofurans

4.2.5 Carbazole and Alkylcarbazoles

4.2.6 Dibenzothiophene and Alkylbenzothiophenes

4.2.7 Fluorene and Alkylfluorenes
4.2.8 Identification of Retene 53
4.2.9 Compound Identification of Laboratory Experiments 54

Chapter–5 GEOCHEMISTRY OF POTWAR BASIN CRUDE OILS 55
Abstract 55
5.1 Introduction 56
5.2 Results and Discussion 59
5.2.1 Normal Alkanes and Isoprenoids Distribution 59
5.2.2 Carbon and Hydrogen Isotopic Compositions 59
5.2.3 Polycyclic Aromatic Hydrocarbons (PAHs) 63
5.2.4 Thermal Maturity of Potwar Basin Oils 65
5.2.5 Lithology and Depositional Environment 70
5.2.5.1 Heterocyclic Aromatic Hydrocarbons 73
5.2.6 Source of OM 74
5.2.6.1 Alkynaphthalenes and alkylphenanthrenes 81
5.2.6.2 Triaromatic steroids (TAS) 83
5.2.7 Biodegradation 87
Conclusions 91

Chapter–6 POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND STABLE HYDROGEN ISOTOPE STUDY AS INDICATOR OF MINOR BIODEGRADATION 93
Abstract 93
6.1 Introduction 94
6.2 Results and Discussion 95
6.2.1 Assessment of Biodegradation 95
6.2.2 Bulk Hydrogen Isotopic Compositions of Saturated Fractions 100
6.2.3 Compound Specific Hydrogen Isotopic compositions of n-alkanes and isoprenoids 101
6.2.4 Affects of Biodegradation on Polycyclic Aromatic Hydrocarbons 106
6.2.4.1 Alkynaphthalenes 106
6.2.4.2 Alkylphenanthrenes

Conclusions

Chapter–7

GEOSYNTHESIS OF HETEROCYCLIC AROMATIC HYDROCARBONS AND FLUORENES BY CARBON CATALYSIS

Abstract

7.1 Introduction

7.2 Results and Discussion

7.2.1 Laboratory Experiments on Active Carbon

7.2.1.1 Probable mechanism of geosynthesis reactions

7.2.2 Distribution of Heterocyclic Aromatic Hydrocarbon in Sediments and Crude Oils

7.2.2.1 Parent compounds

7.2.2.2 Methylated homologous of heterocyclics and Fs

7.2.2.3 Dimethyl homologous of heterocyclics and Fs

a) DMBPs vs DMDBTs

b) DMBPs vs DMCs and DMFs

7.2.3 Paleoredox Conditions and Heterocyclics Formation

Conclusions

REFERENCES

APPENDIX
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table #</th>
<th>Description</th>
<th>Page#</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Aromatic hydrocarbons thermal maturity parameters</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>Geological information of crude oils</td>
<td>22</td>
</tr>
<tr>
<td>2.2</td>
<td>Geological settings and Rock Eval data of sediments from well Mela-1</td>
<td>23</td>
</tr>
<tr>
<td>2.3</td>
<td>Aliphatic biomarker maturity parameters of Mela-1 sediments</td>
<td>27</td>
</tr>
<tr>
<td>3.1</td>
<td>Heating experiments details</td>
<td>33</td>
</tr>
<tr>
<td>4.1</td>
<td>Identifications of pentacyclic triterpanes from Fig. 4.3.</td>
<td>42</td>
</tr>
<tr>
<td>4.2</td>
<td>Identifications of steranes and diasteranes from Fig. 4.4.</td>
<td>43</td>
</tr>
<tr>
<td>4.2</td>
<td>Identification of compounds from Fig. 4.14.</td>
<td>54</td>
</tr>
<tr>
<td>5.1</td>
<td>$n$-Alkanes, isoprenoid ratios and bulk isotope data</td>
<td>60</td>
</tr>
<tr>
<td>5.2</td>
<td>Thermal maturity parameters calculated from aliphatic and aromatic hydrocarbons</td>
<td>66</td>
</tr>
<tr>
<td>5.3</td>
<td>Source OM and depositional environments parameters of Potwar Basin oils</td>
<td>78</td>
</tr>
<tr>
<td>5.4</td>
<td>Biomarkers parameters limits for Potwar Basin oils</td>
<td>80</td>
</tr>
<tr>
<td>5.5</td>
<td>Assessment of biodegradation results of Potwar Basin crude oils</td>
<td>90</td>
</tr>
<tr>
<td>6.1</td>
<td>$n$-Alkanes, isoprenoids, aliphatic biomarkers and diamondoids hydrocarbons ratios</td>
<td>96</td>
</tr>
<tr>
<td>6.2</td>
<td>$\delta D(%o)^*$ values of n-alkanes and isoprenoids (pristane and phytane) from Potwar Basin oils</td>
<td>102</td>
</tr>
<tr>
<td>6.3</td>
<td>Biodegradation ratios (BR) and alkylphenanthrenes ternary plot ratios.</td>
<td>110</td>
</tr>
<tr>
<td>7.1</td>
<td>Concentrations of compounds and elemental kerogen composition for Kohat Basin sediments.</td>
<td>127</td>
</tr>
<tr>
<td>7.2</td>
<td>Ring position relationships between BP and related heterocyclic compounds and Fs</td>
<td>132</td>
</tr>
<tr>
<td>7.3</td>
<td>Concentration and Compound Ratios of Sediments and Crude Oils</td>
<td>136</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Fig. #</th>
<th>Description</th>
<th>Page#</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Possible biological precursors and pathways for the generation of alkynaphthalenes after Püttmann and Villar [180], Strachan et al. [19] and Armstrong et al. [141].</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Generalized comparison of biodegradation sequence between aliphatic and aromatic hydrocarbons of crude oils</td>
<td>7</td>
</tr>
<tr>
<td>1.3</td>
<td>Structurally related compounds</td>
<td>8</td>
</tr>
<tr>
<td>2.1</td>
<td>Geological and Location map of Kohat-Potwar Basin oils (modified from [106,108,110-111])</td>
<td>17</td>
</tr>
<tr>
<td>2.2</td>
<td>Stratigraphy of Kohat-Potwar Basin, Pakistan, and location of crude oils and sediments used in this study (Modified from Wandrey et al., 2004 and references therein)</td>
<td>19</td>
</tr>
<tr>
<td>4.1</td>
<td>Total ion chromatograms (TIC) of saturated hydrocarbon fraction shows ( n )-alkanes (( n )-C\textsubscript{10} to ( n )-C\textsubscript{37} ) and isoprenoids in crude oil (Missakeswal-1); a: 2,6-dimethylundecane (I, see appendix); b: 2,6,10-trimethylundecane (nor-farnesane, II); c: 2,6,10-trimethyldodecane (farnesane, III); d: 2,6,10-trimethyltridecane (IV); e: 2,6,10-trimethylpentadecane (nor-Pristane, V); Pr: pristane, 2,6,10,14-tetramethylpentadecane (VI); Ph: phytane, 2,6,10,14-tetramethylhexadecane (VII). Refer to section 3.4.3 for GC-MS program.</td>
<td>39</td>
</tr>
<tr>
<td>4.2</td>
<td>Mass chromatogram (( m/z ): 191) illustrating tricyclic and tetracyclic terpanes in Dhurnal-1 crude oils. Peak numbers 19-41 denote carbon number of tricyclic terpane (VIII); ( C_{24}^* ): ( C_{24} ) 17,21-secohopane (IX); ( C_{30} ): ( C_{30} ) 17( \alpha )(H)-hopane (Xb). Refer to section 3.4.3 for GC-MS program.</td>
<td>40</td>
</tr>
<tr>
<td>4.3</td>
<td>Mass chromatograms (( m/z ): 191) showing the distribution of pentacyclic triterpanes (hopanes, X-XV) in Adhi-5 crude oil. Identity of peaks refers to Table 4.1. Refer to section 3.4.3 for GC-MS program.</td>
<td>41</td>
</tr>
<tr>
<td>4.4</td>
<td>Mass chromatogram (( m/z ): 217) of Dhurnal-1 crude oil shows the profile of steranes and diasteranes. Peak identity numbers refer to Table 4.2. See section 3.4.3 for GC-MS program.</td>
<td>43</td>
</tr>
<tr>
<td>4.5</td>
<td>Adamantane (XVIII) and methyladamantanes are shown by sum of mass chromatograms (( m/z ): 136+135) and diamantine (XIX) and methyldiamantanes are shown by sum of mass chromatograms (( m/z ): 188+187) from saturated fraction of representative oil sample (Adhi-5). See section 3.4.3 for GC-MS program.</td>
<td>44</td>
</tr>
<tr>
<td>4.6</td>
<td>(a) Sum of mass chromatograms (( m/z ): 154+168) showing</td>
<td>46</td>
</tr>
</tbody>
</table>
biphenyl (BP, XXII) and methylbiphenyls and (b) mass chromatogram (m/z: 182) showing dimethylbiphenyls in aromatic fraction of a representative oil (Adhi-5). DPM, diphenylmethane; numbers on each peak refer to respective methyl and dimethyl biphenyl isomer.

4.7 (a) Naphthalene (N, XXIII), methylnaphthalenes, dimethylnaphthalenes are shown by sum of mass chromatograms (m/z: 128+142+156 respectively) and (b) trimethylnaphthalenes, tetramethylnaphthalenes are shown by sum of mass chromatograms (m/z: 170+184 respectively) in a representative oil (Adhi-5). Numbers on each peak refer to position of methyl substituent.

4.8 Phenanthrene (XXIV), methylphenanthrenes, dimethylphenanthrenes shown by sum of mass chromatograms (m/z: 178+192+206 respectively) from aromatic fraction of Adhi-5. Numbers on each peak refer to respective alkyl phenanthrene isomer.

4.9 (Sum of mass chromatograms (m/z: 168+182) showing DBF (XXV) and methyldibenzofurans in Kohat Basin sediment, depth: 4290 m. Numbers on each peak refer to methyl dibenzofuran isomer.

4.10 (a) sum of mass chromatogram (m/z: 167+181) showing carbazole (C, XXVI) and methylcarbazoles and (b) mass chromatogram (m/z: 195) showing dimethylcarbazoles from Kohat Basin sediment, depth: 4690 m. Numbers on each peak refer to respective methyl and dimethyl carbazole isomer.

4.11 (a) Sum of mass chromatograms (m/z: 184+198) sowing dibenzothiophene (DBT, XXVII) and methyldibenzothiophenes and (b) mass chromatogram (m/z: 212) showing dimethyldibenzothiophenes from Kohat Basin sediment, depth, 4710 m. Numbers on each peak refer to respective methyl and dimethyl dibenzothiophene isomer.

4.12 Sum of mass chromatograms (m/z: 166+180) showing fluorene (F, XXVIII) and methylfluorenes in Kohat Basin sediment, Depth: 4290 m. Numbers on each peak refer to respective methyl substituent.

4.13 Mass chromatograms m/z: 219 and 234 showed Retene (XXI) in aromatic fraction of Adhi-5 crude oil.

4.14 Total ion chromatogram of the extract of laboratory experiment at 300 °C of reactants (biphenyl, activated carbon, NaN₃, Air) for 16 hrs. Identification is given in Table 4.3.

5.1 The plots (a) δ¹³Cᵣₑₛ vs δ¹³Cᵣₑₒ (b) δ¹³Cᵣₑᵥᵉʳ vs δDᵣₑᵥᵉʳ to delineate
5.2 TICs showing distributions of aromatic hydrocarbons in representative samples from the Potwar Basin; N, naphthalene; ..

5.3 (a) Hopanes maturity parameters plot between C₂₉ vs C₃₀ of αβ/(αβ+βα) (c.f. [152]) (b) calculated vitrinite reflectance diagram from $R_{ob}$ (TNR-2; [11]) and $R_c$ (MPI-1; [156]) show different thermal maturation stages of oil generation window.

5.4 (a) Pr/Ph versus DBT/P plot indicates lithology and depositional environment [167] (b) C₃₀ 17α-diahopane/C₃₀ 17α-hopane vs C₂₉ diasteranes/sterane plot shows the affects of clay and depositional environment on Potwar Basin oils (c.f. [45] and references therein).

5.5 Bar diagram shows relative percentages of DBTs, DBFs, Fs in Potwar Basin oils.

5.6 Mass chromatograms (m/z 191) showing distribution of tricyclic (TT) and pentacyclic terpanes (hopanes, H) in Potwar Basin crude oils. numbers on peak indicate TT, 24*, C₂₄-tetracyclic terpane and number with H indicate hopanes.

5.7 Cross plot between C₁₉/(C₁₉+C₂₃) TT and C₂₄ TeT/(C₂₄ TeT + C₂₃ TT) shows difference in source material in Potwar Basin oils (c.f. [173-175]).

5.8 (a) Distribution relationship between TMN ratios of Potwar Basin oils (b) higher plant aromatic biomarkers ratios 1,7-DMP/X and 1-MP/9-MP [5] indicated terrestrial input for group A oil.

5.9 Distribution of triaromatic steroids in Potwar Basin crude oils a) Adhi-5, b) Kal-2, c) Toot-12. Carbon number on peak refers to corresponding TAS (XXa to XXh).

5.10 Distribution relationship between C₂₀/C₂₁ TAS and C₂₇/C₂₉ diasteranes from Potwar Basin oil clearly indicate three groups

5.11 Representative TICs of saturated fractions from Potwar Basin oils, Group A, Adhi-5; group B, Joyamir-4; group C, Dhurnal-1. Number on peaks refers to n-alkanes carbon numbers.

5.12 (a) Plot of Pr/n-C₁₇ vs Ph/n-C₁₈ and (b) API value vs. Pr/n-C₁₇ showing biodegradation trends in crude oils used in this study.

6.1 Total ion chromatograms of saturated hydrocarbon fractions for Potwar Basin crude oils showing different degrees of biodegradation. C₁₇, C₂₅ indicate carbon number of n-alkanes. a; 2,6-dimethylundecane; b: 2,6,10-trimethylundecane (nor-farnesane); c: 2,6,10-trimethyldecane (farnesane); d: 2,6,10-trimethyltridecane; e: 2,6,10-trimethylpentadecane (nor-Pristane); Pr, pristane and Ph, phytane; UCM, unresolved complex mixture.
6.2 Relationship between API gravity and biodegradation parameters (BPI and BP2, [203]) showing API to be controlled by biodegradation rather than any other factor such as mixing.

6.3 $\delta D_{sats}$ vs. $Pr/n-C_{17}$ shows enrichment in deuterium of saturated fractions with increase in biodegradation.

6.4 The $\delta D$ ($\%$) distribution of $n$-alkanes from Potwar oils, (a) $n-C_{14}$ to $n-C_{29}$ $n$-alkanes (b) significant effect of biodegradation is observed in $n$-alkanes, $n-C_{14}$-$n-C_{22}$.

6.5 Plot of $\delta D$ ($\%$) difference between LMW $n$-alkanes ($n-C_{14}$ - $n-C_{22}$) and isoprenoids vs. (a) API gravity, and (b) $Pr/n-C_{17}$

6.6 Biodegradation susceptibility for alkylnaphthalene distributions ($m/z$ 156+170+184; dimethylnaphthalenes, DMNs; trimethylnaphthalenes, TMNs; tetramethylnaphthalenes, TeMNs). Numbers on each peak refer to respective alkylnaphthalene isomer and highlighted peaks show isomer components most affected by rising biodegradation.

6.7 Order of susceptibility of alkylnaphthalenes and alkylphenanthrenes to microbial attack in the Potwar Basin crude oils (cf. [15]). Numbers refer to positions of methyl substituents. Ternary plot was plotted using similar conditions for analysis and identifications as reported by van Aarssan et al. [38] for TMNr (1,3,7/1,3,7+1,2,5)-TMNs, TeMNr (1,3,6,7/1,3,6,7+(1,2,5,6+1,2,3,5)-TeMNs and PMNr (1,2,4,5,7/1,2,4,5,7+1,2,3,5,6)-PMNs.

6.8 Polymethylnaphthalenes biodegradation ratios vs. $Pr/n-C_{17}$ showed a good correlation. A significant decrease in DNBR, TNBR and TeNBR is observed.

6.9 A combined chromatogram of MP’s and DMP’s ($m/z$: 192+206) shows decrease in relative intensity with in increase in biodegradations. The numbers on peaks indicate the respective alkyl substituted isomer of phenanthrene and highlighted peaks show significant depletion as move to more biodegraded sample.

7.1 Total ion chromatograms (TIC) of extracts from laboratory heating experiments. Samples were heated at 300 $^\circ$C for 16 hr. Each blank experiment was identical in composition, temperature and time but without activated carbon. AC, activated carbon; BP, biphenyl; S, sulfur; TMB, 1,2,3,4-tetramethylbenzene; MBPs, methylbiphenyls.

7.2 TICs of extracts from laboratory heating experiments at temperature 270 $^\circ$C for 16 hr. Each blank experiment was identical in composition, temperature and time but without coal, BP, biphenyl; S, sulfur.
7.3 Mass chromatograms (m/z: 198) of the extract of heating experiments of 3-MBP with elemental S in the presence of active carbon at different temperatures.

7.4 TICs of extract of heating experiments of BP with activated carbon using different alkyl precursor compounds, heating temperature and duration was same for all experiments i.e. 300°C and 16 hr. AC, activated carbon; BP, biphenyl; MBPs, methylbiphenyls; TMB, 1,2,3,4-tetramethylbenzene.

7.5 Purposed reaction pathways on activated carbon for formation of heterocyclic aromatic compounds and F from BP. AC, activated carbon; S: sulfur; BP, biphenyl; F, fluorene; DBT, dibenzothiophene; DBF, dibenzofuran; C, carbazole.

7.6 Relationship of reactant (BP)-product (DBT, DBF and F) for Kohat Basin sediments (data given in Table 7.1).

7.7 Relationship between compounds in SOM and the N, S, and O concentration of kerogen from each sample (data given in Table 7.1).

7.8 Representative ion chromatograms show relative distributions of MDBTs (198), MDBFs (m/z: 182), MBPs (m/z: 168), MCs (m/z: 181) and MFs (m/z: 180) from the Kohat Basin, Pakistan sediment (Depth, 4345 m). Symbols relate precursor-product compounds.

7.9 Distributions of MBPs and methyl homologues of DBF, C and F in crude oils from two different basins. a) Chaknaurang, Upper Indus Basin, Pakistan; b) Barrow, Carnarvon Basin, NW Australia. MBPs (m/z 168), MFs (m/z 180), MDBFs (m/z 182) and MCs (m/z 181). Symbols relate precursor-product compounds.

7.10 Relationship between MBPs and MDBTs in Kohat Basin sediments. a) absolute concentration plot shows association between individual isomers of MBPs and MDBTs. b) plot shows ratio of MBPs and MDBTs to the parent BP and DBT in sediment samples.

7.11 Relative distribution of DMBPs and DMDBTs in Kohat Basin sediments (depth, 4680 m). Numbers on peaks indicate dimethyl substituted isomers of BP and DBT (Table 7.2). Symbols relate precursor-product compounds.

7.12 Relative distributions of methyl and dimethyl biphenyls and dibenzo thiophenes in crude oils from two different basins. a) Mela-1, Kohat Basin, Pakistan, b) Wanaea, Carnarvon Basin, Australia. MBPs (m/z 168), DMBPs (m/z 182), MDBTs (m/z 198) and DMDBTs (m/z 212). Symbols relate precursor-product compounds.
7.13 Relative distribution of DMBPs ($m/z$: 182), DMCs ($m/z$: 195) and DMFs ($m/z$: 194) in the Kohat Basin sediment (Depth, 4940 m) and the Carnarvon Basin Griffin crude oil. Numbers on peaks indicate dimethyl substituted isomers. Symbols show precursor-product relationships (Table 3).

7.14 $\delta^{34}$S(‰) of pyrite against concentrations of DBT, DBF, BP, C and Pr/Ph with depth in Kohat Basin sediments Pakistan.
Chapter - 1

INTRODUCTION

1.1 PETROLEUM GEOCHEMISTRY

Petroleum geochemistry is the study of geochemical processes that lead to the formation, migration, accumulation and alteration of crude oils and natural gas [1]. Crude oil is a complex mixture of thousands of organic compounds, formed through processes i.e. deposition, thermal and bacterial alteration of organic matter (OM), catalytic effects of clastic minerals, oxidation and reduction in sedimentary environment for millions of years [2]. A biomarker is compound in geological samples that can structurally related to the natural products of the living organism i.e. animals, higher plants, bacteria, fungi, algae which are the source of OM. The distribution of these compounds is highly diagnostic of source organisms, and their subtle structural transformation could be indicative of depositional environment, thermal maturity and biodegradation. The relative proportions of biomarkers are routinely being used by geochemists to reconstruct ancient depositional environment and to correlate crude oils to their source rocks.

1.2 POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

Aromatic hydrocarbons are important constituents of petroleum and extracts of both recent and ancient sediments [3-7]. PAHs are not synthesized in living organisms and almost absent in natural OM [8]. The majority of PAHs in petroleum are the products of complex chemical transformations of naphthenic and/or olefinic biological ancestors during diagenesis and catagenesis [4,9]. The biological origin of a given PAHs is obvious only in favorable conditions, where a characteristic part of the naphthenic structure has been preserved unchanged.

Distributions of PAHs are potentially useful in many areas of applied petroleum geochemistry. Abundance of certain aromatic hydrocarbons in crude oils and sediments such as 1,2,5-trimethylnaphthalene (1,2,5-TMN), 1,2,5,6-tetramethylnaphthalene (1,2,5,6-TeMN), 9-methylphenanthrene (9-MP), 1,7-
dimethylphenanthrene (1,7-DMP) originate from diterpenoid and triterpenoid natural products [4-5] (Fig. 1.1). The most useful application of aromatic hydrocarbons is evolution of thermal maturity of OM [10-11]. The correlation of oils using aromatic hydrocarbon distributions and alteration of crude oils in reservoirs are other important application discussed [12-13]. Furthermore, affects of biodegradation of aromatic hydrocarbons has been reported in crude oils, coals and sediments [14-17].

**Precursor compounds of PAHs**

The widespread occurrence of PAHs in sedimentary OM is the result of complex chemical transformation of biological precursors under sedimentary conditions. Alteration of functional groups in biological structures commonly occurs through decarboxylation or dehydration and unsaturated bonds provides a starting point for cyclization and aromatization [4,9,18-19] (Fig. 1.1). Specifically, diagenetic and catagenetic transformations of carotenoids, terpenoids and alkaloids have been considered as possible pathways/precursors for the formation of mono-, di- and tri- aromatics [19-24] (Fig. 1.1). Alkynaphthalenes has been suggested to be originated from terrestrial sources [4]. Biological compounds such as cyclic sesquiterpenoids from resins of conifer plants are potential precursors of alkynaphthalenes, 1,2,7-Trimethylnaphthalene is suggested to originate from compounds like β-amyrin that are constituents of angiosperms (Fig. 1.1). It is commonly observed that alkyl substituted aromatics are the major components as compared to their parent (non alkyl substituted) hydrocarbons [25-29]. They are proposed to be the product of both the organic facies as well as the processes (diagenesis and catagenesis) through which OM passes during thermal stress [30]. Clay minerals act as a catalyst to enhance the alkylation and decomposition of parent aromatic hydrocarbons during sedimentary processes [31] and abundant alkynaphthalenes has been attributed to ring isomerization and transalkylation processes [19]. On the basis of laboratory heating experiments and examination of geological samples Bastow [30] suggested precursor-product relationship between certain isomers of tri-, tetra- and penta-methyl naphthalenes and reported methylation of naphthalenes and phenanthrenes is a geosynthetic process. The abundance of certain isomers of alkylphenanthrenes in geological samples indicate specific source precursors for these
Fig. 1.1 Possible biological precursors and pathways for the generation of alkynaphthalenes after Strachan et al. [19] and taken from Armstroff et al. ([23] and references therein).
compounds, such as retene and pimanthrene could have formed through aromatization of tricyclic diterpenoids of plant resins [32] or by the dehydrogenation of alkylated dihydrophenanthrenes [33]. Biphenyls have lowest relative abundance compared to other aromatic series. Minor amounts of these compounds and their alkyl analogues have been identified in marine sediments of Cambrian age [13]. Previous study by Alexander et al. [34] refers to biphenyl carbon skeletons such as ellagic acid in natural products as possible precursors of sedimentary biphenyls.

**Thermal maturity applications of PAHs**

The principal application of C\textsubscript{10+} aromatic hydrocarbons has been as maturity indicators for crude oils and sediments extracts [10,25-26,35-38]. The most common approach exploits changes in the relative abundance between isomers of aromatic hydrocarbons with increase in thermal effects. For example methylnaphthalene ratio (MNR) is thermal maturity parameter derived by dividing thermodynamically less stable isomer 1-methylnaphthalene (1-MN) (α-isomer) with thermodynamically more stable isomer 2-methylnaphthalenes (2MN) (β-isomer) [25]. The concept is the shift of α-methyl group to β- position with increase in thermal maturity [26] whereas methyl shift resulted in a decrease in steric strain, hence β- position is thermodynamically more stable. Similar principal has been used to devised number of polycyclic and sulfur aromatic hydrocarbons maturity parameters [4,38 and references therein) shown in Table 1.1.
Table 1.1 Aromatic hydrocarbons thermal maturity parameters

<table>
<thead>
<tr>
<th>Name and abbreviation</th>
<th>Definition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylnaphthalene ratio, MNR</td>
<td>2-MN/1-MN</td>
<td>[26]</td>
</tr>
<tr>
<td>Dimethylnaphthalene ratio-1, DNR-1</td>
<td>(2,6-DMN + 2,5-DMN)/1,5-DMN</td>
<td>[26]</td>
</tr>
<tr>
<td>Trimethylnaphthalene ratio-1, TNR-1</td>
<td>2,3,6-TMN/(1,4,6-TMN + 1,3,5-TMN)</td>
<td>[10]</td>
</tr>
<tr>
<td>Trimethylnaphthalene ratio-2, TNR-2</td>
<td>(1,3,7-TMN + 2,3,6-TMN)/ (1,3,5-TMN + 1,3,6-TMN + 1,4,6-TMN)</td>
<td>[11]</td>
</tr>
<tr>
<td>Trimethylnaphthalene ratio-1, TMNr</td>
<td>1,3,7-TMN/(1,3,7-TMN + 1,2,5-TMN)</td>
<td>[38]</td>
</tr>
<tr>
<td>Tetramethylnaphthalene ratio, TeMNr</td>
<td>1,3,6,7-TeMN/(1,3,6,7-TeMN + 1,2,5,6-TeMN + 1,2,3,5-TeMN)</td>
<td>[38]</td>
</tr>
<tr>
<td>Pentamethylnaphthalene ratio, PMNr</td>
<td>1,2,4,6,7-PMN/(1,2,4,6,7-PMN + 1,2,3,5,6-PMN)</td>
<td>[39]</td>
</tr>
<tr>
<td>Methylphenanthrene index-1, MPI-1</td>
<td>1.5 × (2-MP + 3-MP)/(P + 1-MP + 9-MP)</td>
<td>[25]</td>
</tr>
<tr>
<td>Methylphenanthrene ratio, MPR</td>
<td>2-MP/1-MP</td>
<td>[26]</td>
</tr>
<tr>
<td>Methyldibenzothiophene ratio, MDR</td>
<td>4-MDBT/1-MDBT</td>
<td>[11]</td>
</tr>
<tr>
<td>Methyldibenzothiophene ratio, MDR'</td>
<td>4-MDBT/(4+1)-MDBT</td>
<td>[40]</td>
</tr>
</tbody>
</table>

MN: methylnaphthalene; DMN: dimethylnaphthalene; TMN: trimethylnaphthalenes; TeMN: tetramethylnaphthalene; PMN: pentamethylnaphthalene; MP: methylphenanthrene; MDBT: methyldibenzothiophene;
Biodegradation of PAHs

The effects of biodegradation on PAHs have been reported in different studies [15,41-43]. In reservoir biodegradation of PAHs starts with smaller rings e.g. benzenes are depleted first followed by naphthalenes and then phenanthrenes [15,41,43-44]. Alkylated PAHs show a range of susceptibility difference but generally methyl substituted isomers are degraded in preference to dimethyl and trimethyl isomers of benzene, naphthalene and phenanthrene [15,41,44]. However study by Huang et al. [43] on Chinese biodegraded oils has reported higher susceptibility of trimethylnaphthalenes over dimethylnaphthalenes and methylphenanthrenes over phenanthrene [43]. Demethylation of alkylnaphthalenes and alkylphenanthrenes was purposed as biodegradation process as reason for this reverse susceptibility orders of depletion [43]. Biodegradation susceptibility order of saturated and aromatic hydrocarbons shows that alkylbenzenes alter along with n-alkanes but persist till the depletion of isoprenoids [45]. Minor alteration of methyl and dimethylnaphthalenes are observed during depletion of n-alkanes however trimethylnaphthalenes show depletion along with isoprenoids while tetramethylnaphthalenes are resistant to biodegradation till the substantial removal of steranes [15]. Biodegradation of alkylphenanthrenes indicates that depletion of methylphenanthrenes starts after complete removal of n-alkanes while dimethylphenanthrenes show resistant to biodegradation till steranes are altered [15,43]. A comparison biodegradation sequences between aliphatic and aromatic compound classes is shown in Fig. 1.2.
**Fig. 1.2** Generalized comparison of biodegradation sequence between aliphatic and aromatic hydrocarbons of crude oils [45-46]. For more detail see Peters and Moldowan, [47]; Fisher et al. [15,48], Triolio et al. [49]. Arrows indicate extent of depletion of compound class where first altered (dashed lines), significant depletion (solid grey line) and completely removed (black arrow). Wenger et al. [46] indicates change in oil quality with extends of biodegradation; L: light, M: moderate, H: heavy.
1.3 HETEROCYCLICS AROMATIC HYDROCARBONS AND FLUORENES IN CRUDE OILS AND SEDIMENTS

PAHs in petroleum are abundant with various structural features. Some of them only contain benzene structures like naphthalene and phenanthrenes while some have heteroatoms (S, O, N) within the benzene structures. The heteroatomic aromatic hydrocarbons i.e. heterocyclics such as dibenzothiophenes (DBTs), dibenzofurans (DBFs), carbazoles (Cs), and fluorenes (Fs) are important constituents of sedimentary OM [6,11-12,50-51]. The origin of these compounds in sedimentary OM is under debate for last three decades. Knowledge of specific source precursors and reaction pathways for the formation of these compounds in crude oils and sediments has not been reported. It is interesting to see that all these compounds show similar structural features except heteroatoms (Fig. 1.3). It is noteworthy that biphenyl shows a structural associations with these heterocyclics compounds (Fig. 1.3). Here it may be supposed that these heterocyclics compounds may have same origin and/or source precursors in sedimentary organic matter.

![Structurally related compounds](image)

**Fig. 1.3** Structurally related compounds
The sulfur heterocyclics aromatic hydrocarbons (dibenzothiophene and alkyl dibenzothiophenes, DBTs) have been used to determine the thermal maturity of sediments, coals and crude oils [4,7,37,52-53]. The oxygen heterocyclic aromatic hydrocarbon, DBFs and related compounds are present in significant abundance in terrestrial OM [6] and have also been suggested as oxidative degradation products of coals [54]. Moreover, thermal maturity and lithology of source rocks are shown to control the distribution of dibenzofuran and alkyl dibenzofurans [55]. Pyrrolic nitrogen (N) compounds have shown dependence on organic facies and thermal maturity of OM [50-51]. Although contrasting results have been reported concluded from Canadian oils that carbazoles concentration are not affected by variation in thermal maturity and depositional environments [56]. Moreover, benzocarbazoles are reported as good migration indicators in petroleum reservoirs [57]. A limited geochemical significance of F are only reported for oil correlation studies along with DBT and DBF distributions [12,58] where it is indicated that the distribution of these compounds depends on the depositional environments of source OM while alkylfluorenes are not yet reported in any from of sedimentary OM so far.

The abundance of heterocyclics aromatic hydrocarbons and fluorenes in crude oils and sediments has been shown a relationship with sedimentary depositional environments. For example sulfur heterocyclics (i.e. DBTs) are higher in marine water depositional environments while oxygen heterocyclics (i.e DBFs and Fs) are higher in freshwater depositional environments [12-13]. It is commonly observed that the generation of heterocyclics in sedimentary environments is controlled by oxic/anoxic depositional conditions. These finding could be used to build an idea that the formation of heterocyclics aromatic hydrocarbons may depend on the abundance of heteroatomic species in sedimentary OM. So the incorporation of hetero-elements in to sedimentary OM is important and brief description about the topic is given below.

1.3.1 Incorporation of N, S, O Elements into Sedimentary OM

The incorporation of heteroatoms into the sedimentary OM takes place during the early diagenesis [2]. The N containing biomacromolecules e.g. amino acids interact
and incorporate into OM at early diagenes is. The abundance of N incorporation depends on the biological source of OM i.e. terrestrial plants contribute less N than phytoplanktons. Depositional settings of OM also affect the relative preservation of N for example clay rich contents interacted with biological OM and incorporate more N [59]. At the end of diagenesis, N content of OM do not change substantially up to the formation of petroleum and natural gas [59]. However the structure of N containing molecules varies with increase in thermal maturity of kerogen and coal [60-61]. Immature coals and kerogen show the presence of N in the form of amide/amine groups [61] whereas pyrrole and pyridine N structures are observed during the formation of petroleum [62]. A minor contribution of \( \text{NH}_4^+ \) ion in kerogen is always observed which decreases with increase in thermal maturity; this could be due to the interaction of pyridine and OH groups in the kerogen [60].

Sulfur (S) is the most abundant hetero-element in all types of sedimentary OM found both in soluble and insoluble OM. The sulfate reducing bacteria produces S which is the source of S at the water/sediment interface and results its incorporation at early stage of diagenesis through abiotic reactions [63-64]. The mechanism of S incorporation into the OM depends on the nature of sulfurized functional groups and can be incorporated via intra- and intermolecular reactions [65]. The former process results in the formation of cyclic alkyl sulfides (like thiolanes, thianes and thiophenes; e.g. Brassell et al. [66] while Intermolecular sulfurization leads to the formation of (poly) sulfide linkages between alkyl chains [67-68]. The occurrence of thiophenes in the S-rich kerogen pyrolysates does not necessarily reflect a ubiquitous contribution of thiophenic moieties to kerogen structure. However, such aromatic sulfur compounds may originate, at least partly, from secondary transformation of (poly)sulfide-containing moieties [69]. In fact, heating (poly)sulfide-linked macromolecules results in the rapid formation of thiophenic compounds [70-72]. Secondary thermal reactions of (poly)sulfide-bound linear carbon skeletons were observed upon kerogen pyrolysis [73]. These findings reflect the importance of incorporated S in kerogen for the formation of sulfur compounds.
During early diagenesis, oxidation of OM is the major cause of decrease in TOC and enrichment of residual OM in oxygen. Thus, oxidation is the partial degradation of immature OM and increase in oxygen/carbon (O/C) ratio in the kerogen. Riboulleau et al. [74] studied the kerogen pyrolysates from Kashpir oil shale (Russia) high abundance of oxygen functional groups (C=O) on different carbons of alkyl chains was observed. These results showed the O insertion at C=C in the kerogen after diagenetic isomerization and random migrations. However in contrast to S incorporation, O incorporation may occur at any stage of kerogen evolution [59].

1.3.2 Sulfur (S) Compounds from Laboratory Simulations

Examples of laboratory experiments of heteroatom species other than S with hydrocarbons are scarce however there are many examples of laboratory chemical reactions between S species and different biological compounds are reported. Common sedimentary hydrocarbon precursors such as terpenes, steroids, alkylated aromatic hydrocarbons, amino acids and humic acids has been used in these simulation experiments [75-76]. S reactions with unsaturated isoprenoids followed by cyclization and aromatization were reported for the formation of benzothiophenes [65,77]. Furthermore, the formation of dialkylated dibenzothiophenes was reported and related to sulphurized triterpenoids source precursors [78]. Direct insertion of a heterosulfur bridge into biaryls and angulary condensed arenes has been reported using hydrogen sulfide and a heterogeneous catalysis [79]. The temperature (450-630 °C) involved in these reactions is considerably higher than sedimentary temperatures. Insertion of S in aromatic hydrocarbons at mild temperatures has been reported using elemental S/pyrite with and without additives as catalyst [80]. This study was related to obtaining information about the early stage of the coalification processes when elemental S is present.

These findings show that there are such examples where heteroatoms species chemically react with sedimentary molecules with and without catalyst. A new approach is established where activated carbon has been successfully used as catalyst to evidenced different sedimentary reactions [81]. A brief introduction for carbon catalysis and
structure comparison between different form of sedimentary OM (kerogen and coal) with activated carbon is given in following section.

1.4 CARBON CATALYSIS

Activated carbons have long been used as a catalysts and catalyst support [82-84]. Carbon catalyst concept extends to study the formation of different sedimentary hydrocarbons where it is supposed that carbonaceous material (kerogen and coal) provide a catalyst support. Evidence that the solid–state carbonaceous material promotes chemical reactions in sediments has been suggested from data obtained from hydrogen exchange reactions between hydrocarbons [81,85]. In these studies, it has been shown that carbon surface adsorbed species reacted with provided compounds to produce structurally related compounds. Following section describe a structure comparison of different form of carbonaceous material i.e. kerogen, coal and activated carbon. This comparison provides an overview that the structure and nature of surface adsorbed species in different forms of carbonaceous material is broadly same.

1.4.1 Kerogen

Forsman [86] recognized two types of kerogen on the basis of functional groups and degradative studies. First, coaly kerogen which contains macromolecules consisting of condensed aromatic rings interconnected by ether, alkoxy and S bridges which attached the aromatic nuclei with hydroxyl, methoxyl groups. Second, non-coaly type kerogen showed nearly open chain structure with cycloparaffine or aromatic rings attached through O, N and S atoms. Later substantional work has been performed on kerogens structure particularly on Green Rive Shale [87-89]. Kerogen structure purposed by Siskin et al. [90] was balanced in all aspects of functional group analysis of the whole kerogen and heteroatoms (N, S, O) distribution. Behar and Vandernbroucke [91] reported a detailed structure evolution with change in diagenesis and catagenesis of the kerogen type II. Chemical structure of kerogen at the beginning of diagenesis showed higher aliphatic structures with higher hydrogen/carbon (H/C) ratio 1.34 while start of catagenesis introduced aromatic moieties which further increased the aromatic clusters at
the end of catagenesis (H/C ratio 0.73). These kerogen structures contain different macromolecular composition depend on rank/stage of diagenesis and catagenesis.

1.4.2 Coal

Significant work has been done on the coal structure models (for review see, van Krevelen, [92]) and mostly focused on the quantitative distribution of functional groups and carbon-carbon bond types. Coal structure at different coalification ranks has been assumed to differ only in functional groups content and bond types [93]. The coal structure showed similar type of saturated and aromatic macromolecules as that of the kerogen [94]. Generally, as move from peat to bituminous to anthracite indicated different coalification stages, the aromatic moieties of coal structure increases. Although the elemental compositions (C, H) changed in same pattern as was reported in case of kerogen but oxygen is exclusive part of bituminous coals [95].

1.4.3 Activated Carbon

Activated carbons structure has been proposed similar to the structure of coal [96] and successful conversion of coal to active carbon has been reported by different studies [97-98]. Boehm [99] studied the structure of active carbon and devised acidic and basic surfaces groups. Different oxygen containing functional groups were reported such as, carboxyl, carbonyl, carboxylic, phenolic, lactoles, ether and quinone. N adsorption on active carbon has been devised by treatment with different nitrogen substances such as NH₃, HCN and reported the formation of nitrogen species such as amide, imide, lactam, pyrroles and pyridines [100]. The carbon-sulfur surface compounds have been reported on a wide variety of charcoals, activated carbons, carbon blacks, and coals. In the case of activated carbons, they are generally formed by heating the carbon in the presence of elementary sulfur [101] or sulfurous gases such as CS₂ [102], H₂S [103] and SO₂ [104].

1.5 SCOPE AND FRAMEWORK OF THE THESIS

Previous studies have described oil correlations from Pakistani crude oils and sediments from Upper Indus (Kohat-Potwar) Basin however these studies have focused on basic geochemical analysis such as total organic carbon (TOC) and Rock Eval
analysis. Very little information is available on biomarkers and virtually no information is available on aromatic hydrocarbons present in Pakistani crude oils and sediments so far. This thesis broadly contained three objectives; first, classification of Potwar Basin oils using aliphatic and PAHs distributions along with stable carbon and hydrogen isotope compositions of saturated and aromatic fractions; Second, assessment of minor biodegradation using PAHs distributions and stable hydrogen isotopes compositions of $n$-alkanes and isoprenoids from selective Potwar Basin crude oils and third, geosynthesis of heterocyclic aromatic hydrocarbons and fluorenes by carbon catalysis laboratory simulation experiments. Distribution of heterocyclics and fluorenes is determined in sediments and crude oils from Kohat Basin, Pakistan. Moreover, carbon catalysis geosynthesis is supported by adding distribution of heterocyclics and fluorenes from Carnarvon Basin, Australian crude oils.

The main objectives of any organic geochemical study are to establish i.e. source of OM, thermal maturity, depositional settings and lithology of OM and affects of biodegradation on hydrocarbons. In chapter 5 saturated and aromatic hydrocarbon parameters used to establish oil-oil correlation study in a suite of 18 crude oils. Bulk stable carbon and hydrogen isotopic compositions of saturated and aromatic hydrocarbon fraction were used to delineate the oil groupings of Potwar Basin. The study gave an insight to petroleum geochemistry of the area which is first ever of its kind.

In chapter 6 affects of minor biodegradation on alkynaphthalenes and alkylphenanthrenes, stable hydrogen isotopic composition of $n$-alkanes and pristane and phytane were reported. It shows that susceptibility to biodegradation of alkynaphthalenes and alkylphenanthrenes varies with the extent of biodegradation. Compound specific isotope analysis of $n$-alkanes and isoprenoids revealed that microbes preferentially consumed isotopically lighter $n$-alkanes and residual compounds become enriched in D of $n$-alkanes while isoprenoids D values are not affected at minor biodegradation.

In chapter 7, it is shown that activated carbon plays a key role in the geosynthesis of heterocyclics aromatic hydrocarbons in subsurface environments. Different heteroatomic species show adsorption on carbon surface at moderate heating
temperatures. These heteroatom adsorbed species reacted with biphenyl and methylbiphenyls to produce heterocyclics aromatic hydrocarbons i.e. dibenzothiophene (DBT), dibenzofuran (DBF), carbazole (C) and fluorene (F) and their methyl homologous. Natural sedimentary OM has been shown a structure association between biphenyls and these heterocyclics aromatic hydrocarbons. Abundance of these compounds are used to show the product precursor relationship between biphenyls and these compounds in sediments and crude oils from Kohat Basin, Pakistan and Carnarvon Basin, Australia. The evidences of various carbon surface species are reported to devise the reaction intermediate and pathways for geosynthesis of these compounds.
Chapter - 2

GEOLOGICAL SETTINGS AND DESCRIPTION OF SAMPLES

2.1 GEOLOGY OF KOHAT-POTWAR GEOLOGICAL PROVINCE

The Kohat-Potwar Basin also called Upper Indus Basin is situated in northern Pakistan and located between lat. 32° and 34° N and, long. 70° and 74° E (Fig. 2.1). It is an onshore basin bounded on the North by Parachinar-Muree fault, on the West by Kurram fault, on the South by Surghar and Salt Ranges and on the East by Jehlum fault. The Kohat-Potwar Basin is a portion of Indian plate deformed by Indian and Eurasian plate collision and overthrust of Himalayas on the north and northeast [105]. The detailed petroleum geology of the area has been described by different authors [106-108].

The geological division between Kohat and Potwar is done naturally by river Indus, the East and West of river represent the Potwar and Kohat Basins respectively (Fig. 2.1). The geological structure of the Potwar Basin is one of the most complex structures of the world which is the result of the Tertiary Himalayan collision between Eurasian and Indian plates [105]. This intense tectonic activity has affected Eastern Potwar the most compared to Western Potwar. The eastern Potwar contains carbonate reservoir rock of Cambrian to Tertiary ages. The basin infilled started with thick Infra-Cambrian evaporate deposits overlain by relatively thin Cambrian to Eocene age platform deposits followed by thick Miocene-Pliocene molasses deposits. The Infra-Cambrian salt provided an easy detachment of Eocene-to-Cambrian (E-C) sequence as a result of intense tectonic activity during Himalayan Orogeny during Pliocene to middle Pleistocene time. This thinner E-C sequence in eastern Potwar affected by compressional forces has generated large number of fold and faults. The E-C layer varies from a few meters to 400 m in the eastern Potwar [109]. The crude oils discovered from this area showed a range of reservoir formations (section 2.2).
Fig. 2.1 Geographical and Location map of Kohat-Potwar Basin oils (modified from [106, 108, 110-111]).
The Kohat Basin is tectonically complex area of northern Pakistan and is a tilted plateau where moderate-steeper dips and asymmetrical structures resulted in a large number of thrusts/normal faults [112]. Eocene through Pliocene are involved in a complex fold and thrust belt in which Eocene salt occupies the cores of many of the anticlines. Upper Eocene is more deformed than Lower Eocene where this area deformation resulted in duplex structures in Kohat formation of Eocene [112]. Kohat Basin showed absence and/or very thin deposition in Cretaceous times due to erosion and emergence out of the area from sea. This emergence was higher in south and east of the Basin evidenced by less deposition in cretaceous sections [112]. Although, the geological information of Kohat Basin is scarce but unconformities and sharp variation in deposition made this area is very unpredictable (see [112]).

2.1.1 Depositional Settings of the Kohat-Potwar Basin

Depositional record of the Kohat-Potwar geological province is given in Fig 2.2. Sedimentation in the Kohat-Potwar area began in the Precambrian and lasted until the Pleistocene. Three major unconformities in the area are Ordovician to Carboniferous, Mesozoic to late Permian and Eocene to Oligocene. The basin infilled started with thick infra-Cambrian evaporates with carbonates and oil-impregnated shales represented by Salt Range Formation which is overlain metamorphic rocks reported as the oldest sedimentary rocks in the Kohat-Potwar Basin [106]. The salt lies unconformably on the Precambrian basement above the Salt Range, massive sandstone and marine shales of Lower Cambrian Jhelum Group, Khewra Formation are deposited. Cambrian rocks comprised sandstone, siltstone, shale and dolomite represented by Kussak, Jutana, and Baghanwala Formations (Fig. 2.2). This whole sequence is marine in origin and terminated by a major unconformity [106].

Permian Nilawahan Group (Fig. 2.2) consists of sandstone, clay, marl and fossiliferous limestone overlie the Cambrian rocks after an unconformity. The lower Permian Tobra and Dandot Formations are comprised of glacial tillits and coarse-grained sandstones with shales. Some fluvial sandstone with occasional shale and coal seams were deposited within the marine sequence of Warcha and Sardhai Formations [106].
Fig. 2.2  Stratigraphy of Kohat-Potwar Basin, Pakistan and location of crude oils and sediments used in this study (Modified from [108] and references therein). Refer to Tables 2.1 and 2.3 for the identity of crude oils (P1-P22) and sediments (S1-S14) respectively.
The Permian rocks are generally preserved in the Potwar Basin but this section is missing in the Kohat Basin [113] (Fig. 2.2). The Musa Khel Group from Triassic strata represented by Mianwali, Tredian Formations contains limestone, dolomite, coarse- to fine-grained sandstone and shale. The origin of Triassic sediments is mainly shallow marine while freshwater sandstone was also reported in Tredian Formation [106].

The Jurassic and Triassic times of deposition are absent or very thin in Kohat and Potwar Basin. The Jurassic Shinawri Formation consists of marine shales, with occasional sandstones and thin bedded limestones and contains frequent fluctuations of the shelf and terrigenous material which is decreased at the top. The depositional environment of Datta Formation is versatile and represents nearshore, swamp, bay, mud flat and delta front [107]. Upper Jurassic is represented by the interbedded shales and thick limestone as much as 1400 m of middle and upper Jurassic Sulaiman limestone group (Fig. 2.2). The Shinawari overlaying Samana Suk Formation contained thick carbonates. During early Cretaceous times, the Indian plate entered into warmer latitudes, marine shale and limestones were deposited over regional erosional surface on the Sulaiman group. This erosional surface is present at the top of the Samana Suk Formation and is overlain by sandstone and shales of lower Cretaceous Chichali Formation. The Cretaceous sequence mainly contained shale and sandstone of Chichali and Lumshiwal Formations with marl and limestone in some of the areas (Fig. 2.2). The shale layers of Chichali Formation indicate reducing environments for sedimentation. The Lumshiwal Formation composed of siltstone and shelly limestone represent marine environment [107]. The Sembar and Goru Formations from Cretaceous strata are present in Kohat Basin while are not deposited in the Potwar Basin (Fig. 2.2).

Paleocene-Eocene depositions represented by Makarwal Group (Fig. 2.2) are composed of shallow marine foraminiferal limestone and grey fossiliferous shale [106]. In early Paleocene, beginning with sedimentation of Hangu sandstone is coastal setting with greater marine influence followed by Lockhart limestone depositions in shallow water environments and that of Patala Formation in shallow marine to deltaic environment [107]. Eocene Nammal and Panoba Formations show transitional contact with Patala Formation which is deposited in shallow marine to lagoonal shales with
limestone. The overlaying Chorgali and Sakaser Formations consist of marine carbonates and shale facies in the Potwar Basin area while evaporite facies consist of anhydrite, gypsum with minor oil shales in the Kohat Basin. The Upper Eocene, Kohat Formation comprised of shales with carbonate of the Oligocene Kirthar Formation. Oligocene was deposited only in Kohat Basin and small area of northern Potwar while missing in most of the Potwar Basin. The collision of Indian and Eurasian plates made regional uplift and transport direction of south to north sediments on the Indian plate was reversed. A carbonate platform was buildup as a result of large volumes of sediments shed by Eurasian plate from Eocene through Miocene [108].

2.2 DESCRIPTION OF CRUDE OILS AND SEDIMENTS

A total of 23 crude oils and 14 sediments were analyzed, Tables 2.1 and 2.2 show geological and geochemical informations. The sediments mainly consist of well cuttings obtained from Oil and Gas Development Corporation Limited, Pakistan (OGDCL). Australian crude oils obtained from Carnarvon Basin were also studied in order to compare the distribution of aromatic hydrocarbons with Pakistani oils and sediments (Table 2.1). These crude oils from Carnarvon Basin have been reported previously and indicate typical non-biodegraded mature hydrocarbon profile [114]. Following sections describe geological information of crude oils and sediments from Pakistan.

2.2.1 Potwar Basin

Potwar Basin is one of the oldest area explored for petroleum in the world while first commercial oil discovery was made in 1914 which was the first of South Asian sub-Continent [106]. Since then Potwar is the main source of hydrocarbons and about 25 wells of crude oils and condensates are explored in the Potwar Basin [115]. Petroleum reservoirs containing significant amount of hydrocarbons in range of medium to high density oils (Table 2.1) have been found in the small area of the Potwar Basin and causes of the vast diversity in physical characteristics of crude oils are unknown so far. 18 Crude oils of different API gravity from very light to heavy (16-48°) and reservoired in various geological formations were selected from the basin (Table 2.1).
Table 2.1 Geological information of crude oils

<table>
<thead>
<tr>
<th>No</th>
<th>Samples</th>
<th>Reservoir</th>
<th>API Gravity (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Name</td>
<td>Depth (m)</td>
<td>Age</td>
</tr>
<tr>
<td>Potwar Basin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>Adhi-5</td>
<td>2680</td>
<td>Cambrian</td>
</tr>
<tr>
<td>P2</td>
<td>Missakeswal-1</td>
<td>2187</td>
<td>Eocene</td>
</tr>
<tr>
<td>P3</td>
<td>Missakeswal-3</td>
<td>2063</td>
<td>Cambrian</td>
</tr>
<tr>
<td>P4</td>
<td>Rajian-1</td>
<td>-</td>
<td>Cambrian</td>
</tr>
<tr>
<td>P5</td>
<td>Rajian-3A</td>
<td>3645</td>
<td>Cambrian</td>
</tr>
<tr>
<td>P6</td>
<td>Kal-1</td>
<td>2773</td>
<td>Cambrian</td>
</tr>
<tr>
<td>P7</td>
<td>Kal-2</td>
<td>2694</td>
<td>Cambrian</td>
</tr>
<tr>
<td>P8</td>
<td>Fimkassar-1</td>
<td>3063</td>
<td>Cambrian</td>
</tr>
<tr>
<td>P9</td>
<td>Fimkassar-4</td>
<td>3318</td>
<td>Cambrian</td>
</tr>
<tr>
<td>P10</td>
<td>Chaknaurang-1A</td>
<td>2687</td>
<td>Cambrian</td>
</tr>
<tr>
<td>P11</td>
<td>Minwal-1</td>
<td>2179</td>
<td>Eocene</td>
</tr>
<tr>
<td>P12</td>
<td>Joyamir-4</td>
<td>2103</td>
<td>Eocene</td>
</tr>
<tr>
<td>P13</td>
<td>Turkwal-1</td>
<td>3612</td>
<td>Eocene</td>
</tr>
<tr>
<td>P14</td>
<td>Pindori-4</td>
<td>-</td>
<td>Eocene</td>
</tr>
<tr>
<td>P15</td>
<td>Dhurnal-1</td>
<td>4096</td>
<td>Eocene</td>
</tr>
<tr>
<td>P16</td>
<td>Dhurnal-6</td>
<td>4174</td>
<td>Eocene</td>
</tr>
<tr>
<td>P17</td>
<td>Toot-10A</td>
<td>4485</td>
<td>Jurassic</td>
</tr>
<tr>
<td>P18</td>
<td>Toot-12</td>
<td>4450</td>
<td>Jurassic</td>
</tr>
<tr>
<td>Kohat Basin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P19</td>
<td>Chanda-1</td>
<td>4750</td>
<td>Jurassic</td>
</tr>
<tr>
<td>P20</td>
<td>Chanda -2</td>
<td>4990</td>
<td>Triassic</td>
</tr>
<tr>
<td>P21</td>
<td>Mela-1</td>
<td>4960</td>
<td>Jurassic</td>
</tr>
<tr>
<td>Carnarvon Basin, Australia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P22</td>
<td>Wanaea</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P23</td>
<td>Griffin</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: Oil samples were collected from following oil companies of Pakistan.
OGDCL, Islamabad, Pakistan
POL, Pakistan
OXY, Pakistan
PPL, Islamabad
Table 2.2  Geological settings and Rock Eval data of sediments from well Mela-1\textsuperscript{a}

<table>
<thead>
<tr>
<th>No</th>
<th>Depth range (m)</th>
<th>Lithology</th>
<th>Age</th>
<th>Geological Formation</th>
<th>TOC average (%)</th>
<th>S\textsubscript{1} (mg/g)</th>
<th>S\textsubscript{2} (mg/g)</th>
<th>HI (mg/g)</th>
<th>Tmax (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>4290-95</td>
<td>Marl</td>
<td>Paleocene</td>
<td>Patala</td>
<td>1.0</td>
<td>4.75</td>
<td>3.01</td>
<td>295</td>
<td>427</td>
</tr>
<tr>
<td>S2</td>
<td>4310-15</td>
<td>Marl</td>
<td>Paleocene</td>
<td>Patala</td>
<td>0.7</td>
<td>3.19</td>
<td>2.29</td>
<td>347</td>
<td>431</td>
</tr>
<tr>
<td>S3</td>
<td>4345-70</td>
<td>Limestone, Shale</td>
<td>Paleocene</td>
<td>Patala</td>
<td>1.1</td>
<td>2.35</td>
<td>2.01</td>
<td>182</td>
<td>431</td>
</tr>
<tr>
<td>S4</td>
<td>4410-40</td>
<td>Limestone</td>
<td>Paleocene</td>
<td>Lockhart</td>
<td>1.0</td>
<td>0.49</td>
<td>0.45</td>
<td>55.5</td>
<td>442</td>
</tr>
<tr>
<td>S5</td>
<td>4510-12</td>
<td>Limestone</td>
<td>Paleocene</td>
<td>Lockhart</td>
<td>0.8</td>
<td>3.77</td>
<td>1.90</td>
<td>241</td>
<td>433</td>
</tr>
<tr>
<td>S6</td>
<td>4534-60</td>
<td>Limestone</td>
<td>Paleocene</td>
<td>Lockhart</td>
<td>0.8</td>
<td>1.00</td>
<td>0.75</td>
<td>71</td>
<td>431</td>
</tr>
<tr>
<td>S7</td>
<td>4650-52</td>
<td>Sandstone</td>
<td>Paleocene</td>
<td>Lockhart</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S8</td>
<td>4680-82</td>
<td>Sandstone</td>
<td>Paleocene</td>
<td>Hangu</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S9</td>
<td>4690-92</td>
<td>Shale, siltstone</td>
<td>Paleocene</td>
<td>Hangu</td>
<td>2.3</td>
<td>7.78</td>
<td>5.78</td>
<td>257</td>
<td>-</td>
</tr>
<tr>
<td>S10</td>
<td>4710-12</td>
<td>Shale, siltstone</td>
<td>Cretaceous</td>
<td>Lumshiwal</td>
<td>1.4</td>
<td>4.24</td>
<td>3.38</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td>S11</td>
<td>4741-42</td>
<td>Shale</td>
<td>Cretaceous</td>
<td>Chichali</td>
<td>1.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S12</td>
<td>4834-50</td>
<td>Shale</td>
<td>Jurassic</td>
<td>Shinawri</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S13</td>
<td>4860-62</td>
<td>Shale, clayston</td>
<td>Jurassic</td>
<td>Shinawri</td>
<td>3.4</td>
<td>2.71</td>
<td>2.78</td>
<td>82</td>
<td>-</td>
</tr>
<tr>
<td>S14</td>
<td>4940-42</td>
<td>Claystone</td>
<td>Jurassic</td>
<td>Datta</td>
<td>0.6</td>
<td>0.61</td>
<td>0.33</td>
<td>55</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: OGDCL, Islamabad, Pakistan
The locations of crude oils are shown in Fig. 2.1 and marked on stratigraphic chart in Fig. 2.2. The source origin of these crude oils is not fully correlated with any specific source rock of the area. Few studies using geochemical properties from cuttings, outcrops and core samples from different geological formations were undertaken and correlated partially with Potwar crude oils [116-117].

The oldest producing reservoir in the Potwar Basin is Precambrian Salt Range Formation. It consists of thick carbonates overlain by evaporates. Marine shales and massive sandstones of lower Cambrian, Khewra Formation have reservoir potential. Khewra Formation has produced Adhi-5, Chaknaurang-1A, Kal-1, Kal-2, Fimkassar-1 and Fimkassar-4 oils used in this study. The overlying Jutana Formation primarily consists of sandy carbonates and nearshore sandstones has reservoired Rajian-1, Rajian-3A and Missakeswal-3 oil fields. The Permian, Tobra Formation composed of glacial tillites, siltstone, and shales, and Fimkassar oil field is produced Khewra/Tobra Formation. The Jurassic Datta Formation has produced oils from Toot-10A and Toot-12 fields. Shallow marine carbonate strata of the Eocene Chorgali and Sakaser Formations form an important hydrocarbon producing horizon in the northern Potwar Basin. Chorgali and Sakaser Formation consist of medium-bedded limestones and fine crystalline dolomites. Both Formations are oil and gas producing reservoirs, Dhurnal-1, Dhurnal-6, joyamir-4, Turkwal-1, Pindori-1, Minwal-1 and Missakeswal-1 are producing from Chorgali and Sakersar Formations.

2.2.2 Kohat Basin

Currently, the most active area for exploration in Upper Indus Basin is Kohat Basin. In early nineties a number of wells were abandoned (e.g. Tolanj-1, Kahi-1 and Sumari-1; for details see Paracha, [112]). But later on, discoveries of oil and gas (Chanda, Mela, Makori and Manzalai) have increased the interest of exploration geoscientist in the area. The details of crude oils used from the Kohat Basin are shown in Table 2.2. The sandstones of Datta formation produced Chanda-1 and Mela-1 are mainly continental in origin, with fine to coarse grained and very high porosity characteristics. While Kingriali formation is predominantly composed of dolomites with minor limestone. The crude oils
show a similar range of API gravities (Table 2.2) and the source rock origin of Kohat Basin oils and gas is not yet reported.

### 2.2.3 Geochemical Description of Sediments

Fourteen sediments cuttings were selected from the Mela-1 well of the Kohat Basin. The location of well is marked in Fig. 2.1 and samples locations marked on the stratigraphic section in Fig. 2.2. The geological information along with Rock-Eval data is shown in Table 2.2. Patala Formation contains total organic carbon (TOC) in fair range (0.7-1.1%), S₁ & S₂ show very good potential in terms of generated hydrocarbons and poor for residual hydrocarbons. Tₘₐₓ, 427-431 °C reveals that sediments are at the onset of hydrocarbon generation, most likely both liquid and gaseous hydrocarbons as supported by hydrogen index (HI) in the range of 182 to 347 mg/g TOC and suggest both type II and type III as main components of OM. Lockhart Formation sediments contain poor to fair amount of TOC, the genetic potential of the Formation is poor except one sample (4510-12 m) where S₁ shows good genetic potential. HI 241 mg/g TOC indicates both oil and gas prone OM (Type-II/III kerogen). Anonymous reports showed recent discoveries of oils and gas condensate in Hangu formation in the area (news). Hangu Formation sample (6490-92 m) shows organic rich sediments (TOC: 2.3 %), S₁ and S₂ values (7.78 and 5.78 mg/g TOC) suggest very good potential in terms of both generated and residual hydrocarbons. HI 257 mg/g TOC indicates OM derived from type II and type-III kerogen. Lumshiwal Formation also contains good amount of TOC, S₁ and S₂ show fair and good potential in terms of generated and residual hydrocarbons. Chichali Formation data is not available while Rock Eval data of single sample of Shinawari Formation shows very good TOC with fair genetic and residual potential but low values of HI (82 mg/g TOC) are consistent with type III/IV kerogen. Datta Formation shows poor TOC and low values for both S₁ and S₂ also indicate very lean potential for hydrocarbons which is further supported by low HI (55 mg/g TOC) and indicate type III kerogen.
Thermal maturity of sediments

$T_{\text{max}}$ data for most of the sediments was not available therefore aliphatic biomarkers parameters were used to assess thermal maturity of sediments from the Kohat Basin. The parameters were calculated from branched/cyclic fractions of sediments extracts and reported in Table 2.3. The $C_{32}$ 22S/(22S+22R) hopane ratio (0.41-0.44) show immature range of thermal maturity for all sediments except single sample (4834-50 m) which indicates marginal thermal maturity. The $T_s/(T_s+T_m)$ ratios (0.42-0.67) are a consistent with marginal range of maturity. The sterane thermal maturity parameters $C_{29}$ $\beta\beta/(\alpha\alpha+\beta\beta)$ and $C_{29}$ 20S/(20S+20R) ratios in the range of 0.58 to 0.61 and 0.43 to 0.48 respectively indicate a immature nature of OM for Patala Formation sediments. In case of Lockhart Formation sediments, sterane maturity parameters show variation in thermal maturity where $C_{29}$ 20S/(20S+20R) ratios (0.50-52) indicate mature range while $C_{29}$ $\beta\beta/(\alpha\alpha+\beta\beta)$ ratio (0.51-59) indicate marginal range of thermal maturity of these sediments. The $C_{32}$ 22S/(22S+22R) ratios (0.42-0.50, Table 2.3) and $C_{29}$ $\beta\beta/(\alpha\alpha+\beta\beta)$ ratios (0.52-0.58) of Hangu, Lumshiwal, Chichali and Shinawri Formations sediments revealed immature thermal maturity while $C_{29}$ 20S/(20S+20R) ratio (0.42-53) indicate immature to onset oil generation thermal maturity. The thermal maturity parameters from steranes and hopanes (Table 2.3) indicate contrasting results where hopanes show immature thermal maturity while steranes show marginal to mature thermal maturity of Kohat Basin sediments.
Table 2.3 Aliphatic biomarker maturity parameters of Mela-1 well sediments

<table>
<thead>
<tr>
<th>No</th>
<th>Sample depth (m)</th>
<th>S/S+R C32-Hop.</th>
<th>T_5/ (T_s+T_m)</th>
<th>S/S+R C29-Ster</th>
<th>ββ/ββ+αα, C29-Ster.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>4290-95</td>
<td>0.42</td>
<td>0.50</td>
<td>0.43</td>
<td>0.58</td>
</tr>
<tr>
<td>S2</td>
<td>4310-15</td>
<td>0.42</td>
<td>0.67</td>
<td>0.48</td>
<td>0.61</td>
</tr>
<tr>
<td>S3</td>
<td>4345-70</td>
<td>0.43</td>
<td>0.42</td>
<td>0.43</td>
<td>0.61</td>
</tr>
<tr>
<td>S4</td>
<td>4410-40</td>
<td>0.42</td>
<td>0.58</td>
<td>0.52</td>
<td>0.59</td>
</tr>
<tr>
<td>S5</td>
<td>4510-12</td>
<td>0.41</td>
<td>0.60</td>
<td>0.50</td>
<td>0.51</td>
</tr>
<tr>
<td>S6</td>
<td>4534-60</td>
<td>0.44</td>
<td>0.56</td>
<td>0.52</td>
<td>0.55</td>
</tr>
<tr>
<td>S7</td>
<td>4650-52</td>
<td>0.43</td>
<td>0.62</td>
<td>0.52</td>
<td>0.56</td>
</tr>
<tr>
<td>S8</td>
<td>4680-82</td>
<td>0.42</td>
<td>0.61</td>
<td>0.42</td>
<td>0.58</td>
</tr>
<tr>
<td>S9</td>
<td>4690-92</td>
<td>0.43</td>
<td>0.44</td>
<td>0.53</td>
<td>0.54</td>
</tr>
<tr>
<td>S10</td>
<td>4710-12</td>
<td>0.44</td>
<td>0.46</td>
<td>0.49</td>
<td>0.52</td>
</tr>
<tr>
<td>S11</td>
<td>4741-42</td>
<td>0.43</td>
<td>0.49</td>
<td>0.49</td>
<td>0.52</td>
</tr>
<tr>
<td>S12</td>
<td>4834-50</td>
<td>0.50</td>
<td>0.59</td>
<td>0.42</td>
<td>0.55</td>
</tr>
<tr>
<td>S13</td>
<td>4860-62</td>
<td>0.44</td>
<td>0.49</td>
<td>0.52</td>
<td>0.55</td>
</tr>
<tr>
<td>S14</td>
<td>4940-42</td>
<td>0.43</td>
<td>0.45</td>
<td>0.44</td>
<td>0.45</td>
</tr>
</tbody>
</table>
EXPERIMENTAL

The experimental work excluding GC-MS analysis and stable carbon and hydrogen isotope analysis reported in this thesis was performed at chemistry department, UET, Lahore. The GC-MS analysis and stable carbon and hydrogen analysis was performed in geochemistry and isotope labs in Australia. However, the work was repeated in order to keep consistencies in the data.

3.1 MATERIALS AND REAGENTS

Solvents

\[ \text{n-Pentane, n-hexane, cyclohexane, methanol, dichloromethane (Mallinkckrocdt, USA)} \]

were used without further purifications. The purity of these solvent were checked by evaporating 10 mL of each solvent to 500 µL followed by analysis of the residue by gas chromatograph-mass spectrometer.

Drying and neutralizing agents

Anhydrous magnesium sulphate (AR grade, Unilab) was pre-rinsed with solvent before use as a drying agent. For use as a neutralizing agent, sodium bicarbonate (AR grade, chemsupply) was dissolved in milli-Q water until saturated solution obtained.

Silica gel

Silica gel 60 (0.063-0.200 mm, Merck) for column chromatography was activated at 160 °C for at least 24 hrs and pre-rinsed with solvent (n-pentane or n-hexane) prior to use.

Molecular sieves

Molecular sieves Type 5A (Merck) were activated at 240 °C for at least 24 hrs prior to every use.
**Copper (precipitated)**

Precipitated copper powder and/or turnings (5 g, DBH chemicals) were activated by rinsing with 3M HCl (5 mL), and then sequential rinsing with milli-Q water till neutral pH, methanol (5 mL), dichloromethane (5 mL) and n-hexane (5 mL), respectively.

**Hydrofluoric acid and hydrochloric acid**

Hydrofluoric acid (50 % w/v, Merck) was used for digestion of molecular sieves. Hydrochloric acid (specific gravity, 1.18, Merck) was used for activation of copper turnings.

### 3.2 GEOCHEMICAL TECHNIQUES

#### 3.2.1 Sample Preparation

**Sediments**

The samples (well cuttings) were washed with water and air dried prior to grinding. The samples were ground to particle size of about 150 µm or less using a ring-mill (Rocklabs).

**Extraction of soluble organic matter (SOM) from sediments**

The extraction of SOM was performed in a Soxhlet apparatus. Prior to each run the apparatus, thimble, cotton wool, activated copper turnings and anti-bumping granules were extracted with mixture of solvents (9:1 v/v dichloromethane : methanol) for at least overnight. The grounded sediment was weighed into a thimble, covered by cotton wool and extracted using mixture of dichloromethane and methanol (9:1, 200 mL). Fresh solvent mixture was introduced as required. The extraction was allowed to proceed for at least 72 hrs for each sample or until the solvent became colorless. The solvent was removed by a rotary evaporator to obtain SOM.
3.2.2 Liquid Chromatography of Crude Oils and SOM

*Preparation of SOM sample*

The soluble organic matter (up to 70 mg) was dissolved in minimum amount of dichloromethane. The activated silica (up to 1.5 gm) was taken in clean vial (10 mL). The SOM solution was carefully adsorbed on activated silica. The dichloromethane was evaporated by heating vial on sand bath at 50 °C. The dried silica adsorbed SOM was fractionated using column chromatography.

*Small scale column chromatography*

In a typical small scale separation, the SOM adsorbed silica gel sample (maximum up to 20 mg SOM) or crude oil (10 mg) was applied on the top of the column (5.5 × 0.5 cm i.d. pasture pipette) of activated silica gel (pre-rinsed with *n*-pentane). The aliphatic hydrocarbons (saturates) were eluted with *n*-pentane (2 mL); the aromatics with a mixture of *n*-pentane and dichloromethane (2 mL, 7:3, respectively); and polar fraction with a mixture of dichloromethane and methanol (2 mL, 1:1).

*Large scale column chromatography*

Soluble organic matter (up to 70 mg, adsorbed on activated silica) and crude oil (50 mg) were separated by large open column chromatography with following details: A glass column (40 × 0.9 cm i.d.) with cotton wool at bottom was washed with dichloromethane prior to use. Activated silica gel (10 g) was packed as slurry in *n*-hexane. The SOM adsorbed silica or crude oil was introduced on the top of the packed column. The aliphatic hydrocarbons (saturates) fraction was eluted with *n*-hexane (35 mL); the aromatic fraction with a mixture of *n*-hexane : dichloromethane (35 mL, 7:3, respectively) and aromatic/polar (fraction-3) with dichloromethane and polar fraction with methanol (35 mL). Each fraction was recovered by removal of solvent on a sand bath by maintaining temperature up to maximum 60 °C.
3.2.3 Isolation of Branched and Cyclic Alkanes

A saturated fraction obtained by liquid chromatography separation was used to isolate branched and cyclic alkanes from straight chain alkanes. The saturated fraction (up to 15 mg) in cyclohexane (1-2 mL) was added in to a 2 mL autosampler vial quarter filled (2 g) with activated 5A molecular sieves. The autosampler vial was capped and placed into pre-heated aluminum block (85 °C) for at least 8 hrs. The resulting mixture was filtered through a small column of silica (5.5 × 0.5 i.d.) and rinsed thoroughly with cyclohexane. The cyclohexane containing branched/cyclic alkanes was collected in pre-weighed vial. The removal of excess cyclohexane under a slow stream of nitrogen yielded branched and cyclic fraction.

Recovery of straight chain alkanes from molecular sieves

The molecular sieve containing n-alkanes were air dried and transferred to a 20 mL Teflon tube. n-Pentane (2-3 mL) was added to cover the sieves along with 1 mL of milli-Q water. The mixture was homogenized by stirring magnetically while placing on an ice bath. Hydrofluoric acid (50 %, 20-30 drops) was added drop wise while stirring until the sieve had dissolved (45-50 minutes). The excess HF was neutralized by adding saturated solution of sodium bicarbonate while stirring. The n-alkanes from sieves were dissolved in n-pentane and separated by passing through a small column of anhydrous magnesium sulfate. The aqueous mixture was further extracted with pentane (approx, 3 × 1 mL). Excess pentane was removed carefully using sand bath (60 °C).

Quantification of aromatic hydrocarbons

Deuterated phenanthrene (d10) was used as internal standard for quantification of aromatic hydrocarbons. The internal standard was prepared by dissolving 4 mg of deuterated phenanthrene in 100 mL of isoctane solution, so each microliter (µL) of solution contained 40 ng of deuterated phenanthrene.
3.3 LABORATORY EXPERIMENTS

3.3.1 Reference Compounds and Glass Tubes Preparation

Reference compounds were purchased from commercial suppliers: biphenyl (Acros Organics), 3-MBP (TCI chemicals), Fluorene, 1-methylfluorene (1-MF), 9-MF, 4-MF, 1,7-DMF (Chron AS, Norway), elemental sulfur (Technical Grade, Asia Pacific Suppliers), NaN₃ (Sigma-Aldrich), nonyl amine, secondary amine (diisopropyl amine), acetonitrile (Sigma-Aldrich), NH₃ gas (unknown), tetramethylbenzene (TMB) (Sigma-Aldrich) and activated carbon (Technical Grade, Asia Pacific Suppliers) were used in laboratory simulation experiments. Active carbon was conditioned at 340 °C (minimum 2 hrs) before use. The coal used in heating experiments was from Collie in Western Australia [118] from the Hebe seam. It was sieved to pass 90 mesh.

Glass tubes (15cm × 0.3cm i.d) were soaked in hydrochloric acid (1M) for at least 12 hours. After that one end of tube was sealed on oxygen-methane flame. The glass tubes were then deactivated by keeping them in dichlorodimethylsilane solution (Alltech, 5% solution in toluene) for more than 24 hours. After washing tubes subsequently with methanol and acetone were ready for heating experiments.

3.3.2 Laboratory Heating Experiments

In a typical experiment 1 mg of the biphenyl or 3-methylbiphenyl reactant with 1 mg of heteroatomic and methylene (alkyl) species compound mentioned in Table 3.1 and 10 mg activated carbon (or coal) were flushed with N₂, and sealed under vacuum before heating in a thermostat at selected temperatures between 200 °C and 300 °C. Heating time was 15-16 hrs for all experiments. The reaction products were extracted with dichloromethane and chromatographed by passing the extract through a small-scale silica column. Blank experiments without carbon (or coal) were carried out in parallel. The reaction products were analyzed using gas chromatography-mass spectrometry (GC-MS).
Table 3.1  Heating experiments details

<table>
<thead>
<tr>
<th>Precursor compound</th>
<th>Species compound</th>
<th>Active carbon</th>
<th>Temp.(^a) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biphenyl</td>
<td>Elemental Sulfur</td>
<td>Active carbon</td>
<td>300</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>Elemental Sulfur</td>
<td>Coal</td>
<td>300</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>Acetonitrile</td>
<td>Active carbon</td>
<td>300</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>NH(_3) gas</td>
<td>Active carbon</td>
<td>300</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>Nonyl amine</td>
<td>Active carbon</td>
<td>300</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>NaN(_3)</td>
<td>Active carbon</td>
<td>300</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>NaN(_3)</td>
<td>Coal</td>
<td>270</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>Air (source of O)</td>
<td>Active carbon</td>
<td>300</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>Tetramethylbenzene (TMB)</td>
<td>Active carbon</td>
<td>300</td>
</tr>
<tr>
<td>3-methylbiphneyl</td>
<td>Air (Source of O)</td>
<td>Active carbon</td>
<td>300</td>
</tr>
<tr>
<td>3-methylbiphneyl</td>
<td>Elemental S</td>
<td>Active carbon</td>
<td>300</td>
</tr>
<tr>
<td>3-methylbiphneyl</td>
<td>Elemental S</td>
<td>Active carbon</td>
<td>250</td>
</tr>
<tr>
<td>3-methylbiphneyl</td>
<td>Elemental S</td>
<td>Active carbon</td>
<td>225</td>
</tr>
<tr>
<td>3-methylbiphneyl</td>
<td>Elemental S</td>
<td>Active carbon</td>
<td>200</td>
</tr>
</tbody>
</table>

\(^a\): heating time was 15-16 hrs for all experiments

Note: Blank experiments were performed with out active carbon/coal
3.4 ANALYTICAL METHODS AND INSTRUMENTATION

3.4.1 Elemental Analysis of Sediments

Analysis was performed on Carlo Erba NA1500 elemental analyzer. Samples were weighed into tin capsules and dropped into a combustion tube at 1000 °C through which a constant stream of helium was maintained. Just prior to sample introduction the helium stream was dosed with a precise volume of pure oxygen. The sample was instantaneously burned followed by intense oxidation of the tin capsule at 1800 °C (flash combustion). The resulting combustion gases are passed over catalysts to ensure complete oxidation and absorption of halogens, sulfur and other interferences. Excess oxygen was removed as the gases were swept through a reduction tube containing copper at 650 °C. Any oxides of nitrogen were reduced to nitrogen. The gases were separated on a chromatographic column into nitrogen (N), carbon dioxide (C) and water vapour (H) and quantitatively measured by a thermal conductivity detector (TCD). The system response was calibrated to known calibration standards.

For oxygen analyses samples were precisely weighed into silver capsules and dropped at preset times into a combustion tube (at 1050 °C) through which a constant stream of helium was maintained. The resulting pyrolysed gases were passed over catalysed carbon to ensure complete conversion of oxygen in the sample to carbon monoxide. The carbon monoxide was separated from other pyrolysis gases on a chromatographic column and quantitatively measured by a thermal conductivity detector (TCD). The system response was calibrated to known calibration standards.

For sulfur analyses samples were precisely weighed into tin capsules and dropped into a combustion tube (at 1000 °C) through which a constant stream of helium was maintained. Just prior to sample introduction the helium stream was dosed with a precise volume of pure oxygen. The sample was instantaneously burned followed by intense oxidation of the tin capsule at 1800 °C (flash combustion). The resulting combustion gases were passed over catalysts to ensure complete oxidation. The gas stream was then dried by means of a water scrubber. Excess oxygen was removed as the
gases are swept through a reduction tube containing copper at 650 °C. Finally the sulfur
dioxide was separated from other interfering gases on a chromatographic column and
quantitatively measured by a thermal conductivity detector (TCD). The system response
was calibrated to known calibration standards.

3.4.2 $\delta^{34}$S of Pyrite from Sediments

The total reduced sulfur from the sediment was obtained by a distillation method
described by Fossing and Jorgensen [119]. Details of this method are outlined in
Jørgensen et al. [120] and Grice et al. [121]. $^{34}$S/$^{32}$S ratios were measured by means of
combustion isotope-ratio mass spectrometry (C-irmMS) using a Thermo Finnigan Delta$^+$
coupled to an elemental analyzer (Eurovectro) via a split interface (Thermo Finnigan
Conflo III). Measured isotope ratios were calibrated with in-house and international
reference materials and are reported in the $\delta$-notation relative to the V-CDT (Vienna
Canon Diablo Troilite) standard.

3.4.3 Gas Chromatography-Mass Spectrometry (GC-MS)

*Full scan mode for compound identification*

GC-MS analysis was performed using a Hewlett-Packard (HP) 5973 Mass
Selective Detector (MSD) interfaced to a HP 6890 gas chromatograph (GC). A 60 m ×
0.25 mm ID capillary column coated with a 0.25 µm 5% phenyl 95% methyl
polysiloxane stationary phase (DB-5 MS, J & W scientific) was used for the analysis.
1µL of the saturated or aromatic fractions (1 mg/mL in n-hexane) was introduced into the
split/splitless injector using the HP 6890 auto-sampler. The injector was operated at 280
in pulsed splitless mode. Helium maintained at a constant flow rate of 1.1 mL/min was
used as carrier gas. The GC oven was programmed from 40 °C to 310 °C at 3 °C/min
with initial and final hold times of 1 and 30 minutes, respectively. The transfer line
between the GC and the MSD was held at 310 °C. The MS source and quadrupole
temperatures were at 230 °C and 106 °C, respectively. Data was acquired in full scan
mode from 50 to 550 amu, with the MS ionization energy 70 eV and the electron multiplier voltage 1800 V.

**Full scan mode for heating experiment extracts**

GC-MS analyses were performed using an Agilent Technologies 6890 gas chromatograph coupled to an Agilent Technologies 5973 mass spectrometer with similar condition as above for heating experiments (section 3.3.2) extracts except following difference. The GC oven was programmed from 40 °C for 1 minute then at 5 °C/min to 310 °C for 10 minutes. The MS mass range was 10-500 a.m.u. with a scan rate of ~3 scans/sec.

**Selected ion monitoring (SIM) mode**

Aliphatic and aromatic hydrocarbons were analyzed by GC-MS in selected ion monitoring mode for better resolutions of compound classes. Similarly, to increase the resolution between individual isomers of alkynaphthalenes was obtained by running GC-MS in SIM mode using WAX column (0.60 m × 0.25 mm × 0.25 µm, DB-WAXETR, J & W scientific). In these analyses GC-MS conditions were kept same as described in full scan mode except MSD was operated in SIM mode.

### 3.4.4 Gas Chromatography-Isotope Ratio Mass Spectrometry

Gas chromatography-isotope ratio mass spectrometry (GC-irMS) was performed using micromass IsoPrime mass spectrometer interfaced to an agilent technologies 6890N Gas Chromatograph for compound specific stable hydrogen isotopic compositions (δD). GC was operated with column of same dimensions used for GC-MS analysis above for δD. During the analysis of a mixture of organic reference compounds (hexadecane and docosane), the GC oven was programmed from 50 °C to 310 °C at 3° C/min with initial and final hold times of 1 and 10 minutes respectively.

δD values were calculated by integration of the m/z 2 and 3 ion currents of the H2 peaks produced by pyrolysis of the GC separated hydrocarbons using chromium powder (350-400 µm, IsoScience Australia Pvt. Ltd.) at 1050 °C. An interfering species, H3+ ions are produced in the mass spectrometer ion source as a result of H2+ ion and H2
molecule collisions [122]. The amount of H$_3^+$ formed depends on the partial pressure of hydrogen, and the species interferes isobarically at m/z 3. Thus, contributions from H$_3^+$ produced in the ion source are corrected by performing m/z 3 measurements at two different pressures of the H$_2$ reference gas to determine the H$_3^+$ factor. An electrostatic sector is used to separate HD$^+$ from the leading edge of the large signal produced at m/z 4 by the constant flow of helium (carrier gas) into the mass spectrometer. δD values are reported relative to that of H$_2$ reference gas pulses produced by allowing hydrogen (UHP, BOC Gases Australia Ltd.) of a known D/H values into the mass spectrometer. The D/H content of the H$_2$ reference gas was monitored daily via analysis of mixture of reference compounds (see above). Average values of at least two analysis and standard deviations are reported. An internal standard (Squalane) with a predetermined δD value of -167‰ was used to monitor accuracy and precision of δD measurements. Isotopic compositions are given in the delta notation relative to Vienna Standard Mean Ocean Water (VSMOW).

3.4.5 Elemental Analysis-Isotope Ratio Mass Spectrometry (Bulk Isotope Analysis)

Bulk isotope analyses were performed on a micromass IsoPrime isotope ratio mass spectrometer interfaced to a EuroVector EuroEA3000 elemental analyzer. For bulk δ$^{13}$C analysis, the sample was accurately weighed (0.05-0.15 mg) into a small tin capsule which was then folded and compressed carefully to remove any tracers of atmospheric gases. The tin capsule containing sample was dropped into a combustion reactor at 1025 °C with help of autosampler. The sample and capsule melted in an atmosphere temporarily enriched with oxygen, where the tin promoted flash combustion. The combustion products, in a constant flow of helium, passed through an oxidation catalyst (chromium oxide). The oxidation products then passed through a reduction reactor at 650 °C containing copper granules, where any oxides of nitrogen (NO, N$_2$O and N$_2$O$_2$) are reduced to N$_2$ and SO$_2$ were separated on a 3 m chromatographic column (PoropakQ) at ambient temperature. After removing of oxides of nitrogen, oxidation products are then passed through a thermal conductivity detector (TCD) followed by the irMs. Isotopic
compositions are given in the delta notation relative to Vienna Peedee belemnite (VPDB).

For bulk δD analysis, the sample was accurately weighed (0.05-0.15 mg) into a small silver capsule which was then folded and dropped into a pyrolysis reactor containing glassy carbon chips held at 1260 °C. The sample was pyrolyzed to form H₂ and CO, along with N₂ if applicable. The pyrolysis products were separated on a 1 m 5A molecular sieve packed chromatographic column held in an oven at 80 °C (isothermal), before passing through a TCD, then into the irMS. δD values were calculated and reported similar to as above for compound specific isotope analysis (CSIA).
Chapter - 4

IDENTIFICATION OF SATURATED AND AROMATIC HYDROCARBONS

4.1 SATURATED HYDROCARBONS

Saturated hydrocarbons were identified using relative retention times, mass spectra and comparison with literature data [45, 123-125 and references therein].

4.1.1 \textit{n}-Alkanes and Isoprenoids

![Total ion chromatograms (TIC) of saturated hydrocarbon fraction shows \textit{n}-alkanes (\textit{n}-C_{10} to \textit{n}-C_{37}) and isoprenoids in crude oil (Missakeswal-1); a: 2,6-dimethylundecane (I, see appendix); b: 2,6,10-trimethylundecane (nor-farnesane, II); c: 2,6,10-trimethyldodecane (farnesane, III); d: 2,6,10-trimethyltridecane (IV); e: 2,6,10,-trimethylpentadecane (nor-Pristane, V); Pr: pristane, 2,6,10,14-tetramethylpentadecane (VI); Ph: phytane, 2,6,10,14-tetramethylhexadecane (VII). Refer to section 3.4.3 for GC-MS program.}

Fig. 4.1 Total ion chromatograms (TIC) of saturated hydrocarbon fraction shows \textit{n}-alkanes (\textit{n}-C_{10} to \textit{n}-C_{37}) and isoprenoids in crude oil (Missakeswal-1); a: 2,6-dimethylundecane (I, see appendix); b: 2,6,10-trimethylundecane (nor-farnesane, II); c: 2,6,10-trimethyldodecane (farnesane, III); d: 2,6,10-trimethyltridecane (IV); e: 2,6,10,-trimethylpentadecane (nor-Pristane, V); Pr: pristane, 2,6,10,14-tetramethylpentadecane (VI); Ph: phytane, 2,6,10,14-tetramethylhexadecane (VII). Refer to section 3.4.3 for GC-MS program.
4.1.2 Tricyclic and Tetracyclic Terpanes

Fig. 4.2 Mass chromatogram (m/z: 191) illustrating tricyclic and tetracyclic terpanes in Dhurnal-1 crude oils. Peak numbers 19-41 denote carbon number of tricyclic terpane (VIII); C\textsubscript{24}*: C\textsubscript{24} 17,21-secohopane (TeT: tetracyclic terpane, IX); C\textsubscript{30}: C\textsubscript{30} 17a(H)-hopane (Xb). Refer to section 3.4.3 for GC-MS program.
4.1.3 Pentacyclic Triterpanes

Fig. 4.3 Mass chromatograms (m/z: 191) showing the distribution of pentacyclic triterpanes (hopanes, X-XV) in Adhi-5 crude oil. Identity of peaks refers to Table 4.1. Refer to section 3.4.3 for GC-MS program.
Table 4.1 Identifications of pentacyclic triterpanes from Fig. 4.3.

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ts</td>
<td>$18\alpha(H)$-22,29,30-trisnorneohopane, C$_{27}$, XIII</td>
</tr>
<tr>
<td>Tm</td>
<td>$17\alpha(H)$-22,29,30-trisnorhopane, C$_{27}$, XII</td>
</tr>
<tr>
<td>29</td>
<td>$17\alpha(H),21\beta(H)$-30-norhopane, C$_{29}$ Xa</td>
</tr>
<tr>
<td>29Ts</td>
<td>$18\alpha(H)$-30-norneohopane, C$_{29}$T$_s$, XV</td>
</tr>
<tr>
<td>30D</td>
<td>$17\alpha(H)$-diahopane, C$_{30}$, XIV</td>
</tr>
<tr>
<td>29M</td>
<td>$17\beta(H),21\alpha(H)$-30-norhopane; C$_{29}$ (moretane), XIa</td>
</tr>
<tr>
<td>30</td>
<td>$17\alpha(H),21\beta(H)$-Hopane, C$_{30}$, Xb</td>
</tr>
<tr>
<td>30M</td>
<td>$17\beta(H),21\alpha(H)$-Hopane, C$_{30}$ (moretane), XIb</td>
</tr>
<tr>
<td>31S</td>
<td>22S $17\alpha(H),21\beta(H)$-homohopane, C$_{31}$, Xc</td>
</tr>
<tr>
<td>31R</td>
<td>22R $17\alpha(H),21\beta(H)$-homohopane, C$_{31}$, Xc</td>
</tr>
<tr>
<td>32S</td>
<td>22S $17\alpha(H),21\beta(H)$-bishomohopane, C$_{32}$, Xd</td>
</tr>
<tr>
<td>32R</td>
<td>22R $17\alpha(H),21\beta(H)$-bishomohopane, C$_{32}$, Xd</td>
</tr>
<tr>
<td>33S</td>
<td>22S $17\alpha(H),21\beta(H)$-trishomohopane, C$_{33}$, Xe</td>
</tr>
<tr>
<td>33R</td>
<td>22R $17\alpha(H),21\beta(H)$-trishomohopane, C$_{33}$, Xe</td>
</tr>
<tr>
<td>34S</td>
<td>22S $17\alpha(H),21\beta(H)$-tetrakishomohopane, C$_{34}$, Xf</td>
</tr>
<tr>
<td>34R</td>
<td>22R $17\alpha(H),21\beta(H)$-tetrakishomohopane, C$_{34}$, Xf</td>
</tr>
<tr>
<td>35S</td>
<td>22S $17\alpha(H),18\beta(H)$-pentakishomohopane, C$_{35}$, Xg</td>
</tr>
<tr>
<td>35R</td>
<td>22R $17\alpha(H),21\beta(H)$-pentakishomohopane, C$_{35}$, Xg</td>
</tr>
</tbody>
</table>
4.1.4 Steranes and Diasteranes

Fig. 4.4 Mass chromatogram (m/z: 217) of Dhurnal-1 crude oil shows the profile of steranes and diasteranes. Peak identity numbers refer to Table 4.2. See section 3.4.3 for GC-MS program.

Table 4.2 Identifications of steranes and diasteranes from Fig. 4.4.

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20S 13β,17α-diacholestane, C27, <strong>XVIIa</strong></td>
</tr>
<tr>
<td>2</td>
<td>20R 13β,17α-diacholestane, C27, <strong>XVIIa</strong></td>
</tr>
<tr>
<td>3</td>
<td>20S 24-methyl-13β,17α-diacholestan, C26, (24(S+R)), <strong>XVIIb</strong></td>
</tr>
<tr>
<td>4</td>
<td>20R 24-methyl-13β,17α-diacholestan, C28, (24(S+R)), <strong>XVIIb</strong></td>
</tr>
<tr>
<td>5</td>
<td>20S 5α, 14α,17α-cholestane, C27, <strong>XVIa</strong></td>
</tr>
<tr>
<td>6</td>
<td>20S 24-ethyl-13β,17α-diacholestan, C29, <strong>XVIIc</strong> + 20R 5α,14β,17β-cholestane, C27, <strong>XVId</strong></td>
</tr>
<tr>
<td>7</td>
<td>20S 5α,14β,17β-cholestane, C27, <strong>XVId</strong></td>
</tr>
<tr>
<td>8</td>
<td>20R 5α,14α,17α-cholestane, C27, <strong>XVIa</strong></td>
</tr>
<tr>
<td>9</td>
<td>20R 24-ethyl-13β,17α-diacholestan, C29, <strong>XVIIc</strong></td>
</tr>
<tr>
<td>10</td>
<td>20S 24-methyl-5α,14α,17α-cholestan, C28, <strong>XVIIb</strong></td>
</tr>
<tr>
<td>11</td>
<td>20R 24-methyl-5α,14β,17β-cholestan, C28, <strong>XVIIe</strong></td>
</tr>
<tr>
<td>12</td>
<td>20S 24-methyl-5α,14β,17β-cholestan, C28, <strong>XVIIe</strong></td>
</tr>
<tr>
<td>13</td>
<td>20R 24-methyl-5α,14α,17α-cholestan, C28, <strong>XVIIb</strong></td>
</tr>
<tr>
<td>14</td>
<td>20S 24-ethyl-5α 14α,17α-cholestan, C29, <strong>XVIc</strong></td>
</tr>
<tr>
<td>15</td>
<td>20R 24-ethyl-5α,14β,17β-cholestan, C29, <strong>XVIf</strong></td>
</tr>
<tr>
<td>16</td>
<td>20S 24-ethyl-5α,14β,17β-cholestan, C29, <strong>XVIf</strong></td>
</tr>
<tr>
<td>17</td>
<td>20R 24-ethyl-5α,14α,17α-cholestan, C29, <strong>XVIc</strong></td>
</tr>
</tbody>
</table>
4.1.5 Diamondiod Hydrocarbons

$m/z$: 136+135

Fig. 4.5 Adamantane (XVIII) and methyladamantanes are shown by sum of mass chromatograms (m/z: 136+135) and diamantine (XIX) and methyldiamantanes are shown by sum of mass chromatograms (m/z: 188+187) from saturated fraction of representative oil sample (Adhi-5). See section 3.4.3 for GC-MS program.
4.2 POLYCYCLIC AROMATIC HYDROCARBONS

Aromatic hydrocarbons were identified using relative retention times, mass spectra and comparison with the literature data [6,30,49,126-133]. Methylfluorenes are not reported in sedimentary OM as per my knowledge and they were identified using relative retention times and comparison with mass spectra of available internal standards i.e. 9-methylfluorene (9-MF), 1-MF, 4-MF and 1,7-dimethylfluorene (1,7-DMF).
4.2.1 Biphenyl and Alkylbiphenyls

**Fig. 4.6** (a) Sum of mass chromatograms (m/z: 154+168) showing biphenyl (BP, XXII) and methylbiphenyls and (b) mass chromatogram (m/z: 182) showing dimethylbiphenyls in aromatic fraction of a representative oil (Adhi-5). DPM, diphenylmethane; numbers on each peak refer to respective methyl and dimethyl biphenyl isomer.
4.2.2 Naphthalene and Alkynaphthalenes

Fig. 4.7 (a) Naphthalene (N, XXIII), methylnaphthalenes, dimethylnaphthalenes are shown by sum of mass chromatograms (m/z: 128+142+156 respectively) and (b) trimethylnaphthalenes, tetramethylnaphthalenes are shown by sum of mass chromatograms (m/z: 170+184 respectively) in a representative oil (Adhi-5). Numbers on each peak refer to position of methyl substituent.
4.2.3 Phenanthrene and Alkylphenanthrenes

Fig. 4.8 Phenanthrene (XXIV), methylphenanthrenes, dimethylphenanthrenes shown by sum of mass chromatograms (m/z: 178+192+206 respectively) from aromatic fraction of Adhi-5. Numbers on each peak refer to respective alkyl phenanthrene isomer.
4.2.4 Dibenzofuran and Alkyldibenzofurans

$m/z: 168+182$

**Fig. 4.9** Sum of mass chromatograms (m/z: 168+182) showing DBF (XXV) and methyldibenzofurans in Kohat Basin sediment, depth: 4290 m. Numbers on each peak refer to methyl dibenzofuran isomer.
4.2.5 Carbazole and Alkylcarbazoles

Fig. 4.10 (a) sum of mass chromatogram (m/z: 167+181) showing carbazole (C, XXVI) and methylcarbazoles and (b) mass chromatogram (m/z: 195) showing dimethylcarbazoles from Kohat Basin sediment, depth: 4690 m. Numbers on each peak refer to respective methyl and dimethyl carbazole isomer.
4.2.6 Dibenzothiophene and Alkyldibenzothiophenes

Fig. 4.11 (a) Sum of mass chromatograms (m/z: 184+198) sowing dibenzothiophene (DBT, XXVII) and methyldibenzothiophenes and (b) mass chromatogram (m/z: 212) showing dimethyldibenzothiophenes from Kohat Basin sediment, depth, 4710 m. Numbers on each peak refer to respective methyl and dimethyl dibenzothiophene isomer.
4.2.7 Fluorene and Alkylfluorenes

Fig. 4.12 Sum of mass chromatograms (m/z: 166+180) showing fluorene (F, XXVIII) and methylfluorenes in Kohat Basin sediment, Depth: 4290 m. Numbers on each peak refer to respective methyl substituent.
4.2.8 Identification of Retene

Identification of Retene was confirmed by monitoring ions 219 and 234 to avoid any interference from tetramethylphenanthrenes (m/z: 234).

Fig. 4.13 Mass chromatograms m/z: 219 and 234 showed Retene (XXI) in aromatic fraction of Adhi-5 crude oil.
4.2.9 Compound Identification of Laboratory Heating Experiments

**Fig. 4.14** Total ion chromatogram of the extract of laboratory experiment at 300 °C of reactants (biphenyl, activated carbon, NaN₃, Air) for 16 hrs. Identification is given in Table 4.3.

**Table 4.3** Identification compounds from Fig. 4.14.

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Compound name</th>
<th>Retention Indices *</th>
<th>Identification</th>
<th>Zenkevich et al., [132]*</th>
<th>Rostad and Pereira, [126]*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Lee</td>
<td>Kovat</td>
<td>Kovat</td>
<td>Lee</td>
</tr>
<tr>
<td>1</td>
<td>Biphenyl</td>
<td>235.64</td>
<td>1394.2</td>
<td>MS</td>
<td>1379</td>
</tr>
<tr>
<td>2</td>
<td>ortho-Hydroxybiphenyl</td>
<td>257.96</td>
<td>1529.9</td>
<td>Kovat</td>
<td>1506</td>
</tr>
<tr>
<td>3</td>
<td>Dibenzofuran</td>
<td>259.51</td>
<td>1539.8</td>
<td>MS</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>ortho-Aminobiphenyl</td>
<td>269.79</td>
<td>1605.2</td>
<td>Kovat and Lee</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Carbazole</td>
<td>308.55</td>
<td>1866.3</td>
<td>MS</td>
<td>-</td>
</tr>
</tbody>
</table>

* Column and temperature program: DB-5MS (60 m × 0.25 mm × 0.25 µm I.D.) 40 °C (1 min) @ 5 °C/min, 310 °C (10 min)

**MS**: Mass spectra

#: HP-5 (30. m × 0.25 mm × 0.25 µm) 50 °C (3 min) 3 °C/min 280 °C (20 min)

#: DB-5 (30. m × 0.25 mm × 0.25 µm) 50 °C (4 min) 6 °C/min 300 °C (20 min)
Chapter - 5

GEOCHEMISTRY OF POTWAR BASIN CRUDE OILS

ABSTRACT

Geochemical classification of eighteen crude oils from the Potwar Basin (Upper Indus), Pakistan was carried out using carbon and hydrogen bulk isotope abundance and distribution of saturated and aromatic hydrocarbons. Aliphatic biomarkers were used as supporting tool to deduce the geochemical characteristics such as thermal maturity, depositional environments, source OM and extent of biodegradation. PAHs distributions in regard to these geochemical characteristics were reported and comprehensive oil correlation of the Potwar Basin was established. GC-MS analysis and bulk stable isotopic compositions of saturated and aromatic fractions reveal that at least three different groups of crude oils are present in the Potwar Basin.

Group A contains terrestrial source of OM deposited in highly oxic/fluvio-deltaic clastic depositional environment shown by high Pr/Ph, high diahopane/hopane, high diasterane/sterane, low DBT/P ratios and higher relative abundance of C_{19} tricyclic and C_{24} tetracyclic terpanes. Aliphatic biomarkers for rest of the oils indicate marine origin however two ranges of values for parameters such as steranes/hopanes, diasteranes/steranes, C_{23}-tricyclic/C_{30} hopane, C_{24}-tetracyclic/C_{30} hopane, tricyclics/hopanes, C_{31}/C_{30} hopane ratios differentiate them into two groups (B and C). Group B oils are generated from clastic rich source rocks deposited in marine suboxic depositional environment than group C oils which are generated from source rocks deposited in marine oxic depositional environment. Group C oils show higher marine OM (algal input) indicated by extended tricyclic terpanes (upto C_{41} or higher) and higher steranes/hopanes ratios. Distribution of PAHs classified Potwar Basin oils into similar three groups based on depositional environments and source OM variations. Abundant biphenyls (BPs) and fluorenes (Fs) are observed in group A oils while group B oils...
showed higher abundance of dibenzothiophenes (DBTs) and negligible presence of dibenzofurans (DBFs) and Fs and group C oils showed equal abundance of DBTs and Fs. This relative abundance of heterocyclic aromatic hydrocarbons in Potwar Basin oils broadly indicate that the distribution of these compounds is controlled by depositional environment of OM where sulfur compounds (i.e. DBTs) are higher in marine source oils while oxygen compounds (DBFs) and Fs are higher in oxic/deltaic depositional environment oils. Higher abundance of aromatic biomarkers the 1,2,5-trimethylnaphthalene (1,2,5-TMN), 1-methylphenanthrene (1-MP) and 1,7-dimethylphenanthrene (1,7-DMP) indicate major source of OM for group A oil is higher plant supported by abundance of conifer plants biomarker retene. Variations in distribution of triaromatic steroids (TAS) in Potwar Basin oils clearly indicate source dependent of these compounds rather than thermal maturity. Higher abundance of C20 and C21 TAS and substantional difference in distribution of long chain TAS (C26, C27, C28) between the groups indicate different source origin of these compounds. Group A shows only C27 and C28 TAS while group B shows C25 to C28 TAS and absence of these compounds in group C oils revealed that the sterol precursors for these compounds are most probably different. Aliphatic and aromatic hydrocarbon maturation parameters indicate higher (late oil generation) thermal maturity for all oils from the Potwar Basin. The crude oils of group A and C are typically non-biodegraded mature crude oils whereas some of the oils from group B showed minor biodegradation indicated by higher Pr/n-C17, Ph/n-C18 and low API gravity.

5.1 INTRODUCTION

The Potwar Basin has shown a number of small and medium size oil and gas discoveries and still active for further explorations. Both heavy and light oils have been discovered in the basin, heavy oils are genetically related to light oils, and bear a close spatial relationship [134]. The properties and composition of these petroleum systems are controlled by complex geological, physicochemical and biological processes during generation as well as accumulation in reservoirs. Biomarker analysis of selected sediments and crude oils has been performed and source to oil correlation has been
reported in a study [116]. However, organic geochemical data particularly PAHs and isotopic compositions from potential source rocks in the Potwar Basin have never been reported, nor has detailed an oil-oil correlation ever been undertaken up to my knowledge. However rock-eval pyrolysis of some Precambrian source rocks has reported and partially correlated with Potwar Basin crude oils [117].

The application of biomarkers and stable isotope analysis has been recognized as powerful tool in exploration petroleum geochemistry. Biomarkers (on structural grounds) in bituminous OM can provide valuable information on: i) the source of their natural product precursors (i.e. Eukaryotes, Prokaryotes and Archeae) ii) paleoenvironmental depositional conditions - marine, lacustrine, hypersaline or fluvio-deltaic iii) lithology of potential petroleum source rocks (carbonate vs. shale) (iv) relative thermal maturity of potential source rocks and v) extent of biodegradation of petroleum hydrocarbons. However, many of the above factors are often interrelated and have been considered collectively for correlation studies [135]. The variation in biomarkers abundances has been used successfully for oil correlation studies between source rocks and/or other oils [e.g. 136-139].

Aromatic structures are almost absent in biological OM, however their ubiquitous occurrence in sedimentary OM suggests that the compounds are the product of sedimentary reactions [4]. The distribution and relative abundance of these compounds have been used as source, depositional environment and thermal maturity indicators of source rocks and petroleum [5-6,11,25,38,140-141]. Alexander et al. [5] suggested aromatic biomarker, retene (XXI) as indicator of terrestrial OM and related it to araucariaceae family of conifers and later on source of retene was specified to the conifer resin [135]. The potential application of aromatic hydrocarbons has been recognized as thermal maturity indicator of source rocks and crude oils [25-26,10-11,38]. Thermal maturity parameters derived by comparing concentrations of thermodynamically least stable isomers (α) to the thermodynamically most stable isomers (β). The principal behind is that the methyl group shifts from α- to β- position with increase in thermal maturity [26]. The alkynaphthalenes maturity parameters have been described by van Aarssen et al. [38]. In alkylphenanthrenes, methylphenanthrenes ratio (MPR) are derived
by dividing $\alpha$-isomer (1-MP) to the $\beta$-isomer (2-MP). Methylphenanthrene index 1(MPI-1) is the most significant molecular maturity parameter from aromatic hydrocarbons which is successfully calibrated with mean vitrinite reflectance ($R_m$) for source rocks and crude oils [4]. The calculated vitrinite reflectance ($R_c$) from MPI-1 differentiates crude oils thermal maturity into immature (0.70), mature (0.85) and postmature (0.95). Among aromatic sulfur hydrocarbons, methyldibenzothiophene ratio (MDR; 4-/1-MDBT) are sensitive to maturity changes which shows good correlation with vitrinite reflectance in range of 0.52 to 1.32% [11]. However MDR showed different thermal maturity trends in early maturation stages [11], moreover MDR showed variation relevant to the expulsion stage of aromatic sulfur hydrocarbons from type II/III kerogens [40].

Stable isotopes of carbon and hydrogen are the most useful tracers in crude oils and sediments because they are the most abundant elements in any shape of sedimentary OM. Variations in stable isotopic compositions or “isotope fractionation” occur in nature due to different physical and chemical processes. Bulk isotope analysis represents the measurement of stable isotopes of total carbon and hydrogen in the samples which indicate the average values of all complex compounds. The entire sample such as whole oil, saturated fraction or aromatic fraction of crude oils and sediment extracts are being under use for bulk isotope determinations. The bulk isotope compositions of saturated and aromatic fractions from crude oils has been applied to represent the source OM input in hundred of oils in the world [142-144] while compound specific isotope analysis is used as a powerful tool in the oil correlation studies [145-146].

In this chapter organic geochemical parameters based on PAHs and stable carbon and hydrogen isotopes of saturated and aromatic fractions supporting with aliphatic biomarkers have been used to investigate the source OM of the Potwar Basin crude oils. A selection of saturated and aromatic biomarker parameters has been determined for oils and source-rocks to establish thermal maturity of OM, depositional paleoenvironmental information, lithology and extent of biodegradation of hydrocarbons. Results were successfully applied to delineate the oils groupings of the Potwar Basin.
5.2 RESULTS AND DISCUSSION

5.2.1 Normal Alkanes and Isoprenoids Distribution

The crude oils analyzed in this study are listed in Table 5.1. The total ion chromatogram (TIC) of the saturated fraction of a representative oil sample is shown in Fig. 4.1 (Chapter 4). \( n \)-Alkanes from \( n\)-C\(_{10}\) to \( n\)-C\(_{37}\) are present in Adhi-5 with no odd or even preference of \( n \)-alkanes as measured by CPI and OEP (Table 5.1). Low molecular weight hydrocarbons (<\( n\)-C\(_{10}\)) were not observed, probably because of evaporative loss during sample processing. Ratios of isoprenoids to \( n \)-alkanes are very low (0.4 and 0.2 for Pr/\( n\)-C\(_{17}\) and Ph/\( n\)-C\(_{18}\) respectively) but Pr/Ph ratio is highest (3.2). Compared to Adhi-5, a group of oils (P2-P14, Table 5.1) display different characteristics i.e. Pr/Ph ratio 1-2 and less abundance of low molecular weight \( n \)-alkanes. Their isoprenoids to \( n \)-alkanes ratios are higher, CPI and OEP of some samples are <1 suggesting even preference for \( C_{22}-C_{30}\) \( n \)-alkanes. The P15-P18 oils contained full suit of \( n \)-alkanes, low values of Pr/\( n\)-C\(_{17}\) and Ph/\( n\)-C\(_{18}\) (0.6-0.9 and 0.4-0.7 respectively, Table 5.1).

This data in combination with API gravity (Table 2.1, chapter 2) broadly classify the samples into three groups. Group A comprising a single oil Adhi-5, of typically mature, non-biodegraded light oil (API: 48°), generated from highly oxic depositional conditions. Group B (P2-P14) of medium to heavy (API: 16-41°) oils. The source rocks generating Group B oils appear to have deposited under sub-oxic depositional conditions. The Group B samples show low maturity likely to be affected by biodegradation. Group C, consists of P15-P18 oils, shows characteristics of narrow range medium gravity (API: 34-38°), mature, non-biodegraded petroleum.

5.2.2 Carbon and Hydrogen Isotopic Compositions

The isotopic composition of crude oil is mainly dependent on the \( \delta^{13}C \) and \( \delta D \) value of the kerogen which in turn, depends on the biological OM and the depositional environment [143,147-148]. Biodegradation and thermal maturity have little effect on the stable carbon isotopic composition of the whole oil [149]. Since isotopic compositions of oils change with type of OM, therefore bulk \( \delta^{13}C \) of saturated and aromatic fractions of
Table 5.1  
*n*-Alkanes, isoprenoid ratios and bulk isotope data

<table>
<thead>
<tr>
<th>No</th>
<th>Oil and well</th>
<th>Pr/Ph</th>
<th>Pr*/n-C17</th>
<th>Ph*/n-C18</th>
<th>CPI</th>
<th>OEP</th>
<th>δ¹³C sat</th>
<th>δ¹³C aros</th>
<th>δD sat</th>
<th>δD aros</th>
<th>δ¹³C a ver</th>
<th>δD a ver(‰)</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Adhi-5</td>
<td>3.2</td>
<td>0.4</td>
<td>0.2</td>
<td>1.0</td>
<td>1.0</td>
<td>-26.4</td>
<td>-24.5</td>
<td>-117</td>
<td>-111</td>
<td>-25.4</td>
<td>-114</td>
<td>A</td>
</tr>
<tr>
<td>P2</td>
<td>Missakeswal-1</td>
<td>1.5</td>
<td>1.0</td>
<td>0.7</td>
<td>0.9</td>
<td>1.0</td>
<td>-23.1</td>
<td>-20.8</td>
<td>-155</td>
<td>-130</td>
<td>-21.9</td>
<td>-142</td>
<td>B</td>
</tr>
<tr>
<td>P3</td>
<td>Missakeswal-3</td>
<td>2.0</td>
<td>1.0</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
<td></td>
<td>-</td>
<td></td>
<td>-22.4</td>
<td>-21.0</td>
<td>B</td>
</tr>
<tr>
<td>P4</td>
<td>Rajian-1</td>
<td>1.2</td>
<td>1.3</td>
<td>0.9</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
<td></td>
<td>-</td>
<td></td>
<td>-22.4</td>
<td>-21.0</td>
<td>B</td>
</tr>
<tr>
<td>P5</td>
<td>Rajian-3A</td>
<td>1.3</td>
<td>1.3</td>
<td>0.9</td>
<td>1.0</td>
<td>1.0</td>
<td>-22.4</td>
<td>-21.0</td>
<td>-132</td>
<td>-125</td>
<td>-21.7</td>
<td>-128</td>
<td>B</td>
</tr>
<tr>
<td>P6</td>
<td>Kal-1</td>
<td>1.3</td>
<td>1.4</td>
<td>0.9</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
<td></td>
<td>-</td>
<td></td>
<td>-22.4</td>
<td>-21.0</td>
<td>B</td>
</tr>
<tr>
<td>P7</td>
<td>Kal-2</td>
<td>1.5</td>
<td>1.2</td>
<td>0.8</td>
<td>1.0</td>
<td>0.9</td>
<td>-23.0</td>
<td>-21.1</td>
<td>-149</td>
<td>-135</td>
<td>-22.0</td>
<td>-142</td>
<td>B</td>
</tr>
<tr>
<td>P8</td>
<td>Fimkassar-1</td>
<td>1.3</td>
<td>1.1</td>
<td>0.8</td>
<td>1.0</td>
<td>0.9</td>
<td>-</td>
<td></td>
<td>-</td>
<td></td>
<td>-22.4</td>
<td>-21.0</td>
<td>B</td>
</tr>
<tr>
<td>P9</td>
<td>Fimkassar-4</td>
<td>1.4</td>
<td>0.8</td>
<td>0.6</td>
<td>1.0</td>
<td>1.0</td>
<td>-22.9</td>
<td>-22.2</td>
<td>-126</td>
<td>-132</td>
<td>-22.2</td>
<td>-137</td>
<td>B</td>
</tr>
<tr>
<td>P10</td>
<td>Chaknaurang-1A</td>
<td>1.2</td>
<td>1.3</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>-22.6</td>
<td>-21.9</td>
<td>-132</td>
<td>-141</td>
<td>-22.2</td>
<td>-137</td>
<td>B</td>
</tr>
<tr>
<td>P11</td>
<td>Minwal-1</td>
<td>1.0</td>
<td>1.3</td>
<td>1.0</td>
<td>0.9</td>
<td>0.9</td>
<td>-23.0</td>
<td>-21.1</td>
<td>-136</td>
<td>-136</td>
<td>-22.1</td>
<td>-136</td>
<td>B</td>
</tr>
<tr>
<td>P12</td>
<td>Joyamir-4</td>
<td>1.0</td>
<td>1.1</td>
<td>1.0</td>
<td>0.9</td>
<td>0.8</td>
<td>-22.3</td>
<td>-21.0</td>
<td>-145</td>
<td>-129</td>
<td>-21.6</td>
<td>-137</td>
<td>B</td>
</tr>
<tr>
<td>P13</td>
<td>Turkwal-1</td>
<td>1.2</td>
<td>1.1</td>
<td>0.8</td>
<td>1.0</td>
<td>0.9</td>
<td>-22.3</td>
<td>-21.0</td>
<td>-145</td>
<td>-129</td>
<td>-21.6</td>
<td>-137</td>
<td>B</td>
</tr>
<tr>
<td>P14</td>
<td>Pindori-4</td>
<td>1.5</td>
<td>0.8</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
<td>-23.1</td>
<td>-20.5</td>
<td>-145</td>
<td>-139</td>
<td>-21.8</td>
<td>-142</td>
<td>B</td>
</tr>
<tr>
<td>P15</td>
<td>Dhurnal-1</td>
<td>1.4</td>
<td>0.9</td>
<td>0.7</td>
<td>1.0</td>
<td>1.0</td>
<td>-25.0</td>
<td>-22.0</td>
<td>-148</td>
<td>-139</td>
<td>-23.5</td>
<td>-144</td>
<td>C</td>
</tr>
<tr>
<td>P16</td>
<td>Dhurnal-6</td>
<td>1.4</td>
<td>0.9</td>
<td>0.7</td>
<td>1.0</td>
<td>1.0</td>
<td>-25.1</td>
<td>-22.1</td>
<td>-</td>
<td></td>
<td>-23.6</td>
<td>-</td>
<td>C</td>
</tr>
<tr>
<td>P17</td>
<td>Toot-10A</td>
<td>1.6</td>
<td>0.6</td>
<td>0.4</td>
<td>1.0</td>
<td>1.0</td>
<td>-26.1</td>
<td>-21.5</td>
<td>-129</td>
<td>-122</td>
<td>-23.8</td>
<td>-126</td>
<td>C</td>
</tr>
<tr>
<td>P18</td>
<td>Toot-12</td>
<td>1.6</td>
<td>0.8</td>
<td>0.6</td>
<td>1.0</td>
<td>1.0</td>
<td>-26.1</td>
<td>-21.4</td>
<td>-</td>
<td></td>
<td>-23.7</td>
<td>-</td>
<td>C</td>
</tr>
</tbody>
</table>

CPI: \(2(C_{23} + C_{25} + C_{27} + C_{29})/(C_{22} + 2(C_{24} + C_{26} + C_{28}) + C_{30})\); OEP: \((C_{21} + 6\times C_{23} + C_{25})/(4\times C_{22} + 4\times C_{24})\)

δ¹³C (‰) with respect to VPDB reported with in standard deviation of 0.2‰.

δD (‰) with respect to VSMOW with in standard deviation of 3.

-: not determined

\(\delta^{13}C_{\text{aver}}: (\delta^{13}C_{\text{sats}}, \delta^{13}C_{\text{aros}})/2\)

\(\deltaD_{\text{aver}}: (\deltaD_{\text{sats}} + \deltaD_{\text{aros}})/2\)
oils are useful along with biomarker parameters in distinguishing crude oils from different source and depositional settings [143-148].

Crude oils listed in Table 5.1 were examined for bulk stable carbon and hydrogen isotopic compositions. Cross plots $\delta^{13}C$ of saturated and aromatic fractions were used to clearly delineate different groups of petroleum in the Potwar Basin (Fig. 5.1a, Table 5.1). The crude oils P2-P14 showed higher values of $\delta^{13}C$ (isotopically heaviest) and cluster together on right hand side of the plot (Fig. 5.1a, group B). More negative (isotopically lighter) $\delta^{13}C$ values (-25 to -26.1‰) are observed from the Dhurnal and Toot well samples (Fig. 5.1a, group C, P15-P18). Among the sample suite of oils analysed, Adhi-5 was isotopically lightest (more negative) in $\delta^{13}C$ of both saturated and aromatic fractions. It was designated as group A (Fig. 5.1a, Table 5.1, P1). The isotopic composition of crude oils with in each group is most probably controlled by both source and depositional settings as indicated by $n$-alkanes and isoprenoid distributions and saturated and aromatic hydrocarbons distributions (following sections). Group B oils showed enrichment in $\delta^{13}C_{sats}$ having values up to 3-4‰ compared to group C (Fig. 5.1a; Table 5.1). The difference observed between $\delta^{13}C$ of the saturated hydrocarbon fractions between the groups indicates the difference in source organisms. Another plot represents the difference between $\delta^{13}C$ and $\delta D$ average values of both saturated and aromatic fractions of crude oils (Table 5.1) and same results were achieved (Fig. 5.1b). The crude oils were separated into similar three groups hence provided an additional evidence for the existence of at least three groups of petroleum in the Potwar Basin. The difference in stable carbon and hydrogen isotopic compositions of saturated and aromatic fractions is consistent with source variations.
Fig. 5.1  The plots (a) $\delta^{13}C_{\text{sats}}$ vs $\delta^{13}C_{\text{aros}}$ (b) $\delta^{13}C_{\text{aver}}$ vs $\deltaD_{\text{aver}}$ to delineate groupings of petroleum in the Potwar Basin.
5.2.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Distributions of PAHs were evaluated from GC-MS analysis of aromatic fractions. Representative TICs of aromatic fractions from each group of the Potwar oils are shown in Fig. 5.2. The PAHs profiles of oils generally show variations in relative abundance between different classes of aromatic hydrocarbons where diaromatic (two rings) and triaromatic (three rings) are the predominant components in each representative oil chromatogram (Fig. 5.2). Group A chromatogram shows higher abundance of diaromatic than triaromatic hydrocarbons where BPs are the most abundant compounds from the all diaromatic hydrocarbons. Similarly Fs are comparatively abundant than phenanthrenes in the triaromatic hydrocarbons of the same oil. Significant abundance of BPs and Fs from naphthalenes and phenanthrenes separated group A oil from other groups of oils (Fig. 5.2a). Similarly naphthalenes and phenanthrenes are the predominant aromatic components in group B representative chromatogram (Fig. 5.2b). However significant presence of triaromatic steroids (TAS) and DBTs differentiates group B from group A and C where later groups showed less or absence of TAS and comparatively low abundance of DBTs (Figs. 5.2b and 5.2c). Again, naphthalenes and phenanthrenes are present in higher abundance in group C oil however naphthalenes showed a double order of the abundance than phenanthrenes (Fig. 5.2c) and low abundance of TAS, DBTs, Fs, and BPs in representative chromatogram of group C oil differentiates this group from other groups. Distribution of PAHs indicate that at least three types of crude oils are present in Potwar Basin.

Generally aromatic hydrocarbons are not diagnostic compounds for the evaluation of source OM characteristics of mature crude oils and sediments. However variations in relative distribution of aromatic hydrocarbons indicate a difference in source and depositional environment of OM. Following sections explained the distribution of each class of above described aromatic compounds in Potwar Basin oils and they were used for evaluation of thermal maturity and source of OM, lithology and depositional environment in combination with commonly used aliphatic biomarkers.
Fig. 5.2 TICs showing distributions of aromatic hydrocarbons in representative samples from the Potwar Basin; N, naphthalene; MN, methyl naphthalenes; DMN, dimethyl naphthalenes; TMN, trimethyl naphthalenes; TeMN, tetramethyl naphthalenes; BP, biphenyl; MBP, methylbiphenyl; DMBP, dimethylbiphenyl; P, phenanthrene; MP, methylphenanthrenes; DMP, dimethylphenanthrenes; TMP, trimethyl phenanthrenes; MDBT, methyldibenzothiophenes; DMDBT, dimethyldibenzothiophenes; MF, methylfluorenes; DMF, dimethylfluorenes; TAS, triaromatic steroids
5.2.4 Thermal Maturity of Potwar Basin Oils

A combination of saturated and aromatic hydrocarbons parameters were used to determine the thermal maturity of the Potwar Basin oils. The data listed in Table 5.2 was obtained from GC-MS analysis of branched/cyclic and aromatic hydrocarbon fractions. The hopane based parameters were calculated from peak areas of 191 Dalton mass chromatograms. The proportion of 22S relative to (22S + 22R) for C_{32} homohopanes (Xd) is a maturity parameter for immature to early oil window. During maturation the ratio 22S/(22S + 22R) shows distinct change from 0 to 0.6 whereas equilibrium lies between 0.57 and 0.62 [150]. For C_{32} homologue 22S/(22S+22R) ratio varies between 0.57 and 0.64 suggesting high maturity for all the oils samples analysed in this study from the Potwar Basin (Table 5.2). These ratios reach equilibrium in the early oil window so have limited application for studying the relative maturities of crude oils and condensates. The other hopane based maturity parameter is the ratio of 17\alpha(H),21\beta(H)- hopane to 17\beta(H),21\alpha(H)-hopanes [\alpha\beta/(\alpha\beta+\beta\alpha)] for C_{29}- and C_{30}- compounds, which equilibrate at somewhat higher thermal maturities [45,151]. The observed values for the parameter are in the range of 0.81 to 1.0 (Table 5.2, mostly > 0.9) which are typical of oils generated from mature source rocks [152]. The plot of hopane maturity parameter between C_{29}- and C_{30}- [\alpha\beta/(\alpha\beta+\beta\alpha)] is shown in Fig. 5.3a [152], most of the oil samples fall within an equilibrium and higher range of thermal maturity except Adhi-5 which show low thermal maturity. The slight difference in [\alpha\beta/(\alpha\beta+\beta\alpha)] ratios with in the Potwar Basin shows the affects of source and depositional environment variations on these values, which are known to have effects on these ratios [153-154]. The Ts/(Ts+Tm) ratios show a wide range from 0.31 to 0.73; however narrow range of this ratio is observed within individual groups. For example, group B shows Ts/(Ts+Tm) ratio in the range of 0.31 to 0.45 while group C shows exceeding values of 0.67 to 0.70. Group A representing a single oil Adhi-5 shows intermediate value (0.53). Pindori-4 (P14, Table 5.2) shows maximum value of 0.73 which is different from other oils of group B. Three different ranges of Ts/(Ts+Tm) indicates that this ratio is controlled by the source organic facies and depositional environment, which are the factors known to have a control on this ratio [155].
Table 5.2 Thermal maturity parameters calculated from aliphatic and aromatic hydrocarbons

<table>
<thead>
<tr>
<th>No</th>
<th>Oil and Well</th>
<th>Ts/(Tt+Tm)</th>
<th>αβ/(αβ+βα), C_{29} Hop</th>
<th>αβ/(αβ+βα), C_{30} Hop</th>
<th>(S/S+R) C_{29} Hop</th>
<th>(ββ/(αα+ββ)) C_{29} Ster</th>
<th>(S/S+R) C_{29}ster</th>
<th>MAI</th>
<th>MDI</th>
<th>DNR-1 (%)</th>
<th>TNR-1 (%)</th>
<th>TNR-2 (%)</th>
<th>R_c (%)</th>
<th>MDR (%)</th>
<th>Rcs (%)</th>
<th>MDR'</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Adhi-5</td>
<td>0.53</td>
<td>0.83</td>
<td>0.81</td>
<td>0.62</td>
<td>0.59</td>
<td>0.41</td>
<td>0.59</td>
<td>0.46</td>
<td>6.8</td>
<td>1.04</td>
<td>0.94</td>
<td>0.75</td>
<td>0.85</td>
<td>6.4</td>
<td>0.98</td>
</tr>
<tr>
<td>P2</td>
<td>Missakeswal-1</td>
<td>0.40</td>
<td>0.93</td>
<td>0.86</td>
<td>0.61</td>
<td>0.66</td>
<td>0.43</td>
<td>0.63</td>
<td>0.47</td>
<td>7.6</td>
<td>1.43</td>
<td>1.04</td>
<td>1.02</td>
<td>1.07</td>
<td>1.04</td>
<td>8.6</td>
</tr>
<tr>
<td>P3</td>
<td>Missakeswal-3</td>
<td>0.36</td>
<td>0.92</td>
<td>0.86</td>
<td>0.62</td>
<td>0.65</td>
<td>0.41</td>
<td>-</td>
<td>-</td>
<td>7.2</td>
<td>1.38</td>
<td>1.02</td>
<td>0.99</td>
<td>1.02</td>
<td>1.01</td>
<td>7.8</td>
</tr>
<tr>
<td>P4</td>
<td>Rajian-1</td>
<td>0.36</td>
<td>0.94</td>
<td>0.87</td>
<td>0.60</td>
<td>0.64</td>
<td>0.44</td>
<td>-</td>
<td>-</td>
<td>6.3</td>
<td>1.61</td>
<td>1.03</td>
<td>0.80</td>
<td>0.88</td>
<td>5.5</td>
<td>0.91</td>
</tr>
<tr>
<td>P5</td>
<td>Rajian-3A</td>
<td>0.37</td>
<td>0.93</td>
<td>0.88</td>
<td>0.58</td>
<td>0.63</td>
<td>0.45</td>
<td>0.62</td>
<td>0.52</td>
<td>5.7</td>
<td>1.44</td>
<td>0.98</td>
<td>0.90</td>
<td>0.94</td>
<td>5.6</td>
<td>0.92</td>
</tr>
<tr>
<td>P6</td>
<td>Kal-1</td>
<td>0.38</td>
<td>0.93</td>
<td>0.90</td>
<td>0.56</td>
<td>0.61</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td>6.2</td>
<td>1.64</td>
<td>1.05</td>
<td>0.96</td>
<td>0.85</td>
<td>5.9</td>
<td>0.94</td>
</tr>
<tr>
<td>P7</td>
<td>Kal-2</td>
<td>0.41</td>
<td>0.94</td>
<td>0.87</td>
<td>0.57</td>
<td>0.63</td>
<td>0.45</td>
<td>0.62</td>
<td>0.50</td>
<td>7.8</td>
<td>1.50</td>
<td>1.00</td>
<td>0.92</td>
<td>0.95</td>
<td>6.5</td>
<td>0.99</td>
</tr>
<tr>
<td>P8</td>
<td>Fimkasser-1</td>
<td>0.40</td>
<td>0.93</td>
<td>0.88</td>
<td>0.59</td>
<td>0.61</td>
<td>0.47</td>
<td>0.64</td>
<td>0.53</td>
<td>8.1</td>
<td>1.85</td>
<td>1.15</td>
<td>1.04</td>
<td>1.03</td>
<td>6.4</td>
<td>0.98</td>
</tr>
<tr>
<td>P9</td>
<td>Fimkasser-4</td>
<td>0.45</td>
<td>0.92</td>
<td>0.88</td>
<td>0.61</td>
<td>0.64</td>
<td>0.47</td>
<td>-</td>
<td>-</td>
<td>8.0</td>
<td>1.61</td>
<td>1.12</td>
<td>1.11</td>
<td>0.93</td>
<td>6.8</td>
<td>1.01</td>
</tr>
<tr>
<td>P10</td>
<td>Chaknaurang-1A</td>
<td>0.35</td>
<td>0.96</td>
<td>0.89</td>
<td>0.57</td>
<td>0.59</td>
<td>0.48</td>
<td>0.64</td>
<td>0.53</td>
<td>8.4</td>
<td>1.96</td>
<td>1.14</td>
<td>0.97</td>
<td>0.91</td>
<td>4.7</td>
<td>0.85</td>
</tr>
<tr>
<td>P11</td>
<td>Minwal-1</td>
<td>0.31</td>
<td>0.94</td>
<td>0.90</td>
<td>0.59</td>
<td>0.59</td>
<td>0.46</td>
<td>0.62</td>
<td>0.50</td>
<td>5.7</td>
<td>2.31</td>
<td>1.24</td>
<td>1.07</td>
<td>0.85</td>
<td>4.5</td>
<td>0.84</td>
</tr>
<tr>
<td>P12</td>
<td>Joyamir-4</td>
<td>0.38</td>
<td>0.93</td>
<td>0.85</td>
<td>0.60</td>
<td>0.62</td>
<td>0.45</td>
<td>0.64</td>
<td>0.53</td>
<td>6.9</td>
<td>2.17</td>
<td>1.18</td>
<td>1.07</td>
<td>0.90</td>
<td>4.4</td>
<td>0.83</td>
</tr>
<tr>
<td>P13</td>
<td>Turkwal-1</td>
<td>0.45</td>
<td>0.97</td>
<td>0.92</td>
<td>0.60</td>
<td>0.63</td>
<td>0.45</td>
<td>0.59</td>
<td>0.48</td>
<td>5.5</td>
<td>1.39</td>
<td>0.95</td>
<td>0.95</td>
<td>1.26</td>
<td>1.16</td>
<td>8.2</td>
</tr>
<tr>
<td>P14</td>
<td>Pindori-4</td>
<td>0.73</td>
<td>1.00</td>
<td>1.00</td>
<td>0.64</td>
<td>0.63</td>
<td>0.47</td>
<td>0.65</td>
<td>0.48</td>
<td>6.8</td>
<td>1.25</td>
<td>0.95</td>
<td>0.97</td>
<td>1.14</td>
<td>1.08</td>
<td>11.6</td>
</tr>
<tr>
<td>P15</td>
<td>Dhurnal-1</td>
<td>0.67</td>
<td>1.00</td>
<td>1.00</td>
<td>0.63</td>
<td>0.61</td>
<td>0.45</td>
<td>0.62</td>
<td>0.47</td>
<td>7.7</td>
<td>1.29</td>
<td>0.91</td>
<td>1.01</td>
<td>1.16</td>
<td>1.10</td>
<td>11.5</td>
</tr>
<tr>
<td>P16</td>
<td>Dhurnal-6</td>
<td>0.66</td>
<td>1.00</td>
<td>1.00</td>
<td>0.63</td>
<td>0.61</td>
<td>0.43</td>
<td>-</td>
<td>-</td>
<td>7.1</td>
<td>1.23</td>
<td>0.96</td>
<td>0.98</td>
<td>1.14</td>
<td>1.08</td>
<td>10.7</td>
</tr>
<tr>
<td>P17</td>
<td>Toot-10A</td>
<td>0.70</td>
<td>1.00</td>
<td>0.92</td>
<td>0.61</td>
<td>0.63</td>
<td>0.44</td>
<td>-</td>
<td>-</td>
<td>7.4</td>
<td>1.39</td>
<td>1.00</td>
<td>1.07</td>
<td>1.04</td>
<td>9.2</td>
<td>1.18</td>
</tr>
<tr>
<td>P18</td>
<td>Toot-12</td>
<td>0.70</td>
<td>0.90</td>
<td>0.92</td>
<td>0.61</td>
<td>0.62</td>
<td>0.47</td>
<td>0.61</td>
<td>0.50</td>
<td>8.5</td>
<td>1.23</td>
<td>0.94</td>
<td>0.96</td>
<td>1.05</td>
<td>8.5</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Ts/(Ts + Tm): 18α(H)-22,29,30-trisnorhopane/18α(H)-22,29,30-trisnorhopane + 17α(H)-22,29,30-trisnorhopane; αβ/(αβ + βα), C_{29} Hop: 17α(H),21β(H)-30-norhopane/17α(H),21β(H)-30-norhopane; αβ/(αβ + βα), C_{30} Hop: 17α(H),21β(H)-hopane/17α(H),21β(H)-hopane; (S/S+R), C_{29} hop: 22S/22S+22R, 17α(H)-bishomohopane; (ββ/(αα+ββ)) C_{29} Ster: 14β(H),21β(H)-hopane/14β(H),21β(H)-hopane; 20S/20S+20R 14α(H),21α(H)-ethylcholestan; MAI: methyl adamantane index (1-MA/1-MA + 2-MA), [162]; MDI: methyl diamantane index (4-MD/1-MD + 3-MD + 4-MD), [162]; DNR-1: dimethylnapthalene ratio 1 (2,6- + 27-DMN/1,5-DMN), [26]; TNR-1: trimethylnapthalene ratio 1 (2,3,6-TMN/1,4,6- + 1,3,5-TMN), [10]; TNR-2: trimethylnapthalene ratio 2 (2,3,6- + 1,3,7-TMN)/1,4,6- + 1,3,5- + 1,3,6-TMN); R_c: calculated vitrinite reflectance (0.6 × MPI-1 + 0.4), [156]; MDR: 4-MDBT/1-MDBT, [11]; Rcs: 0.07×MDR + 0.5; [4]; MDR': 4-MDBT/(4-MDBT + 1-MDBT), [40]; -: not determined
Fig. 5.3  (a) Hopanes maturity parameters plot between C₂₉ vs C₃₀ of αβ/(αβ+βα) (c.f. [152]) (b) calculated vitrinite reflectance diagram from $R_{cb}$ (TNR-2; [11]) and $R_e$ (MPI-1; [156]) show different thermal maturation stages of oil generation window.
The sterane based maturity parameters, 20S/(20S+20R) ethylcholestane and ββ/(αα+ββ) ethylcholestane, lie within a close range of 0.41 to 0.48 and 0.59 to 0.66 respectively (Table 5.2) whereas the equilibrium for these parameters occurs between 0.52 to 0.55 and 0.67 to 0.71 respectively [150]. The observed values are lower than equilibrium values supporting a similar moderate maturity of analysed samples [150]. Despite the fact that 20S/(20S+20R) ratio is a useful maturity parameter, factors other than thermal maturities which are likely to affect this ratio are reversal of this ratio within high maturity interval [157-158], could be responsible for lower values. Moreover, ββ/(αα+ββ) ratio is also influenced by source rock mineral matrix and migration, where equilibrium for carbonate source oils is reached at comparatively lower values [159] and more migrated oils show higher values of this ratio [160]. However in this study it is suggested that the highest values of 20S/(20S+20R) and ββ/(αα+ββ) to reach equilibrium for the Potwar basin oils is 0.48 and 0.66 respectively.

Few limitations have been put forward to thermal maturity parameters described above; for example, sterane and hopane isomerization i.e. S/(S + R) parameters reach effective end-points or equilibrium before the main part of oil window, therefore not very effective for mature oils and condensates [161]. In this scenario parameters based on diamondoid and aromatic hydrocarbons are more effective for better evaluation of thermal maturity of mature oils and condensates. Chen et al. [162] suggested methyl adamantane index (MAI) and methyl diamantane index (MDI) as maturity indicators for crude oils and condensates from Chinese basins. The MAI and MDI values were calculated using m/z 136, 137 and m/z 188, 187, respectively from saturated fractions and are listed in Table 5.2. The MAI (0.59-0.65) and MDI (0.46-0.53) values clearly indicate the same range of thermal maturities for these crude oils. The calibration of MAI and MDI with vitrinite reflectance (R_o) reported by Chen et al. [162] for Chinese crude oils and condensates show that MAI > 0.5 and MDI > 0.4 is equivalent to R_o > 1.1 and R_o > 1.3, respectively. The thermal maturity of Potwar Basin oils is based on equivalent vitrinite reflectance shows the post oil generation window.
The commonly used thermal maturity parameter from aromatic hydrocarbons is methylphenanthrene index 1 (MPI-1) and appears to be as useful as vitrinite reflectance for maturity assessment [4,25]. The MPI-1 and calculated vitrinite reflectance ($R_c$) values of the samples are listed in Table 5.2. The MPI-1 and $R_c$ is in the range of 0.75 to 1.26 and 0.85 to 1.15 respectively show higher maturity of source rocks generating these oils. The $R_c$ for Adhi-5 (0.85, Table 5.2) showed mature status of thermal maturity while all other values (>0.9) indicate postmature level of thermal maturity for Potwar Basin oils [4]. Dimethylnaphthalene ratio (DNR-1, see Table 5.2 for definition) is another useful aromatic hydrocarbon maturity parameter for samples having mean vitrinite reflectance ($R_o$) equal or higher than 1% where it shows linear increase in value from 2 to 12 with increase in thermal maturity [4,163]. The DNR-1 > 5.5 (Table 5.2, mostly ~7-8) clearly revealed that thermal maturity of the Potwar Basin oils is reached late oil generation window. Trimethylnaphthalene ratio 1 (TNR-1, see Table 5.2 for definition) has been calibrated with sterane isomerization ratio (20S/20R) where sterane isomerization ratio of oils reached to equilibrium value when TNR-1 ratio became >1 [10]. TNR-1 values for Potwar Basin oils are shown in Table 5.2 that show >1 (mostly >1.2) for all samples indicate maturity of source rocks generating these oils reached to postmature level [10]. Similarly, trimethylnaphthalene ratio 2 (TNR-2, see Table 5.2 for definition) is another useful aromatic hydrocarbon thermal maturity parameter which was calibrated with mean vitrinite reflectance ($R_o$) and show good agreement with increase in thermal maturity. The TNR-2 value (0.9-1.2, Table 5.2) and calculated vitrinite reflectance $R_{cb}$ values (>0.95, Table 5.2) from TNR-2 indicate thermal maturity of the oil samples from the Potwar Basin reached to late oil generation window [11]. A cross plot (Fig. 5.3b) were drawn from calculated vitrinite reflectance values i.e. $R_{cb}$ (TNR-2) vs $R_c$ (MPI-1) clearly indicate thermal maturity of Potwar Basin oils reached to late oil generation window.

Few anomalies are observed in alkylnaphthalenes maturity parameters. For example, TNR-1 shows a wide range of values from 1.04 to 2.31 for Potwar Basin oils although most of the oils lie between 1 and 2 but high values for some of the group B oils are observed (TNR-1 > 2.0, Table 5.2). These differences in TNR-1 ratios are most
probably due to the effects of biodegradation on aromatic fractions in group B oils (Chapter 6). Affects of biodegradation on alkynaphthalenes have been shown to affect different isomers and thus different susceptibilities towards biodegradation [17] and thermal maturity parameters are adversely changed using certain isomers in thermal maturity ratio calculations [38,164].

A number of studies have used alkyl dibenzothiophenes as maturity parameters [11,40,37,53,165]. Commonly used parameter, methyl dibenzothiophene ratio (MDR) derived based on similar chemical phenomenon as for MPI-1 i.e. a methyl shift from thermally less stable isomer (1-MDBT) to thermally more stable isomer (4-MDBT) with increase in thermal maturity [11]. Moreover, MDR was calibrated with vitrinite reflectance and reported as \( R_{cs} \) [165]. DMR and calculated vitrinite reflectance \( (R_{cs}) \) from Potwar Basin crude oils are shown in Table 5.2. A wide range of values are observed for DMR (4.4-11.6) and \( R_{cs} \) (0.83-1.36) indicate peak to late oil generation window thermal maturity of these oils. DMR has shown to be affected by variation in expulsion stages of 1-MDBT and 4-MDBT isomers from kerogen [40] and Dzou et al. [166] pointed out its limitation for coal samples where it does not show linear relationship between 0.5 to 1.0% vitrinite reflectance. Radke and Willsch [40] introduced a revised form of MDR as MDR’ where it was calculated by traditional biomarker maturity parameters way i.e. 4-MDBT/(4-MDBT + 1-MDBT). The values for MDR’ given in Table 5.2 indicate narrow range of values (0.81-0.92) and results revealed higher thermal maturity for Potwar Basin oils [40].

### 5.2.5 Lithology and Depositional Environment

The crude oils listed in Table 5.1 were examined for lithology and depositional environment using aliphatic and aromatic hydrocarbon parameters. Pristane (VI) to phytane (VII) (Pr/Ph) ratio is a commonly used for depositional environment. Pr/Ph ratios > 3.0 have been described for terrestrial input deposited under oxic conditions and low Pr/Ph ratios i.e. < 1 indicate anoxic/hypersaline or carbonate environment while Pr/Ph ratios 1 to 3 have been associated with marine oxic/dysoxic conditions [1, 45]. The
ratio of dibenzothiophene (XXVII) to phenanthrene (XXIV) (DBT/P) is an indicator of source rock lithology. The DBT/P ratio >1 indicates a carbonates type facies, whereas incorporation of sulfur into OM produces higher DBT while DBT/P ratio <1 indicates a shale type lithology, where sulfur reacts with iron species in the clay minerals and in turn produces less DBT. DBT/P were measured from GC-MS analysis of the aromatic fraction using m/z 184 and 178 for DBT and P respectively, while Pr/Ph ratios were determined from TIC of saturated fractions. Cross plot of DBT/P vs Pr/Ph suggested by Hughes et al. [167] has been used to infer lithology-depositional environment of the OM and results are shown in Fig. 5.4a. The largest set of oils from the Potwar Basin (Group B and C) are shown to have originated from marine-lacustrine shale source rocks and Pr/Ph ratio in the range 1.0 to 2.0 support a marine oxic/dysoxic depositional environment (Table 5.1). While group A oil (Adhi-5) shows a higher Pr/Ph ratio (3.2) indicating highly oxic fluvio-deltaic depositional environment of OM. However, a study on crude oils from NW Germany showed contrast results where marine sulfur rich samples indicate lacustrine, sulfur poor lithology/depositional environment and caution was referred to use this Hughes diagram [7].

C\textsubscript{\text{30}} 17α-diahopane (C\textsubscript{\text{30})*, XIV} has been suggested to be a rearranged product of regular hopanes [168] by clay-mediated acidic catalysis and it mostly occurs in marine clastic oxic-suboxic depositional environments, where oxic/clay rich depositional conditions rearrange hopanes to diahopanes [45]. The C\textsubscript{\text{30}} 17α-diahopane/ C\textsubscript{\text{30}} 17α-hopane ratio is shown to be high in clastic source rocks and oxic depositional environment. Similarly, the regular steranes change to rearranged steranes by clay mediated rearrangement reactions in source rocks [169] and diasterane/sterane ratios have been widely used for evaluation of source rock lithology of OM [45]. Low diasterane/sterane ratios in petroleum indicate anoxic clay-poor source rocks that are characteristics of carbonates while higher diasterane/sterane ratios refer to oxic clastic source rocks indicative of marine and deltaic environments [45].
Fig. 5.4  (a) Pr/Ph versus DBT/P plot indicates lithology and depositional environment [167]  (b) $C_{30}$ $17\alpha$-diahopane/$C_{30}$ $17\alpha$-hopane vs $C_{29}$ diasteranes/sterane plot shows the affects of clay and depositional environment on Potwar Basin oils (c.f. [45] and references therein).
A plot between C$_{30}$ 17α-diahopane/C$_{30}$ 17α-hopane vs C$_{29}$ diasteranes/sterane ratios is shown in Fig. 5.4b and samples from the Potwar Basin fall into three groups. Groups B and C were similar in Hughes diagram (Fig. 5.4a) are separated into two different groups, however both groups (B and C) showed consistent for depositional environment is marine. Although both groups located near to each other in the diagram but showed two different places in diagram indicate slight variation in lithology and depositional environment of OM between these groups (Fig. 5.4b). This variation revealed that group B shows relatively higher diasteranes/sterane ratios compared to the group C indicating that the group B oils are generated from comparatively more clastic rocks, while group C show higher diahopane/hopane ratios indicating that the group C oils were generated from comparatively more oxic deposited source rocks [45]. The oil from group A (Adhi-5) shows higher values of diahopane/hopane and diasteranes/sterane ratio (0.38 and 0.97, respectively) separating this oil from all the other oils (Fig. 5.4b) which indicate a clay rich oxic depositional environment as indicated by Hughes diagram (Fig. 5.4a). The Adhi-5 was probably generated from oxic/clay rich source rocks and is consistent with the C$_{30}$ 17α-diahopane/C$_{29}$ 18α-30-norneohopane (C$_{29}$Ts, XV) ratio. The C$_{30}$ 17α-diahopane/C$_{29}$Ts ratio has been suggested as a good indicator of oxic/suboxic depositional settings of OM [45] and this ratio for group A oil is significantly high (2.23) indicating an oxic environment of deposition. An anomaly (high value) is observed in the C$_{30}$ 17α-diahopane/C$_{30}$ 17α-hopane vs C$_{29}$ diasteranes/sterane diagram for the Pindori-4 crude oil (Fig. 5.4b). The reason for this anomaly could be related to any factor such as source organic facies, amount of clay contents and total organic carbon that has been suggested to be affecting diahopane/hopane and/or diasteranes/sterane ratios ([45,170] and references therein).

**5.2.5.1 Heterocyclic aromatic hydrocarbons**

Distribution of heterocyclic aromatic hydrocarbons such as DBTs, dibenzofurans (DBFs) and Fs has been related to the source rock lithology and depositional environment
Whereas abundance of DBTs was related to marine source rocks while abundant Fs and DBFs were referred to freshwater source rocks [12].

Relative distribution of DBTs, DBFs and Fs were calculated from sum of the peak areas of parent compounds (non-alkylated) and methyl substituted isomers. A bar diagram was constructed that indicate relative percentages of DBTs, DBFs and Fs in Potwar Basin oils (Fig. 5.5). Groups A show abundance of Fs than DBTs while DBFs are also present in considerable abundance. Group B oils show higher abundance of DBTs while DBFs and Fs are present in almost negligible concentrations while group C oils show almost equal abundance of Fs and DBTs except last two oils (P17-P18). These results reveal that group B oils showed a strong influence of marine suboxic deposition of OM [12] where sulfur heterocyclic aromatic hydrocarbons (DBTs) are present in abundance. While group A show oxic depositional environment of OM indicated by abundant Fs consistent with previous reported results [12-13]. Group C crude oils showed mixed distribution of Fs and DBTs where Dhurnal oils (P15 and P16) showed comparable equal abundance of Fs and DBTs while Toot oils (P17 and P18) indicate higher Fs than DBTs. These results most probably indicate indigenous variation in depositional environment. Similarly, three mixed concentration profiles of Fs and DBTs distribution has been reported from marine source rocks and crude oils for oil-source rock correlation study [13].

5.2.6 Source of OM

Source OM of Potwar Basin oils were initially assessed using distribution of aliphatic biomarkers and subsequently PAHs distributions are used to classify the source origin of the petroleum. Specifically, alkynaphthalenes, alkylphenanthrenes and triaromatic steroids are reported as aromatic biomarkers from Potwar Basin oils.

Distribution of tricyclic terpanes (TT) and hopanes is shown in \( m/\ell \) 191 mass chromatograms (Fig. 5.6) of the representative samples from all delineated groups of Potwar Basin. The parameters for the assessment of source OM from tricyclic and pentacyclic terpanes and steranes are listed in Table 5.3. Group A oil shows significantly
Fig. 5.5 Bar diagram shows relative percentages of DBTs, DBFs, Fs in Potwar Basin oils.
low concentration of tricyclic terpane except for C_{19}-TT and C_{24}-tetracyclic terpane (TeT, IX), both compounds are indicator of terrestrial source OM [45,173]. The correlation diagram C_{19}/(C_{19}+C_{23}) TT vs C_{24} TeT/(C_{24} TeT + C_{23} TT) shown in Fig. 5.7 clearly differentiates three groups of petroleum on the bases of difference in source OM [174-175]. Group A oil (Adhi-5) located in the top right corner of the plot indicating source OM is terrestrial origin. Group B and C located in lower left corner of the diagram indicate marine source OM (Fig. 5.7). However difference in positions of group B and C in the diagram (Fig. 5.7) revealed slight variation in source OM for these oils. Moreover, TT and hopane parameters such as C_{23} TT/C_{30} 17\alpha(H)-hopane, and C_{24} TeT/C_{30} 17\alpha(H)-hopane ratios (Table 5.3) indicated typically marine OM for group B and C oils [45] however two different ranges of these ratios indicate difference in source input in Potwar Basin oils (Table 5.4). The triterpane distribution of group B oil is typical mature marine crude oil (Fig. 5.6b) and the major compounds in the chromatograms are 30 and 29 17\alpha(H)-hopanes. Hopanes are in higher relative abundance compared to TT and this feature differentiates group B oils from other two groups. The representative mass chromatogram m/z 191 for group C oil shows significantly higher abundance of extended TT upto C_{41} and possibly higher (Fig. 5.6c) whereas C_{23} TT is the most abundant compound while hopanes show significantly lower abundance. This is the important feature of group C oils to differentiate from other groups of oils. Total TT/hopanes ratio for group C oils is significantly high compared to the rest of the oils indicate a difference in source OM for this group (Tables 5.3 and 5.4). The higher abundance of TT in Potwar Basin oils is probably associated with algal source of OM. Similarly, higher total sterane/hopane ratio >0.6 (~1.0 for most of the oils, Table 5.4) for group C oils reflects greater eukaryotic input (higher algal input). It could be conclude that at least three groups of petroleum have been produced from different source rocks within the Potwar Basin. A comprehensive Table 5.4 is constructed to show different ranges of aliphatic and aromatic biomarkers ratios of source and depositional environment interpretations for Potwar Basin oils.
Fig. 5.6 Mass chromatograms (m/z 191) showing distribution of tricyclic (TT) and pentacyclic terpanes (hopanes, H) in Potwar Basin crude oils. Numbers on peak indicate TT, 24*, C24-tetracyclic terpane and number with H indicate hopanes.
Table 5.3  Source OM and depositional environments parameters of Potwar Basin oils

<table>
<thead>
<tr>
<th>No</th>
<th>oil and well</th>
<th>$C_{19}^*/(C_{19}+C_{23})$ TT</th>
<th>$C_{24}$TeT/($C_{24}$TeT+$C_{23}$TT)</th>
<th>$C_{23}$ TT/$C_{30}$ hopane</th>
<th>$C_{24}$-TeT/$C_{30}$ hopane</th>
<th>$C_{29}$/$C_{30}$ αβ hop</th>
<th>$C_{30}^*/C_{29}$ αβ hop</th>
<th>Ster/hop</th>
<th>Dia/Ster</th>
<th>Total TT/Hop</th>
<th>$C_{27}$/$C_{29}$, dia</th>
<th>$C_{29}$/$C_{21}$ TAS</th>
<th>1-MP/9-MP</th>
<th>1,7-DMP/X</th>
<th>1,2,6-/1,2,4-TMN</th>
<th>125-/127-TMN</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Adhi-5</td>
<td>0.88</td>
<td>0.87</td>
<td>0.87</td>
<td>0.29</td>
<td>0.60</td>
<td>0.38</td>
<td>0.29</td>
<td>0.97</td>
<td>0.83</td>
<td>1.76</td>
<td>0.93</td>
<td>0.53</td>
<td>2.49</td>
<td>3.46</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>Missakeswal-1</td>
<td>0.49</td>
<td>0.47</td>
<td>0.38</td>
<td>0.26</td>
<td>0.63</td>
<td>0.34</td>
<td>0.24</td>
<td>0.55</td>
<td>0.70</td>
<td>1.25</td>
<td>0.75</td>
<td>0.28</td>
<td>1.46</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>Missakeswal-3</td>
<td>0.46</td>
<td>0.49</td>
<td>0.35</td>
<td>0.22</td>
<td>0.63</td>
<td>0.34</td>
<td>0.24</td>
<td>0.30</td>
<td>0.70</td>
<td>1.25</td>
<td>0.75</td>
<td>0.28</td>
<td>1.58</td>
<td>1.93</td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>Rajian-1</td>
<td>0.40</td>
<td>0.56</td>
<td>0.42</td>
<td>0.15</td>
<td>0.57</td>
<td>0.36</td>
<td>0.23</td>
<td>0.45</td>
<td>0.79</td>
<td>1.77</td>
<td>0.76</td>
<td>0.28</td>
<td>1.58</td>
<td>2.31</td>
<td></td>
</tr>
<tr>
<td>P5</td>
<td>Rajian-3A</td>
<td>0.40</td>
<td>0.55</td>
<td>0.45</td>
<td>0.15</td>
<td>0.57</td>
<td>0.36</td>
<td>0.23</td>
<td>0.45</td>
<td>0.79</td>
<td>1.77</td>
<td>0.76</td>
<td>0.28</td>
<td>1.58</td>
<td>2.31</td>
<td></td>
</tr>
<tr>
<td>P6</td>
<td>Cal-1</td>
<td>0.39</td>
<td>0.54</td>
<td>0.44</td>
<td>0.17</td>
<td>0.54</td>
<td>0.42</td>
<td>0.27</td>
<td>0.45</td>
<td>0.82</td>
<td>1.68</td>
<td>0.75</td>
<td>0.25</td>
<td>1.52</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>P7</td>
<td>Cal-2</td>
<td>0.38</td>
<td>0.52</td>
<td>0.49</td>
<td>0.22</td>
<td>0.60</td>
<td>0.51</td>
<td>0.34</td>
<td>0.72</td>
<td>1.66</td>
<td>0.71</td>
<td>0.26</td>
<td>1.44</td>
<td>1.74</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>P8</td>
<td>Fimkassar-1</td>
<td>0.41</td>
<td>0.57</td>
<td>0.44</td>
<td>0.15</td>
<td>0.49</td>
<td>0.39</td>
<td>0.27</td>
<td>0.70</td>
<td>1.70</td>
<td>0.75</td>
<td>0.27</td>
<td>1.52</td>
<td>1.75</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>P9</td>
<td>Fimkassar-4</td>
<td>0.45</td>
<td>0.52</td>
<td>0.30</td>
<td>0.18</td>
<td>0.35</td>
<td>0.68</td>
<td>0.72</td>
<td>0.77</td>
<td>1.53</td>
<td>0.76</td>
<td>0.28</td>
<td>1.36</td>
<td>1.33</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>P10</td>
<td>Chaknaurang-1A</td>
<td>0.33</td>
<td>0.61</td>
<td>0.38</td>
<td>0.11</td>
<td>0.40</td>
<td>0.26</td>
<td>0.83</td>
<td>2.04</td>
<td>0.77</td>
<td>2.04</td>
<td>0.25</td>
<td>1.47</td>
<td>2.04</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>P11</td>
<td>Minwal-1</td>
<td>0.30</td>
<td>0.63</td>
<td>0.39</td>
<td>0.07</td>
<td>0.38</td>
<td>0.20</td>
<td>0.87</td>
<td>2.28</td>
<td>0.81</td>
<td>0.25</td>
<td>1.57</td>
<td>2.44</td>
<td>2.44</td>
<td>2.44</td>
<td></td>
</tr>
<tr>
<td>P12</td>
<td>Joyamir-4</td>
<td>0.38</td>
<td>0.55</td>
<td>0.43</td>
<td>0.20</td>
<td>0.33</td>
<td>0.59</td>
<td>0.45</td>
<td>0.72</td>
<td>1.35</td>
<td>0.25</td>
<td>1.55</td>
<td>2.36</td>
<td>2.36</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>P13</td>
<td>Turkwal-1</td>
<td>0.44</td>
<td>0.55</td>
<td>0.47</td>
<td>0.19</td>
<td>0.35</td>
<td>0.46</td>
<td>0.84</td>
<td>1.43</td>
<td>0.74</td>
<td>0.27</td>
<td>1.64</td>
<td>1.57</td>
<td>1.57</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td>P14</td>
<td>Pindori-4</td>
<td>0.49</td>
<td>0.51</td>
<td>1.93</td>
<td>2.03</td>
<td>0.75</td>
<td>0.86</td>
<td>1.24</td>
<td>2.37</td>
<td>0.83</td>
<td>0.97</td>
<td>0.69</td>
<td>0.28</td>
<td>1.50</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td>P15</td>
<td>Dhurnal-1</td>
<td>0.34</td>
<td>0.44</td>
<td>1.54</td>
<td>1.22</td>
<td>0.61</td>
<td>0.32</td>
<td>1.50</td>
<td>0.66</td>
<td>1.28</td>
<td>0.96</td>
<td>0.79</td>
<td>0.32</td>
<td>2.20</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>P16</td>
<td>Dhurnal-6</td>
<td>0.33</td>
<td>0.45</td>
<td>1.16</td>
<td>0.93</td>
<td>0.51</td>
<td>0.29</td>
<td>1.45</td>
<td>1.68</td>
<td>1.23</td>
<td>1.24</td>
<td>0.72</td>
<td>0.34</td>
<td>1.77</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>P17</td>
<td>Toot-10A</td>
<td>0.36</td>
<td>0.40</td>
<td>0.86</td>
<td>0.58</td>
<td>0.26</td>
<td>0.74</td>
<td>0.26</td>
<td>1.07</td>
<td>1.18</td>
<td>0.76</td>
<td>0.34</td>
<td>1.84</td>
<td>1.40</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td>P18</td>
<td>Toot-12</td>
<td>0.32</td>
<td>0.44</td>
<td>0.50</td>
<td>0.57</td>
<td>0.23</td>
<td>0.58</td>
<td>2.15</td>
<td>1.27</td>
<td>1.04</td>
<td>0.79</td>
<td>0.33</td>
<td>2.16</td>
<td>1.15</td>
<td>1.15</td>
<td></td>
</tr>
</tbody>
</table>

$C_{19}^*/(C_{19}+C_{23})$ TT: $C_{19}$-tricyclic terpene/(C_{19}-tricyclic terpene + C_{23} tricyclic terpene); $C_{24}$TeT/($C_{24}$TeT+$C_{23}$TT): $C_{24}$-tetracyclic terpene/(C_{24}-tetracyclic terpene + C_{23} tricyclic terpene); $C_{23}$ TT/C30-hopane: C_{23} tricyclic terpene/C_{30}-αβ hopane C_{24} TeT: C_{24} tetracyclic terpene/C_{30}-αβ hopane; $C_{30}^*/C_{30}$ αβ-hopane: 30, αβ-diahopane/ C_{30} αβ- hopane; C_{30}^*/C_{29} Ts: 30, αβ-diahopane/18α(H)-30-norneohopane; C_{31} (R+S)/C_{30} hop: C_{31} αβ-homohopane (22S+22R)/C_{30} αβ-hopane; Ster/hop: total steranes/total hopanes; Dia/ster C_{32}: βα/(αα+ββ) ethylecholestan e; total TT/Hop: total tricyclics/hopanes; C_{27}/C_{29} dia, βα-cholestan e/βα-ethylecholestan e, R+S; C_{29}/C_{21} TAS, C_{29}/C_{21} triaromatic steroids; 1-MP/9-MP: 1-methylphenanthrene/9- methylphenanthrene; 1,7-DMP/X; 1,7-dimethylphenanthrene/(1,3-+3,9-+2,10+3,10-DMP); TMN: trimethylphthalene
Fig. 5.7  Cross plot between $\frac{C_{19}}{C_{19} + C_{23}}$ TT and $\frac{C_{24} \text{ TeT}}{C_{24} \text{ TeT} + C_{23} \text{ TT}}$ shows difference in source material in Potwar Basin oils [c.f. 173-175].
Table 5.4  Biomarkers parameters limits for Potwar Basin oils

<table>
<thead>
<tr>
<th>Parameters*</th>
<th>Group A</th>
<th>Group B</th>
<th>Group C</th>
<th>Interpretation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C19/(C19+C23) TT</td>
<td>~0.9</td>
<td>0.5-0.3</td>
<td>~0.3</td>
<td>Gp A terrestrial,</td>
<td>[45, 175]</td>
</tr>
<tr>
<td>C24TeT/ (C24TeT+C23TT)</td>
<td>~0.8</td>
<td>&gt;0.5</td>
<td>&lt;0.5</td>
<td>Gp A terrestrial</td>
<td>[173-175]</td>
</tr>
<tr>
<td>C23 TT/C30 hopane</td>
<td>&lt;0.1</td>
<td>0.23-0.46</td>
<td>&gt;0.5 (~1.0)</td>
<td>Gp B and C marine, C higher marine input</td>
<td>[45]</td>
</tr>
<tr>
<td>C24-TeT/C30 hopane</td>
<td>&lt;0.3</td>
<td>0.3-0.5</td>
<td>&gt;0.5</td>
<td>Gp B and C marine OM input</td>
<td>[45]</td>
</tr>
<tr>
<td>Total TT/Hopanes</td>
<td>-0.2</td>
<td>0.3-0.6</td>
<td>1.0-2.5</td>
<td>Gp C shows algal source OM</td>
<td>[45,176]</td>
</tr>
<tr>
<td>C31(R+S)/C30- αβ hopane</td>
<td>-</td>
<td>&gt;0.8</td>
<td>&lt;0.5</td>
<td>Gp B showed more reducing depositional settings than Gp C</td>
<td>[45,177]</td>
</tr>
<tr>
<td>Steranes/hopanes</td>
<td>~0.3</td>
<td>&lt;0.4</td>
<td>&gt;0.6 (~1.0)</td>
<td>Higher marine (algal) input in Gp C</td>
<td>[45, 178]</td>
</tr>
<tr>
<td>βα/(ββ+αα) C27</td>
<td>-</td>
<td>&gt;0.45</td>
<td>&lt;0.45</td>
<td>Gp B generated from more clastic than Gp C</td>
<td>[45, 179]</td>
</tr>
<tr>
<td>βα/(ββ+αα) C29</td>
<td>~1.0</td>
<td>&gt;0.4</td>
<td>&lt;0.3</td>
<td>Gp A and Gp B showed greater clay affects</td>
<td>[45, 155]</td>
</tr>
<tr>
<td>Total diasteranes/steranes</td>
<td>&gt;1.0</td>
<td>0.65-1.0</td>
<td>&lt;0.4</td>
<td>Gp B shows higher clastic/mineral affects</td>
<td>[45]</td>
</tr>
<tr>
<td>Retene</td>
<td>Present</td>
<td>Absent</td>
<td>Absent</td>
<td>Gp A terrestrial</td>
<td>[5,32]</td>
</tr>
<tr>
<td>1,7-DMP/X</td>
<td>~0.53</td>
<td>&lt;0.28</td>
<td>&gt; 0.32</td>
<td>Gp A indicate terrestrial input</td>
<td>[5]</td>
</tr>
</tbody>
</table>

*: definition in Tables 5.2 and 5.3
Gp: Group
Abundance of certain methyl substituted isomers of naphthalene (XXIII) and phenanthrene (XXIV) has been reported as aromatic biomarkers derived from specific class of natural products [5,19,180]. β-Amyrine from higher plants angiosperm has been showed a source precursor for alkynaphthalenes [19,180]. Similarly abietane and pimarane type biological precursors from diterpenoids are more likely the source of alkylphenanthrenes [32]. Budzinski et al. [181] related a range of alkylphenanthrenes with marine and terrestrial source OM along with affect of thermal maturation. Distribution of certain isomers of alkynaphthalenes and alkylphenanthrenes were determined to evaluate the contribution of specific class of biological precursors to the source OM of Potwar Basin oils.

In alkynaphthalenes, abundance of 1,2,7-TMN, 1,2,5-TMN and 1,2,5,6-TeMN (see XXIII for naphthalene numbering system) in sediments and crude oils are suggested to be originate from angiosperms [19,182]. Aromatic seco-hopanes are also reported as source for 1,2,5-TMN and 1,2,5,6-TeMN [180]. The 1,2,6-TMN, 1,2,5,7-TeMN and 1,2,3,5-TeMN are supposed to be generated from microbial origin [183] while 1,2,4-TMN in marine sediments suggested as biomarker for tocopherole [66a]. In Potwar Basin oils, there is no noticeable abundance of any certain isomer of alkynaphthalenes were observed. However different alkynaphthalenes ratios were calculated and reported in Table 5.3. Fig. 5.8a shows a cross plot between 1,2,5-/1,2,7-TMN vs 1,2,6-/1,2,4-TMN ratios differentiate Potwar Basin oils into three groups. 1,2,7-TMN and 1,2,5-TMN has been exclusively suggested as angiosperm markers [19] however non-angiosperm natural products are also related to the source of 1,2,5-TMN [141]. The abundance of 1,2,5-TMN relative to 1,2,7-TMN in group A oils indicate different source precursor for these naphthalene isomers than those of angiosperms which is further supported by the absence of oleanane (a angiosperm biomarker) and its related products in saturated fractions (Fig. 5.6). Grice et al. [184] suggested that the origin of 1,2,5-TMN in boghead coals is drimanes by reporting similar δ13C values for both compounds.
Fig. 5.8 (a) Distribution relationship between TMN ratios of Potwar Basin oils (b) higher plant aromatic biomarkers ratios 1,7-DMP/X and 1-MP/9-MP [5] indicated terrestrial input for group A oil.
Source of 1,2,5-TMN in group A oil is also most likely the drimanes which are significantly abundant components in branch/cyclic fraction of group A oil (result not showed). Group B and C oils locate near to each other in the TMN ratios diagram indicate similar type of source for TMNs however both groups cluster at different places in the diagram indicate some difference in the source input [4,19].

In alkylphenanthrenes, 9-MP is related to the marine character of OM while 1-MP related to the terrestrial origin [181] and 1-MP/9-MP ratio was calculated from Potwar Basin oils reported in Table 5.3. 1,7-DMP/X ratio (X is 1,3-, 3,9, 2,10, 3,10-DMP isomers coeluted peak Radke et al., [11]) is successfully used for correlation study of crude oils having different source OM from various ages [5]. A plot between 1-MP/9-MP vs 1,7-DMP/X ratios (Fig. 5.8b) separated Potwar Basin oils in three groups where group A oil shows a separate place in the top right corner of the diagram (Fig. 5.8b). The abundance of 1-MP and 1,7-DMP clearly indicate terrestrial source precursor for these compounds in group A oil. 1,7-DMP has been suggested a biomarker from pimarane type diterpenoids abundant in ambers and resins [32,185]. Moreover the significant abundance of conifer resin aromatic biomarker retene (XXI, Fig. 4.12, Chapter 4) is observed in group A oil indicate that major contribution of source OM for this oil is higher plant resins. Group B and C oils show similar place in the diagram that show similar origin of alkylphenanthrenes however different position in the diagram indicate some difference in OM input.

5.2.6.2 Triaromatic steroids (TAS)

The distribution of TAS was monitored by ion 231 from aromatic fractions and Fig. 5.9 shows representative ion chromatograms (m/z: 231) from each group of Potwar Basin oils. Short (C₁₉ to C₂₂, XXa to XXc) and long chain (C₂₅ to C₂₈, XXe to XXh) TAS with different distributions are observed within the groups. Generally, short chain C₂₀ and C₂₁ compounds are present in higher abundance than long chain compounds. While
Fig. 5.9 Distribution of triaromatic steroids in Potwar Basin crude oils a) Adhi-5, b) Kal-2, c) Toot-12. Carbon number on peak refers to corresponding TAS (XXa to XXh).
distribution of long chain TAS clearly differentiates Potwar Basin oils into three groups. Where group A shows only C\textsubscript{27} and C\textsubscript{28} compounds while group B shows C\textsubscript{25} to C\textsubscript{28} compounds (Fig. 5.9). The absence (or below detection limit) of long chain TAS in group C oil representative chromatogram clearly differentiate this group from other two groups (Fig. 5.9c).

Generally, TAS from C\textsubscript{26} to C\textsubscript{28} compounds have been supposed to be originated from demethylation and aromatization of monoaromatic steroids from corresponding C\textsubscript{27} to C\textsubscript{29} compounds [47,186]. While short chain compounds has been apparently generated from homolytic scission of long chain triaromatic steroids with increase in thermal maturity [187-188]. Monoaromatic and TAS are very effective thermal maturity parameters for late oil generation window although it has been reported that these parameters are potentially source dependent [45]. Significantly higher abundance of C\textsubscript{20} and C\textsubscript{21} compounds and comparatively negligible concentrations of C\textsubscript{19} and C\textsubscript{22} compounds in oils indicate a different source precursor for these compounds. In long chain TAS, the presence of only two compounds (C\textsubscript{27} and C\textsubscript{28}) in group A, C\textsubscript{25} to C\textsubscript{28} compounds in group B and totally absent in group C oils clearly revealed that TAS from Potwar Basin are source dependent. Because full range of regular and rearranged steranes (C\textsubscript{27}, C\textsubscript{28}, C\textsubscript{29}) are significantly abundant in Potwar Basin oils that has been suggested as source for aromatic steroids [45]. But the presence and absence of certain carbon number triaromatic steroids indicate different source precursor for these compounds.

TAS (C\textsubscript{26}, C\textsubscript{27}, C\textsubscript{28}) has been shown effective correlation parameters and indicate similar associations with biological precursors (terrestrial, marine and lacustrine input) as referred by regular steranes and monoaromatic steroids [45,189-190]. Long chain TAS i.e. C\textsubscript{26}, C\textsubscript{27}, C\textsubscript{28} are not fully observed in all samples of Potwar Basin oils, however short chain compounds (C\textsubscript{20} and C\textsubscript{21}) are present all samples. A correlation diagram (Fig. 5.10) between C\textsubscript{20}/C\textsubscript{21} triaromatic steroids and C\textsubscript{27}/C\textsubscript{28} diasteranes differentiate Potwar Basin oils into three groups revealed that variation in relative abundance of aromatic steroids is controlled by source input.
Fig. 5.10 Distribution relationship between $C_{20}/C_{21}$ TAS and $C_{27}/C_{29}$ diasteranes from Potwar Basin oil clearly indicate three groups.
5.2.7 Biodegradation

The presence of heavy oils in reservoirs is mostly related by secondary processes such as biodegradation, water washing and phase separation [14,45-46]. Light to very heavy oils from Potwar Basin are present that indicate the alteration of hydrocarbons composition in reservoirs. A number of commonly used parameters have been used to assess the extent/level of biodegradation in Potwar Basin oils. Representative total ion chromatograms (TICs) of the saturated hydrocarbons fractions from each group of oils are shown in Fig. 5.11. The chromatograms from group A and C show full suite of \( n \)-alkanes and isoprenoids with no unresolved complex mixture (UCM) that indicates no signs of biodegradation. While TIC of saturated hydrocarbon fraction from representative group B oil shows substantial UCM and lack of \( n \)-alkanes indicating that these oils have been biodegraded and the remaining fraction has become enriched in high molecular weight unresolved components. Isoprenoids show resistance to biodegradation compared to the \( n \)-alkanes because \( n \)-alkanes are removed earlier than isoprenoids by bacteria during biodegradation. Hence isoprenoid/\( n \)-alkane ratios from saturated fractions increases with increase in biodegradation [191] and Pr/\( n \)-C\(_{17}\) and Ph/\( n \)-C\(_{18}\) ratios greater than 1 typically show the affects of biodegradation on crude oils. The plot of Pr/\( n \)-C\(_{17}\) vs. Ph/\( n \)-C\(_{18}\) (Fig. 5.12a) shows a trend consistent with biodegradation; these latter ratios increase with rising biodegradation. The top right corner of the diagram (Fig. 5.12a) shows Pr/\( n \)-C\(_{17}\) ratio > 1 indicates the affects of biodegradation on these oils. The API gravity is a bulk property that directly relates to gross compositions of crude oils. The Potwar Basin crude oils show a wide range of API gravities (16-48°; Table 5.1). Low API gravity (16-26.6°) for some of the oils particularly from eastern Potwar is consistent with biodegradation. A plot of API gravity vs Pr/\( n \)-C\(_{17}\) (Fig. 5.12b) shows inverse relationship, a high Pr/\( n \)-C\(_{17}\) and low API gravity (Fig. 5.12b) indicative of the oils affected by biodegradation. The results shows that extent of biodegradation for some of the crude oils in this study reaching up to level 3 on the biodegradation scale [46]. The extent of biodegradation on each crude oil of Potwar Basin is represented with level of biodegradation in Table 5.5. It is observed that some of the oils from group B are affected by minor biodegradation while group A and C are non-biodegraded (Table 5.5).
Fig. 5.11 Representative TICs of saturated fractions from Potwar Basin oils, Group A, Adhi-5; group B, Joyamir-4; group C, Dhurnal-1. Number on peaks refers to \( n \)-alkanes carbon numbers.
Fig. 5.12  (a) Plot of Pr\textsubscript{n}-C\textsubscript{17} vs Ph\textsubscript{n}-C\textsubscript{18} and (b) API value vs. Pr\textsubscript{n}-C\textsubscript{17} showing biodegradation trends in crude oils used in this study.
Table 5.5  Assessment of biodegradation results of Potwar Basin crude oils

<table>
<thead>
<tr>
<th>No</th>
<th>Oil and well</th>
<th>Group#</th>
<th>Bio/non-biodegraded</th>
<th>Biodegradation Level*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Adhi-5</td>
<td>A</td>
<td>Non-biodegraded</td>
<td>0</td>
</tr>
<tr>
<td>P2</td>
<td>Missakeswal-1</td>
<td>B</td>
<td>Non-biodegraded</td>
<td>0</td>
</tr>
<tr>
<td>P3</td>
<td>Missakeswal-3</td>
<td>B</td>
<td>Non-biodegraded</td>
<td>0</td>
</tr>
<tr>
<td>P4</td>
<td>Rajian-1</td>
<td>B</td>
<td>Biodegraded</td>
<td>2</td>
</tr>
<tr>
<td>P5</td>
<td>Rajian-3A</td>
<td>B</td>
<td>Biodegraded</td>
<td>2</td>
</tr>
<tr>
<td>P6</td>
<td>Kal-1</td>
<td>B</td>
<td>Biodegraded</td>
<td>3</td>
</tr>
<tr>
<td>P7</td>
<td>Kal-2</td>
<td>B</td>
<td>Biodegraded</td>
<td>2</td>
</tr>
<tr>
<td>P8</td>
<td>Fimkassar-1</td>
<td>B</td>
<td>Biodegraded</td>
<td>1</td>
</tr>
<tr>
<td>P9</td>
<td>Fimkassar-4</td>
<td>B</td>
<td>Biodegraded</td>
<td>1</td>
</tr>
<tr>
<td>P10</td>
<td>Chaknaurang-1A</td>
<td>B</td>
<td>Biodegraded</td>
<td>3</td>
</tr>
<tr>
<td>P11</td>
<td>Minwal-1</td>
<td>B</td>
<td>Biodegraded</td>
<td>3</td>
</tr>
<tr>
<td>P12</td>
<td>Joyamir-4</td>
<td>B</td>
<td>Biodegraded</td>
<td>3</td>
</tr>
<tr>
<td>P13</td>
<td>Turkwal-1</td>
<td>B</td>
<td>Biodegraded</td>
<td>1</td>
</tr>
<tr>
<td>P14</td>
<td>Pindori-4</td>
<td>B</td>
<td>Non-biodegraded</td>
<td>0</td>
</tr>
<tr>
<td>P15</td>
<td>Dhurnal-1</td>
<td>C</td>
<td>Non-biodegraded</td>
<td>0</td>
</tr>
<tr>
<td>P16</td>
<td>Dhurnal-6</td>
<td>C</td>
<td>Non-biodegraded</td>
<td>0</td>
</tr>
<tr>
<td>P17</td>
<td>Toot-10A</td>
<td>C</td>
<td>Non-biodegraded</td>
<td>0</td>
</tr>
<tr>
<td>P18</td>
<td>Toot-12</td>
<td>C</td>
<td>Non-biodegraded</td>
<td>0</td>
</tr>
</tbody>
</table>

*Wenger et al., [46]
CONCLUSIONS

The hydrocarbon compositions of 18 crude oils from the Potwar Basin were examined using biomarkers, aromatic and heterocyclic aromatic hydrocarbons distribution and stable isotopic compositions of saturated and aromatic fractions, in order to evaluate source OM, maturity, lithology and depositional environment and level of biodegradation. These geochemical characteristics differentiate Potwar Basin oils into three groups (A, B and C) with following key geochemical differences.

- **Group A** oil showed higher Pr/Ph with low DBT/P reveals fluvio-deltaic source rocks deposited in highly oxic depositional environments. Abundance of C$_{19}$ TT and C$_{24}$ TeT along with higher abundance of diagnostic aromatic biomarkers i.e. 1,2,5-TMN, 1-MP, 2,7-DMP and retene revealed terrestrial source OM for group A oil. Group A oil showed more negative (isotopically lighter) in $\delta^{13}$C of both saturated and aromatic fractions from all other oils clearly differentiates. Abundant BPs along with MFs is also important feature of this group separate it from other groups. The saturate hydrocarbons profile showed typical non biodegraded crude oil.

- Rest of oils from Potwar Basin analysed in this study are marine in origin however $\delta^{13}$C and $\delta$D stable isotopes and biomarker parameters including TT, TeT, hopanes, aromatic and heterocyclic aromatic hydrocarbons separated these oils into 2 sub-groups (B and C). Group B oils showed heaviest $\delta^{13}$C of both saturated and aromatic fractions. DBTs aromatic hydrocarbons are abundant components in group B along with significant presence of short and long chain TAS distinguished this group from others. Some of the group B crude oils are showed depletion in low molecular weight hydrocarbons particularly $n$-alkanes, by minor biodegradation (upto level 2-3) while OM is generated from marine clastic rocks deposited in marine suboxic/dysoxic depositional environments. TT are less abundance than hopanes.
• Group C represented typically non-biodegraded matured marine crude oils deposited in marine oxic environments which are generated from source OM enriched in algal source input indicated by higher extended TT. Group C oils showed light $\delta^{13}C$ of saturated fractions than group B oils however $\delta^{13}C$ of aromatic fractions of group B and C are not very different. Significant presence of short chain TAS and totally absent of long chain TAS are important feature of this group oils. TT are more abundant than hopanes.
Chapter - 6

POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND STABLE HYDROGEN ISOTOPE STUDY AS INDICATOR OF MINOR BIODEGRADATION

ABSTRACT

Distribution of PAHs and stable hydrogen isotopic composition (δD) of n-alkanes and isoprenoids has been used to assess the minor biodegradation in a suite of crude oils from Potwar Basin, Pakistan. The biomarker study revealed that crude oils share a similar source and thermal maturity. The low level of biodegradation under natural reservoir conditions was established on the basis of biomarker distributions. Bulk stable hydrogen isotope of saturated fractions of crude oils show an enrichment in D with increase in biodegradation and show a straight relationship with biodegradation indicators i.e. Pr/n-C17, API gravity. For the same oils, δD values for the n-alkanes relative to the isoprenoids are enriched in deuterium (D). The data are consistent with the removal of D-depleted low-molecular-weight (LMW) n-alkanes (C_{14}-C_{22}) from the oils. The δD values of isoprenoids do not change during the minor biodegradation and are similar for all the samples. The average D enrichment for n-alkanes with respect to the isoprenoids is found to be as much as 35‰ for the most biodegraded sample. The relative susceptibility of alkynaphthalenes and alkylphenanthrenes at low levels of biodegradation was discussed. The dimethylnaphthalene, trimethylnaphthalene and tetramethylnaphthalene biodegradation ratios were purposed that showed significant differences with increasing biodegradation and are suggested as good indicators for assessment of low level of biodegradation.
6.1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) from sedimentary OM have been widely used to assess thermal maturity [4,10,38,156] and multiple accumulation histories of oils in reservoirs [38]. The higher relative abundance of certain PAHs isomers (e.g. 1,6-DMN, 1,2,5-TMN, 1,2,7-TMN and 1,2,5,6-TeMN) in sediments and thermally immature oils is generally related to source(s) [38,181]. The effects of biodegradation on PAHs in reservoirs have been reported in several studies [15,17,41,48,129]. Susceptibility of PAHs to biodegradation is dependent on the number of aromatic rings and alkyl substituents on the rings. Generally, the susceptibility to biodegradation decreases with an increase in the number of aromatic rings and in the number of alkyl substituents on the aromatic moieties [41,44,192]. Alkylbenzenes are the first aromatic compounds to be removed from oil during in-reservoir biodegradation [43,44]. For alkynaphthalenes and alkylphenanthrenes the thermodynamically more stable isomers are generally more susceptible to biodegradation [15,41]. For the alkylbiphenyls, the sterically-hindered isomers with alkylation in the 4 position are less susceptible than other isomers [49].

The application of compound specific isotope analysis (CSIA) has become a powerful tool for assessment of source, thermal maturity and biodegradation [17,149,193-197]. In general, biodegradation leads to $^{13}$C enrichment in the residual compounds by removing isotopically lighter $^{12}$C compounds from crude oils [44,198-201]. The greater mass difference between hydrogen and deuterium compared with other stable isotopes (e.g. carbon) results in a larger fractionation. In vitro biodegradation studies of crude oils have demonstrated that fractionation of the LMW $n$-alkanes (i.e. $n$-C$_{15}$ to $n$-C$_{18}$) can lead to 25‰ enrichment in D, whereas the HMW $n$-alkanes show little isotopic change [193]. Sun et al. [149] reported a significant isotopic fractionation in moderately biodegraded oils, a D enrichment in the $n$-alkanes of up to ca. 35‰ being observed. Microbes preferentially utilize the lighter isotopes i.e. $^{12}$C and H, so the residue becomes enriched in $^{13}$C and D [202].

In this study, a suite of eight crude oils from Potwar Basin (group B, section 5.2.6, Table 5.5) was analyzed for compound specific stable hydrogen isotopes of
saturated hydrocarbons and PAHs distributions. The affects of biodegradation on $\delta$D values of $n$-alkanes and isoprenoids (Pr, Ph) and susceptibility to biodegradation of PAHs is investigated. The notion behind the approach is that, during minor biodegradation, microbes consume isotopically lighter compounds and the remaining compound classes become enriched in isotopically heavy compounds. Biodegradation susceptibilities order for individual isomers of alkynaphthalenes and alkylphenanthenes is suggested from non-biodegraded to minor biodegraded crude oils from Potwar Basin.

6.2 RESULTS AND DISCUSSION

Bulk and compound specific hydrogen isotope analysis and distribution of PAHs have been used to evaluate their applications for assessment of minor biodegradation in Potwar Basin crude oils. A sample suit composing non-biodegraded to minor biodegraded crude oils has been used (Table 6.1). The crude oils believed to share a similar source and thermal maturity (Chapter 5, group B).

6.2.1 Assessment of Biodegradation

Evaluation of the extent of biodegradation was reported using different biodegradation indicators (Pr/$n$-C$_{17}$, Ph/$n$-C$_{18}$, API gravity) and it has been observed that a range of non-biodegraded to minor biodegraded crude oils are present in Potwar Basin (Chapter 5, Section 5.2.7). A suite of eight crude oils show similar source OM and thermal maturity were selected for detail assessment and affects of biodegradation on hydrocarbons (Table 6.1). The sequential affects of biodegradation on saturated fractions from these selected crude oils is shown by TIC of saturated hydrocarbons fractions in Fig 6.1. For the Missakeswal-1 oil, the saturated hydrocarbons (Fig. 6.1a) show a typical non-biodegraded profile, having a full suite of $n$-alkanes, while the Rajian-3A oil (Fig. 6.1b) shows a lack of the lower MW $n$-alkanes. In the Joyamir-4 oil (Fig. 6.1c) there is a significant increase in the relative abundance of the UCM, the $n$-alkanes are significantly lower in abundance and there is a lack of the lower MW isoprenoids. These finding show that crude oils from this set of oils show a range from non-biodegraded to minor biodegradation up to level 2 to 3 [46]. Similarly, API gravity with in this set of eight
crude oils show a subtle change from very light oil (Pindori-4, API gravity: 41°) to very heavy oil (Joyamir-4, API gravity: 16.1°). A significant presence of \( n \)-alkanes in saturated fractions along with substantial UCM in very heavy oil (Fig. 6.1c) indicates the possibility of mixing of heavy biodegraded oils with non-biodegraded oils in the reservoirs [124,203,205].

**Table 6.1** \( n \)-Alkanes, isoprenoids, aliphatic biomarkers and diamondoids hydrocarbons ratios

<table>
<thead>
<tr>
<th>Oil#</th>
<th>Name</th>
<th>API Gravity</th>
<th>Pr/Ph</th>
<th>Pr/ ( n )-C(_{17} )</th>
<th>Ph/ ( n )-C(_{18} )</th>
<th>BP1</th>
<th>BP2</th>
<th>MA/A</th>
<th>MDIA/DIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>P14</td>
<td>Pindori-4</td>
<td>41</td>
<td>1.5</td>
<td>0.8</td>
<td>0.5</td>
<td>0.65</td>
<td>0.01</td>
<td>5.3</td>
<td>2.5</td>
</tr>
<tr>
<td>P2</td>
<td>Missakeswal-1</td>
<td>36.2</td>
<td>1.5</td>
<td>1.0</td>
<td>0.7</td>
<td>0.84</td>
<td>0.04</td>
<td>5.3</td>
<td>2.6</td>
</tr>
<tr>
<td>P13</td>
<td>Turkwal-1</td>
<td>-</td>
<td>1.2</td>
<td>1.1</td>
<td>0.8</td>
<td>0.93</td>
<td>0.11</td>
<td>6.4</td>
<td>2.6</td>
</tr>
<tr>
<td>P7</td>
<td>Kal-2</td>
<td>26.6</td>
<td>1.3</td>
<td>1.2</td>
<td>0.9</td>
<td>0.99</td>
<td>0.06</td>
<td>5.0</td>
<td>2.5</td>
</tr>
<tr>
<td>P5</td>
<td>Rajian-3A</td>
<td>22.7</td>
<td>1.3</td>
<td>1.3</td>
<td>0.9</td>
<td>1.07</td>
<td>0.09</td>
<td>5.2</td>
<td>2.4</td>
</tr>
<tr>
<td>P10</td>
<td>Chaknaurang-1A</td>
<td>18.4</td>
<td>1.2</td>
<td>1.3</td>
<td>0.9</td>
<td>1.11</td>
<td>0.15</td>
<td>5.2</td>
<td>2.3</td>
</tr>
<tr>
<td>P11</td>
<td>Minwal-1</td>
<td>16</td>
<td>1.0</td>
<td>1.3</td>
<td>1.0</td>
<td>1.10</td>
<td>0.18</td>
<td>4.9</td>
<td>2.4</td>
</tr>
<tr>
<td>P12</td>
<td>Joyamir-4</td>
<td>16.1</td>
<td>1.0</td>
<td>1.3</td>
<td>1.0</td>
<td>1.15</td>
<td>0.06</td>
<td>4.9</td>
<td>2.4</td>
</tr>
</tbody>
</table>

\( \text{Pr/Ph: Pristane/Phytane} \)
\( \text{BP1: (Pr+Ph)/(n-C\(_{17}\)+n-C\(_{18}\)), Peak areas of pristane and phytane from m/z 183 and n-C\(_{17}\) and n-C\(_{18}\) from m/z 57[203]} \)
\( \text{BP2: 17\alpha 21\beta (H) hopane/(Pr+Ph). Peak area of hopane from m/z 191 and pristane, phytane from m/z 183 [203]} \)
\( \text{MA/A: ratio of methyladamantanes (1-MA +2-MA)/adamantane (A, \text{XVIII}). Peak areas of 1-MA + 2-MA from m/z 135 and adamantane from m/z 136 [204,124]} \)
\( \text{MDIA/DIA: ratio of methyldiamantanes (1-MD + 3-MD + 4-MD)/Diamantane (DIA, \text{XIX}). Peak areas of 1-MD + 3-MD + 4-MD from m/z 187 and adamantane from m/z 188 [204,124]} \)
Fig. 6.1 Total ion chromatograms of saturated hydrocarbon fractions for Potwar Basin crude oils showing different degrees of biodegradation. C_{11} to C_{36} indicate carbon number of \( n \)-alkanes. a: 2,6-dimethylundecane; b: 2,6,10-trimethylundecane (nor-farnesane); c: 2,6,10-trimethyldodecane (farnesane); d: 2,6,10-trimethyltridecane; e: 2,6,10,trimethylpentadecane (nor-Pristane); Pr, pristane and Ph, phytane; UCM, unresolved complex mixture.
In reservoir mixing

The relative abundance of the UCM in saturated hydrocarbon fractions rises when the LMW components are removed [46]. In the case of the Potwar Basin oils herein, the presence of both UCM and \( n \)-alkanes (Fig. 6.1c) might suggest petroleum being comprised mixture of non-biodegraded oil with a severely biodegraded oil. The API gravity of 16° (Joyamir-4) in the most biodegraded oil point to the possibility of in-reservoir petroleum mixing. Components such as the 25-norhopanes are associated with oils that have undergone significant biodegradation [205-206]. None of the oils from the Potwar Basin was found to contain these components. Other than des-methylhopanes, other hydrocarbon classes were examined to assess the level of mixing of the samples (e.g. [124,203,207]). The mixing of a severely biodegraded crude oil with a fresh oil charge has also been shown to affect various thermal maturity parameters [203,207] and results in significant changes in \( \delta^{13}C \) and \( \delta D \) [208]. Interestingly the Potwar Basin oils show a similar range of thermal maturity (Chapter 5, Section 5.2.3) and so appear not to be mixtures. Koopmans et al. [203] proposed a mixing model for biodegraded petroleum, based on \( (\text{Pr} + \text{Ph})/(n\text{-C}_{17} + n\text{-C}_{18}) \) and \( 17\alpha,21\beta(\text{H}) \text{hopane}/(\text{Pr} + \text{Ph}) \), and showed some correlation with biodegradation and with viscosity. These parameters are strongly affected when oils consist of mixtures with different levels of biodegradation. The \( (\text{Pr} + \text{Ph})/(n\text{-C}_{17} + n\text{-C}_{18}) \) and \( 17\alpha,21\beta(\text{H}) \text{hopane}/(\text{Pr} + \text{Ph}) \) values for the Potwar Basin oils are shown in Table 6.1. These ratios have been plotted against API values and show a very good correlation \( (R^2 0.95 \text{ and } 0.83, \text{ respectively, Fig. 6.2}) \) indicating that the oils do not appear to mixtures. Diamondoids are one of the most resistant hydrocarbons to biodegradation [124]. The mixing of non-biodegraded with heavily biodegraded oils has shown variations in the ratio of methyl adamantanes/adamantanes (MA/A) and methyl diamantanes/diamantanes (MDIA/DIA; [124]). The diamondoid ratios for the Potwar oils are similar (Table 6.1), again indicating little or no mixing. The available biomarker distributions in the samples do not provide any firm evidence for in-reservoir mixing, but the possibility of in-reservoir mixing cannot be conclusively excluded since many petroleum reservoirs appear to contain mixtures. Further work for the determination of possible biodegradation mixing is carrying on.
Fig. 6.2  Relationship between API gravity and biodegradation parameters (BP1 and BP2, [203]) showing API to be controlled by biodegradation rather than any other factor such as mixing.
6.2.2 Bulk Hydrogen Isotopic Compositions of Saturated Fractions

A progressive change in $\delta D$ values of bulk hydrogen isotopes of saturated fractions of crude oils has been observed (Chapter 5, Table 5.1). It has been shown that Pr/$n$-C$_{17}$ is a good indicator to show the affects of biodegradation on Potwar Basin crude oils (Chapter 5, section 5.2.6). A cross plot of $\delta D_{\text{sats}}$ vs Pr/$n$-C$_{17}$ is used to show the affect of minor biodegradation on $\delta D$ of saturated fractions (Fig. 6.3). A straight relationship between variables shows that with increase in biodegradation indicated by increase in Pr/$n$-C$_{17}$ is accompanied by increase in $\delta D$ i.e. $\delta D$ of saturated fractions move to more positive. That means with increase in biodegradation the $\delta D$ of saturated fractions become isotopically heavy. This revealed that lighter isotopes of saturated fractions are preferentially removed by microbes and remaining saturated fractions become enriched in deuterium (D) and this is in agreement with previous study [202].

![Diagram](image)

**Fig. 6.3** $\delta D_{\text{sats}}$ vs. Pr/$n$-C$_{17}$ plot shows straight relationship that increase in biodegradation is accompanied by enrichment in deuterium of saturated fractions.
6.2.3 Compound Specific Hydrogen Isotopic Compositions of \( n \)-Alkanes and Isoprenoids

Table 6.2 shows \( \delta^D \) values for \( n \)-alkanes and isoprenoids (Pr and Ph) in a suit of crude oils ranging from non-biodegraded to minor biodegraded samples. Non-biodegraded crude oils (Pindori-4 and Missakeswal-1, Table 6.2) show more negative (lighter) values while minor biodegraded crude oils (Rajian-3A and Minwal-1, Table 6.2) show less negative (heavy) values for stable hydrogen isotopes of LMW \( n \)-alkanes. The \( \delta^D \) values for Pr and Ph are generally similar for all crude oils. This shows non-biodegraded oils contained isotopically lighter compounds compare to the minor biodegraded oils.

Based on extant studies by Sessions et al. [209] the D/H fractionation that occurs between water is ca. 158‰ and ca. 235‰ for alkyl and isoprenoid lipids, respectively. This leads to the fact that isoprenoid lipids are being depleted in deuterium relative to \( n \)-alkyl lipids in organisms. Similar differences have been reported for relatively ‘immature’ sediments dating from recent to Devonian (e.g. [197,210-212]), whereby isoprenoid alkanes (e.g. Pr and Ph) are depleted in D relative to \( n \)-alkanes by up to about 80‰. However, thermal maturity appears to have influence on this trend. With rising maturity, Pr and Ph become enriched in D, whereas the \( \delta^D \) values for \( n \)-alkanes generally remain constant until a very high maturity level is reached [197,213]. These studies have shown that hydrogen isotopic exchange occurs more readily for isoprenoids that contain tertiary carbon centers, via a mechanism involving carbocation-like intermediates. The \( \delta^D \) compositions for individual \( n \)-alkanes from the same suit of oils are shown in Fig. 6.4. Two different profiles are clearly visible across the \( n \)-alkanes \( \delta^D \) plots, one in the LMW region and other in the HMW region of the plot (Fig. 6.4a).

The LMW \( n \)-alkanes (\( n-C_{14} \) to \( n-C_{22} \)) show a significant enrichment in D with increasing level of biodegradation. These results are also consistent with respect to \( ^{13}C \) enrichment observed for LMW \( n \)-alkanes in previous biodegradation studies [214]. The HMW \( n \)-alkanes (\( >n-C_{22} \)) are less affected by minor biodegradation and
Table 6.2  $\delta$D(‰)* values of $n$-alkanes and isoprenoids from Potwar Basin oils

<table>
<thead>
<tr>
<th>Sample</th>
<th>P14</th>
<th>P2</th>
<th>P7</th>
<th>P5</th>
<th>P11</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-alkanes' name</td>
<td>Pindori-4</td>
<td>Missakeswal-1</td>
<td>Kal-2</td>
<td>Rajian-3A</td>
<td>Minwal-1</td>
</tr>
<tr>
<td>$n$-C$_{14}$</td>
<td>-151</td>
<td>-165</td>
<td>-130</td>
<td>-129</td>
<td>-119</td>
</tr>
<tr>
<td>$n$-C$_{15}$</td>
<td>-159</td>
<td>-169</td>
<td>-130</td>
<td>-129</td>
<td>-124</td>
</tr>
<tr>
<td>$n$-C$_{16}$</td>
<td>-157</td>
<td>-166</td>
<td>-132</td>
<td>-133</td>
<td>-122</td>
</tr>
<tr>
<td>$n$-C$_{17}$</td>
<td>-164</td>
<td>-168</td>
<td>-137</td>
<td>-139</td>
<td>-125</td>
</tr>
<tr>
<td>$n$-C$_{18}$</td>
<td>-165</td>
<td>-169</td>
<td>-135</td>
<td>-140</td>
<td>-126</td>
</tr>
<tr>
<td>$n$-C$_{19}$</td>
<td>-164</td>
<td>-167</td>
<td>-138</td>
<td>-141</td>
<td>-128</td>
</tr>
<tr>
<td>$n$-C$_{20}$</td>
<td>-160</td>
<td>-166</td>
<td>-133</td>
<td>-135</td>
<td>-128</td>
</tr>
<tr>
<td>$n$-C$_{21}$</td>
<td>-161</td>
<td>-165</td>
<td>-135</td>
<td>-126</td>
<td>-135</td>
</tr>
<tr>
<td>$n$-C$_{22}$</td>
<td>-154</td>
<td>-163</td>
<td>-141</td>
<td>-129</td>
<td>-135</td>
</tr>
<tr>
<td>$n$-C$_{23}$</td>
<td>-150</td>
<td>-168</td>
<td>-132</td>
<td>-123</td>
<td>-138</td>
</tr>
<tr>
<td>$n$-C$_{24}$</td>
<td>-148</td>
<td>-150</td>
<td>-130</td>
<td>-117</td>
<td>-135</td>
</tr>
<tr>
<td>$n$-C$_{25}$</td>
<td>-141</td>
<td>-153</td>
<td>-128</td>
<td>-119</td>
<td>-135</td>
</tr>
<tr>
<td>$n$-C$_{26}$</td>
<td>-133</td>
<td>-126</td>
<td>-126</td>
<td>-116</td>
<td>-132</td>
</tr>
<tr>
<td>$n$-C$_{27}$</td>
<td>-135</td>
<td>-123</td>
<td>-123</td>
<td>-117</td>
<td>-126</td>
</tr>
<tr>
<td>$n$-C$_{28}$</td>
<td>-132</td>
<td>-127</td>
<td>-122</td>
<td>-115</td>
<td>-118</td>
</tr>
<tr>
<td>$n$-C$_{29}$</td>
<td>-135</td>
<td>-129</td>
<td>-117</td>
<td>-118</td>
<td>-118</td>
</tr>
<tr>
<td>Aver $n$-C$_{14-29}$</td>
<td>-151</td>
<td>-155</td>
<td>-131</td>
<td>-127</td>
<td>-128</td>
</tr>
<tr>
<td>Aver $n$-C$_{14-22}$</td>
<td>-159</td>
<td>-166</td>
<td>-135</td>
<td>-132</td>
<td>-127</td>
</tr>
<tr>
<td>Pristane, Pr</td>
<td>-154</td>
<td>-165</td>
<td>-157</td>
<td>-142</td>
<td>-157</td>
</tr>
<tr>
<td>Phytane, Ph</td>
<td>-149</td>
<td>-157</td>
<td>-152</td>
<td>-141</td>
<td>-168</td>
</tr>
<tr>
<td>Aver, (Pr + Ph)</td>
<td>-152</td>
<td>-161</td>
<td>-155</td>
<td>-142</td>
<td>-162</td>
</tr>
</tbody>
</table>

Difference ($\Delta \delta$)

| (Pr+Ph)- ($n$-C$_{14-22}$) | 7 | 5 | -20 | -10 | -35 |

*: $\delta$D (‰) with respect of VSMOW with in standard deviation of 5‰.
Fig. 6.4  The δD (‰) distribution of \( n \)-alkanes from Potwar oils, (a) \( n-C_{14} \) to \( n-C_{29} \) \( n \)-alkanes (b) significant effect of biodegradation is observed in \( n \)-alkanes, \( n-C_{14} \) to \( n-C_{22} \).
their $\delta D$ values are probably representative of the original OM source for $n$-alkanes. The average $\delta D$ values for the $n$-alkanes were calculated for $n$-$C_{14}$ to $n$-$C_{22}$ (Table 6.2) since these compounds are most affected by biodegradation. The $\delta D$ of isoprenoids (average of Pr and Ph) are shown in Table 6.2. A difference in $\delta D$ values between isoprenoids and $n$-alkanes represented as $\Delta \delta$, has been calculated by subtracting the average $\delta D$ of LMW $n$-alkanes from the average $\delta D$ of Pr and Ph (Table 6.2). Interestingly the oils show a large $\Delta \delta$ offset between the $n$-alkanes and isoprenoids. These oils were shown to be the most biodegraded on the basis of molecular compositional differences (API gravity, isoprenoids/ $n$-alkanes). The plots of $\Delta \delta$ against API values and Pr/$n$-$C_{17}$ is shown in Fig. 6.5 and shows a good correlation ($R^2 = 0.86$ and $R^2 = 0.67$, respectively) also consistent with an increase in biodegradation as these parameters decrease and increase, respectively. It appears that the $n$-alkanes have been fractionated during biodegradation, the order of difference being consistent with that reported for microbes, whereby molecules containing the lighter isotope (i.e. H) are preferentially consumed, leading to enrichment in D for the residual components, i.e. $n$-alkanes [202]. The $\delta D$ values for the isoprenoids (Pr and Ph) are fairly similar for all the oils and therefore do not appear to have been affected by biodegradation. For the least biodegraded oil, Pindori-4 (Table 6.2), high API gravity and the similar $\delta D$ values for $n$-alkanes, Pr and Ph are consistent with trends reported for non-biodegraded oils [197]. On the other hand, the largest $\Delta \delta$ offset (35‰) and lowest API value is observed for the Minwal-1 oil, which is the most biodegraded oil of the suite. The other oils fall between these two end-members. Using molecular parameters to assess light to moderate biodegradation levels of oils is difficult because components are removed in a quasi-stepwise fashion. This study shows that $\delta D$ differences for $n$-alkanes and isoprenoids, together with molecular parameters can be used to assess low biodegradation levels (2-3) of petroleum.
Fig. 6.5  Plot of δD(‰) difference between LMW n-alkanes \((n-C_{14} - n-C_{22})\) and isoprenoids vs. (a) API gravity, and (b) Pr/n-C\textsubscript{17}
6.2.4 Effects of Biodegradation on PAHs

6.2.4.1 Alkylnaphthalenes

The biodegradation susceptibility of PAHs and their alkyl analogous is often more complicated to discuss than that of aliphatic hydrocarbons. Certain aromatic hydrocarbons isomers are more affected towards biodegradation than others [15,41,43]. Combination of mass chromatograms from aromatic fractions for the dimethyl- (DMNs), trimethyl- (TMNs) and tetramethyl-naphthalenes (TeMNs) of selected least to most biodegraded samples are shown in Fig. 6.6. The depletion in aromatic hydrocarbons can be seen from the relative intensities of various aromatic compounds by biodegradation identified in the aromatic fractions (Fig. 6.6). Methylnaphthalenes (MNs) appear to be the highly susceptible alkylnaphthalenes based on their decrease in relative intensities compared to other alkylnaphthalenes biodegradation increases. A significant depletion in the 2-MN isomer relative to the 1-MN isomer is observed with rise in levels of biodegradation (Fig. 6.7). Similar trends can also be seen for other higher alkylnaphthalenes i.e. DMN, TMN and TeMN isomers (Fig. 6.6) at the higher biodegradation levels. It indicates DMNs are more depleted by biodegradation than TMNs and TMNs show more depletion to biodegradation than TeMNs. This biodegradation susceptibility sequence between alkylnaphthalenes (DMNs, TMNs and TeMNs) showed similar trends reported in previous results [41]. With in the DMNs, the 2,6-DMN is more susceptible to biodegradation than similar isomer i.e. 2,7-DMN (Figs. 6.6a and b). In highly biodegraded sample from the set of oils (level-3, Minwal-1, Fig. 6.6c), the 2,7- and 2,6- isomers are significantly altered in DMNs and the 1,7-DMN and 1,3-DMN appear to be the highly resistant to the biodegradation. Biodegradation susceptibilities of aromatic hydrocarbons have been reported by laboratory simulation and reservoir studies [see 45]. It has been reported that the 2,6- and 2,7-DMNs indicate similar susceptibility towards biodegradation. The sequence of susceptibility to the biodegradation for DMNs (Fig. 6.7) relates to the thermodynamic stability of the isomers. For TMN isomers, similar biodegradation affects to the DMNs observed (Fig. 6.6). The 1,3,7-, 1,6,7- and 1,3,6- isomers from TMNs indicate to be more depleted to biodegradation than the 1,2,4-TMN and 1,2,5-TMN
Fig. 6.6  Biodegradation susceptibility for alkynaphthalene distributions \((m/z \ 156+170+184; \text{dimethylnaphthalenes, DMNs; trimethylnaphthalenes, TMNs; tetramethylnaphthalenes, TeMNs})\). Numbers on each peak refer to respective alkynaphthalene isomer and highlighted peaks show isomer components most affected by rising biodegradation.
Order of susceptibility of alkynaphthalenes and alkylphenanthrenes to microbial attack in the Potwar Basin crude oils (cf. [15]). Numbers refer to positions of methyl substituents. Ternary plot was plotted using similar conditions for analysis and identifications as reported by van Aarssen et al. [38] for TMNr (1,3,7/1,3,7+1,2,5)-TMNs, TeMNr (1,3,6,7/1,3,6,7+(1,2,5,6+1,2,3,5)-TeMNs and PMNr (1,2,4,5,7/1,2,4,5,7+1,2,3,5,6)-PMNs.
isomers (Fig. 6.6). Fisher et al. [41] reported a significant abundance of the 1,3,6-TMN in a minor biodegraded oil while Huang et al. [42] reported the 2,3,6-TMN as being the highly susceptible isomer to biodegradation from reservoirs studies. For the Potwar Basin oil samples, the order of most to least biodegradation susceptibility for the TMNs is 1,3,7- & 1,6,7- > 1,3,6-. The exception of the 1,2,4- and 1,2,5-TMN isomers, generally TMNs show a decrease in relative intensity with rising biodegradation (Figs. 6.6b and c). With in TeMNs, most of the isomers are not altered during biodegradation with out few exceptions. The most resistant TeMN isomer in the Potwar Basin oils to biodegradation is the 1,3,5,7-TeMN isomer and the least resistant the 1,3,6,7-TeMN isomer, consistent with the data reported by Fisher et al. [41]. However, slight differences in the relative intensities of some the TeMNs peaks are showing changed with rise in the biodegradation (Fig. 6.7). These observations indicate biodegradation level for the Potwar oils to be at a minor level of biodegradation.

The susceptibility sequence to the biodegradation of various isomers of naphthalene is reported in Fig. 6.7. Fisher et al. [41] proposed different polymethylnaphthalene ratios to determine the biodegradation level in a number of coastal sediments. They were designated those ratios by different names, DMN biodegradation ratio (DBR: 1,6-DMN/1,5-DMN), TMN biodegradation ratio (TBR:1,3,6-TMN/1,2,4-TMN) and TeMN biodegradation ratio (TeBR: 1,3,6,7-TeMN/1,3,5,6-TeMN) indicating affective assessment for biodegradation samples up to about level 6 of biodegradation. In the Potwar Basin oils, the effect of biodegradation appears to be light, up to about a level of 3. In light of this biodegradation sequence we are proposing different methylnaphthalenes biodegradation ratios (MBRs) to determine the low level biodegradation particularly in oil samples. These MBRs ratios were calculated by dividing the area of the most susceptible isomer from respective methyl naphthalenes to the least susceptible methyl naphthalene isomer and are shown in Table 6.3. It is noteworthy to observe that isomers which are structurally similar were applied in these Biodegradation Ratios (BRs) from every alkynaphthalenes. It contains DMN biodegradation ratio (DNBR: 1,6-DMN/1,2-DMN), TMN biodegradation ratio (TNBR: 1,3,7-TMN/1,2,7-TMN) and TeMN biodegradation ratio (TeNBR: 1,3,6,7-TeMN/1,3,5,7-TeMN) (Table 6.3). Although these alkynaphthalene isomers are
<table>
<thead>
<tr>
<th>Oil #</th>
<th>Name</th>
<th>Biodeg. Level*</th>
<th>DNBR&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TNBR&lt;sup&gt;b&lt;/sup&gt;</th>
<th>TeNBR&lt;sup&gt;c&lt;/sup&gt;</th>
<th>TMN&lt;sup&gt;d&lt;/sup&gt;</th>
<th>TeMN&lt;sup&gt;e&lt;/sup&gt;</th>
<th>PMN&lt;sup&gt;f&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>P14</td>
<td>Pindori-4</td>
<td>0</td>
<td>6.5</td>
<td>5.7</td>
<td>2.3</td>
<td>0.85</td>
<td>0.82</td>
<td>0.60</td>
</tr>
<tr>
<td>P2</td>
<td>Missakeswal-1</td>
<td>0</td>
<td>5.8</td>
<td>5.0</td>
<td>1.6</td>
<td>0.81</td>
<td>0.80</td>
<td>0.59</td>
</tr>
<tr>
<td>P13</td>
<td>Turkwal-1</td>
<td>1</td>
<td>4.4</td>
<td>4.9</td>
<td>1.4</td>
<td>0.77</td>
<td>0.79</td>
<td>0.57</td>
</tr>
<tr>
<td>P7</td>
<td>Kal-2</td>
<td>2</td>
<td>5.1</td>
<td>3.9</td>
<td>1.0</td>
<td>0.70</td>
<td>0.71</td>
<td>0.49</td>
</tr>
<tr>
<td>P5</td>
<td>Rajian-3A</td>
<td>2</td>
<td>4.6</td>
<td>3.4</td>
<td>0.8</td>
<td>0.64</td>
<td>0.70</td>
<td>0.47</td>
</tr>
<tr>
<td>P10</td>
<td>Chaknaurang-1A</td>
<td>3</td>
<td>3.9</td>
<td>2.3</td>
<td>0.6</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>P11</td>
<td>Minwal-1</td>
<td>3</td>
<td>3.8</td>
<td>2.1</td>
<td>0.4</td>
<td>0.46</td>
<td>0.51</td>
<td>0.39</td>
</tr>
<tr>
<td>P12</td>
<td>Joyamir-4</td>
<td>3</td>
<td>4.2</td>
<td>2.1</td>
<td>0.4</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

*: from Table 5.5.

<sup>a</sup> DNBR: dimethylnaphthalene biodegradation ratio; 1,6-DMN / 1,2-DMN

<sup>b</sup> TNBR: trimethylnaphthalene biodegradation ratio; 1,3,7-TMN / 1,2,7-TMN

<sup>c</sup> TeNBR: tetramethylnaphthalene biodegradation ratio; 1,3,6,7-TeMN / 1,3,5,7-TeMN

<sup>d</sup> TMN<sub>r</sub>: (1,3,7 / 1,3,7+1,2,5)-trimethylnaphthalenes [38]

<sup>e</sup> TeMN<sub>r</sub>: (1,3,6,7 / 1,3,6,7+(1,2,5,6+1,2,3,5)-tetramethylnaphthalenes [38]

<sup>f</sup> PMN<sub>r</sub>: (1,2,4,5,7 / 1,2,4,5,7+1,2,3,5,6)-pentamethylnaphthalenes [38]

n.d.: not determined
Fig. 6.8  Polymethynaphthalenes biodegradation ratios vs. Pr/n-C$_{17}$ showed a good correlation. A significant decrease in DNBR, TNBR and TeNBR is observed.
structurally similar they tend to show a significant difference in susceptibility to biodegradation (Figs. 6.7 and 6.8). The plots were drawn between these biodegradation ratios and Pr/n-C_{17} (Fig. 6.8). Each plot shows a good correlation with Pr/n-C_{17} ($R^2$ for DNBR, 0.83; TNBR, 0.88; TeNBR, 0.96). The isomers which appear to have a higher resistance to biodegradation have greater steric hindrance than those with less resistance to biodegradation. For example, the most resistant, the 1,2-DMN isomer, has methyl substitutions on adjacent carbon atoms, while the least resistant 1,6-DMN isomer has the methyl groups positioned well apart. Similar results are observed for TNBR and TeNBR [41].

Van Aarssen et al., [38] developed a ternary diagram to illustrate the effect of maturity, biodegradation and mixing of oils, based on the distribution of alkylnaphthalenes. It has been shown that alkylnaphthalene ratios (TMNr, TeMNr and PMNr; see Fig. 6.7 for definitions) affected by biodegradation plot away from the maturity centre of the ternary plot. The alkylnaphthalene ratios for the Potwar Basin oils (TMNr; TeMNr and PMNr; Table 6.3; c.f. [38]) were plotted in a ternary diagram (Fig. 6.7). The order of susceptibility to biodegradation for the isomers used in TMNr is 1,3,7-TMN > 1,2,5-TMN and for the TeMNr isomers 1,3,6,7-TeMN > 1,2,5,6-TeMN and 1,2,3,5-TeMN (Fig. 6.7). Hence, biodegradation led to a decrease in the TMNr and TeMNr values (Fig. 6.7). These results support a low level of biodegradation for the Potwar Basin oils.

6.2.4.2 Alkylphenanthrenes

The affects of biodegradation on alkylphenanthrenes were reported using variations in the distribution of methylphenanthrenes (MPs) and dimethylphenanthrenes (DMPs). Combined representative chromatograms for the MPs and the DMPs from non-biodegraded to minor biodegraded oil samples are shown in Fig. 6.9. The relative intensity of the MPs compare to the DMPs is decreases with increase in biodegradation (Fig. 6.9) that indicates MPs showed less resistance to biodegradation than the DMPs. It shows that increase in alkylation on aromatic rings results in the decrease in susceptibility to biodegradation which is consistent with previous studies [14,41,44,192].
Fig. 6.9 A combined chromatogram of MPs and DMPs ($m/z$: 192 + 206) shows decrease in relative intensity with an increase in biodegradations. The numbers on peaks indicate the respective alkyl substituted isomer of phenanthrene and highlighted peaks show significant depletion as move to more biodegraded sample.
For the MPs isomers, it is observed that the 2-MP isomer is less resistant to biodegradation while the 9-MP and 1-MP isomers show higher resistance to biodegradation. The relative intensity of the 9-MP increases with increase in biodegradation as moved from top to bottom in Fig. 6.9 while relative intensity of the 2-MP and 3-MP isomers decreases. For the DMPs isomers, the susceptibility to the biodegradation of the individual isomers is less clear due to large number of possible isomers and coelution of different substitution isomers on common stationary phases (Fig. 6.9). But rate of depletion for each peak is found considerable and most to least susceptible order for DMPs is given in Fig. 6.7. The 2,7-DMP, 2,6+3,5-DMPs and the 2,3-DMP isomers are depleted faster than from all DMPs isomers as move from non-biodegraded to minor biodegraded oil samples (Fig. 6.9). In minor biodegraded oil sample (Fig. 6.9c) the four coeluted isomers (1,3+2,10+3,9+3,10-DMPs) peak observed degraded relative to following peak representing the 2,5+2,9+1,6-DMPs isomers which are most resistant to biodegradation indicated by continuous increase in relative intensity with increase in biodegradation (Fig. 6.9). The susceptibility order for DMPs (Fig. 6.7) is consistent with field study of Chinese biodegraded oils [43] while contradiction is observed from laboratory biodegradation study [128] where 2,7-DMP was the most refractory isomer to the biodegradation. It shows that affects of minor biodegradation (up to level 3) on the MP and DMP isomers are not severe and only slight depletion is observed across the biodegradation sequences (Fig. 6.9).

CONCLUSIONS

The δD values of selected aliphatic hydrocarbons (n-alkanes and isoprenoids) in eight crude oils of similar thermal maturity from the Potwar Basin, Pakistan have been measured. High Pr/n-C_{17} and Ph/n-C_{18} values and low API gravity values of some of the oils are consistent with relatively low levels of biodegradation up to level 3. There is no indication of mixing, based on various known molecular parameters. The δD values for the LMW n-alkanes relative to the isoprenoids were found to be enriched in D because of the removal of D-depleted LMW n-alkanes. The Δδ between the n-alkanes and isoprenoids of the most biodegraded oil was found to be as much as 35‰. A
significant change in the alkynaphthalene and alkylphenanthrene distributions is used to assess the affects of biodegradation on individual isomers. Different biodegradation ratios were successfully purposed i.e. dimethylnaphthalene Biodegradation ratio (DNBR: 1,6/1,2), Trimethylnaphthalene biodegradation ratio (TNBR: 1,3,7/1,2,7) and Tetramethylnaphthalene biodegradation ratio (TeNBR: 1,3,6,7/1,3,5,7) showed significant variation in values with increase in biodegradation indicate a valuable parameters for the assessment of low level of biodegradation.

The affects of biodegradation on methyl and dimethylphenanthrenes showed that with increase in alkylation of phenanthrene decrease in biodegradation extent is observed in Potwar Basin crude oils.
Chapter - 7

GEOSYNTHESIS OF HETEROCYCLIC AROMATIC HYDROCARBONS AND FLUORENES BY CARBON CATALYSIS

ABSTRACT

Laboratory experiments have shown that activated carbon catalyses the reactions of biphenyls (BPs) with surface adsorbed reactants that incorporate S, O, N or methylene forming some common constituents of sedimentary OM namely, dibenzothiophene (DBT, XXVII), dibenzofuran (DBF, XXV), carbazole (C, XXVI) and fluorene (F, XXVIII). A relationship between the % abundance of the hetero element in kerogen and the abundance of the related heterocyclic compound in the associated soluble organic matter supports the hypothesis that these reactions occur in nature. More specific supporting evidence was obtained from the good correlation observed between methyl and dimethyl isomers of the reactant BPs and the methyl and dimethyl isomers of the proposed product heterocyclics compounds.

It is suggested that these heterocyclic aromatic hydrocarbons distributions reported for sediments and crude oils from the Kohat Basin (Pakistan) and Carnarvon Basin (Australia) are the result of a catalytic reactions of compounds with BP ring systems and surface adsorbed species of the hetero element on the surface of carbonaceous material. Furthermore, the abundances of these compounds (DBT, DBF and BP) show similar concentration profiles throughout the Kohat Basin sediments suggesting that share a common source. These compounds also correlate well with changes in the paleoredox conditions. These data tends to point towards a common precursor perhaps lignin phenols of land plants. Coupling of phenols leads to BP, which has been demonstrated in our laboratory experiments to be the source of C, DBT, DBF, and F.
7.1 INTRODUCTION

Heterocyclic aromatic compounds occur widely in sediments and petroleum [6,12,50-51,131]. The common members of this group include, dibenzothiophenes (DBTs), dibenzofurans (DBFs) and carbazoles (Cs). These compounds comprise a BP cyclic ring system with incorporation of a hetero-atom forming a third five-membered ring. It is convenient for the purposes of this study to include the fluorenes (Fs) in this group although in this case it is carbon which forms the third ring. It is require to evaluate that all these compounds show similar arrangements of structure except difference in heteroatoms. The mechanism of formation of these structurally similar compounds has not been reported, although their abundance in sediments and crude oils has been related to depositional environments [12,51,215], thermal maturity [37,56], source organic facies [6,131,216], and migration effects [57]. A brief overview of these suggestions now follows.

The changes in relative abundances of benzothiophenes (BTs) and DBTs has been the basis for proposed thermal maturity indicators for OM [52,165,217]. The high abundances of DBF and alkylated DBFs in coals led to the suggestion of their relationship with oxidative degradation [54] and their terrestrial origin from lower vascular plants, fungi and lichens [6]. The difference in distribution of DBF and alkylated DBFs has also been reported changes in lithology and thermal maturity [36,55]. Relative abundances of DBFs and DBTs have been reported in different depositional environments where marine carbonates show higher amounts of DBT while freshwater/lacustrine sediments show higher amounts of DBFs [12-13]. Fenton et al. [215] reported a high relative abundance of DBT, DBF and BP in a Permian/Triassic section from East Greenland. Their abundances coincide with a shift in $\delta^{34}$S of pyrite as well as with the disappearance of the major vegetation types occurring during the Permian/Triassic mass extinction event. In the latter study, the compounds have been suggested to be derived from the same precursor i.e. lignin phenols, BP is formed through phenol coupling. DBT and DBF have been suggested to have formed through reaction of BP with S and O species [215]. Pyrrolic N containing compounds in
petroleum have been suggested as indicators of migration [57]. Less work has been done on occurrence and distribution of Cs in sedimentary OM. The source of pyrrolic N has been reported as facies dependent and concentration of both Cs and benzocarbazoles (BCs) increases with rise in thermal maturity [50-51,216]. While contrasting results have been reported from Canadian oils indicating thermal maturity and depositional environment show no effect on the distribution of Cs [56]. The geochemical significance of Fs is not well known except those reported in a few oil correlation studies [12-13] while alkylated Fs are not yet reported in any from of sedimentary OM. These contrasting concentrations and the relative distributions of heterocyclic aromatic hydrocarbons in sediments and crude oils may be due to lack of knowledge about the source and mechanism of formation of these compounds.

In this chapter, number of evidence reported for the geosynthesis of heterocyclics aromatic hydrocarbons. The formation of DBTs, DBFs, Cs and Fs is shown to occur in laboratory experiments through carbon surface reactions to introduce a third ring in BPs. Evidence that these conversions have also occurred in sediments is provided by relative abundance data showing precursor product relationship between BPs and the heterocyclic compounds in crude oils and sediments reported from the Kohat Basin (Pakistan). Distribution of heterocyclic aromatic hydrocarbons were reported from the Carnarvon Basin, Australia crude oils to show the global feature of this hypothesis i.e. precursor product relationship between BPs and heterocyclics. Furthermore, abundances of DBT, BP, C and DBF throughout the Kohat Basin (Pakistan) sediments have been measured and compared with $\delta^{34}$S of pyrite minerals and pristane to phytane (Pr/Ph) ratio to establish their relationship with the paleoredox conditions. Paleoredox conditions appear to play a role in the formation of these components and the availability of the hetero atom to undergo carbon surface catalysis.

### 7.2 RESULTS AND DISCUSSION

Evidence that the solid–state carbonaceous material promotes chemical reactions in sediments has been suggested from data obtained from hydrogen exchange
reactions between hydrocarbons [81]. Here data and results are reported from laboratory experiments showing reactions of S, O, N and C species on carbonaceous surfaces with BPs form the heterocyclic and F ring systems. Distribution association is observed between heterocyclics and BPs in sediments and crude oils revealed that kerogen is catalysing such reactions in sedimentary OM.

7.2.1 Laboratory Experiments on Activated Carbon

Laboratory experiments have shown that carbon surfaces catalyse the reaction between BP and surface reactants. Mass chromatograms (Fig. 7.1) of the reaction products from heating experiments with activated carbon at 300 °C in deactivated, evacuated glass tubes indicate significant concentrations of each of the compounds of interest in the reaction products. Blank experiments without carbon (Fig. 7.1 blanks) showed no significant products and activated carbon when heated alone gave no products.

The carbon catalysed formation of DBT from reaction of BP and elemental S under these reaction conditions is shown in Fig. 7.1a. The reaction was repeated by replacing activated carbon with sub-bituminous coal and again a significant abundance of DBT was observed (see below). This surface reaction extend by providing sources of reactive O, N and C for reaction with BP. Fig. 1(b) shows a chromatogram indicating formation of DBF. The surface O was provided to the activated carbon by molecular oxygen [84]. This experiment was carried out after sealing the reaction tube without evacuation to provide a source of O contained in air. Reaction of BP with surface N was made possible by using sodium azide [218]. The reaction product contained both aminobiphenyl and C as shown in Fig. 1(c). The reaction of 1,2,3,4- tetramethylbenzene with BP under the same reaction conditions that resulted in formation of the heterocyclic products from O and N donors produced F and MBP isomers as shown in Fig. 1(d).

A set of these experiments have also been carried out replacing activated carbon with crushed coal. GC-MS analysis of the reaction products under these reaction conditions with coal is shown in Fig. 7.2a. Clearly the S species in the presence of coal
Fig. 7.1 Total ion chromatograms (TIC) of extracts from laboratory heating experiments. Samples were heated at 300 °C for 16 hr. Each blank experiment was identical in composition, temperature and time but without activated carbon. AC, activated carbon; BP, biphenyl; S, sulfur; TMB, 1,2,3,4-tetramethylbenzene; MBPs, methylbiphenyls.
reacted with BP to produce DBT. Similar type of reaction was repeated where N species reacted with BP at a reaction temperature of 270 °C. The chromatogram of the reaction products showed significant C compared with that from the blank experiment (Fig. 7.2b). These results indicate that carbonaceous surfaces other than activated carbon facilitate these reactions.

A similar experiment using activated carbon with 3-MBP was carried at different heating temperatures from 200 °C to 300 °C. GC-MS chromatograms of experiment extract showed the presence of 4-MDBT and 2-MDBT (Fig. 7.3). At low heating temperatures the 2-MDBT isomer showed higher abundance while with increase in heating temperature of reaction produced higher concentration of 4-MDBT. Blank experiments without activated carbon gave no significant MDBTs. The reaction has inserted S into the BP ring system without isomerization of the methyl group suggesting that 1-MDBT and 3-MDBT would be formed from reaction of 2- and 4- MBP respectively. The systematic change in the relative abundances of product with increase in reaction temperature suggests that the position of the methyl substituent influences the reaction energy of activation. This surface reaction at higher reaction temperatures favours the formation of the heterocyclic compound with the methyl substituent adjacent to the heteroatom. The preferential position of S addition to the BP system is an important feature of the process that can also be recognized in the formation of DBTs under natural conditions in sediments.

### 7.2.1.1 Probable mechanism of geosynthesis reactions

Catalysis by carbon surfaces is a known process [84,99] and formation of active adsorbed surface reactants involves free radical reactions. Since carbon surfaces have low polarity but are electrical conductors the reactions they facilitate are more likely to involve radical rather than ionic intermediates. In this section possible reaction intermediate and pathways for the formation of heterocyclic aromatic hydrocarbons and fluorenes are reported with laboratory experiments results as evidenced obtained from carbon catalyses surface reactions.
**Fig. 7.2**  TICs of extracts from laboratory heating experiments at temperature 270 °C for 16 hr. Each blank experiment was identical in composition, temperature and time but without coal, BP, biphenyl; S, sulfur.
Fig. 7.3 Mass chromatograms (m/z: 198) of the extract of heating experiments of 3-MBP with elemental S in the presence of active carbon at different temperatures.
It is interesting to observe that both methylation of BP and methylene substitution of BP to yield MBP isomers and F are present in extract of laboratory reaction of BP and TMB (Fig. 7.4b). This formation of MBPs and F from BP could involve surface carbenoid (or carbene) species [219]. A similar distribution of these products resulted when the TMB was substituted with nonyl amine (Fig. 7.a) or acetonitrile (Fig. 7.4c) indicating that the reactive methylene species can be formed on the solid carbon surface by methylene abstraction from different compound types. The formation of C from BP could similarly involve a nitrogen radical species such as nitrene [220] by direct insertion or via 2-aminobiphenyl (Fig. 7.1c). A similar set of radical processes appear to be responsible for formation of DBF from BP and adsorbed oxygen. The proposed reaction sequence for formation of these compounds is shown in Fig. 7.5.

7.2.2 Distribution of Heterocyclic Aromatic Hydrocarbon in Sediments and Crude Oils

In order to assess the likelihood that the precursor-product relationships observed in the laboratory experiments have also occurred in sedimentary OM relative abundances of the parent compounds (non-alkylated) and their proposed products have been examined in sediments and crude oils. Both the parent (unsubstituted) and methyl substituted isomers of these compounds are common constituents in sediments and crude oils.

7.2.2.1 Parent compounds

A sequence of sediments from the Kohat Basin, Pakistan have been analysed for heterocyclic aromatic hydrocarbons. The quantitative measurements were performed by comparing peak areas of compounds (BP, DBT, DBF, F, C) with deuteriated phenanthrene and reported in Table 7.1. Fig. 7.6 shows the relationships between the concentrations of the BP and the heterocyclic aromatic hydrocarbons and F in these sediments. Formation of DBT, DBF, C and F support the interpretation that BP is related to the formation of this group of compounds by its reaction with a species containing the hetero element contained in the kerogen. The abundance of O and S species vary significantly with depositional environments and
Fig. 7.4 TICs of extract of heating experiments of BP with activated carbon using different alkyl precursor compounds, heating temperature and duration was same for all experiments i.e. 300 °C and 16 hr. AC, activated carbon; BP, biphenyl; MBPs, methylbiphenyls; TMB, 1,2,3,4-tetramethylbenzene.
Fig. 7.5  Purposed reaction pathways on activated carbon for formation of heterocyclic aromatic compounds and F from BP. AC, activated carbon; S: sulfur; BP, biphenyl; F, fluorene; DBT, dibenzothiophene; DBF, dibenzofuran; C, carbazole.
Table 7.1 Concentrations of compounds and elemental kerogen composition for Kohat Basin sediments.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Concentration (µg/g TOC)</th>
<th>Elemental composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BP</td>
<td>DBT</td>
</tr>
<tr>
<td>S1</td>
<td>2.88</td>
<td>8.52</td>
</tr>
<tr>
<td>S2</td>
<td>1.06</td>
<td>2.66</td>
</tr>
<tr>
<td>S3</td>
<td>2.23</td>
<td>6.78</td>
</tr>
<tr>
<td>S5</td>
<td>0.22</td>
<td>0.74</td>
</tr>
<tr>
<td>S7</td>
<td>1.80</td>
<td>3.67</td>
</tr>
<tr>
<td>S8</td>
<td>1.35</td>
<td>1.81</td>
</tr>
<tr>
<td>S10</td>
<td>7.26</td>
<td>19.49</td>
</tr>
<tr>
<td>S12</td>
<td>1.52</td>
<td>0.68</td>
</tr>
<tr>
<td>S13</td>
<td>2.01</td>
<td>3.29</td>
</tr>
<tr>
<td>S14</td>
<td>0.27</td>
<td>0.31</td>
</tr>
</tbody>
</table>

BP, biphenyl; DBT, dibenzothiophene; DBF, dibenzofuran; C, carbazole; F, fluorene; S, sulfur; O, oxygen; N, nitrogen; -: below detection limit; n.d.: not determined.
abundant DBTs have been proposed to differentiate between marine and carbonate-evaporate crude oils and sediments [167,171]. It has been reported that freshwater-lacustrine oils showed higher abundance of DBFs than DBTs [6]. Fan et al. [12] reported distribution relationship between DBT, DBF and F in a large suit of crude oils and source rocks from different sedimentary environments. They have concluded that the relative abundance of DBF and F was higher in freshwater environments while DBT was higher in marine environments. The abundance of S in marine and carbonate-evaporate environments and less abundance of S (hence more O) in freshwater-lacustrine environments could be related in this scenario to that the formation of heterocyclic aromatic hydrocarbons depend on the nature of kerogen surface species. The elemental composition (%) of kerogen for S, O, and N was determined from similar suite of sediments of Kohat Basin Pakistan and reported in Table 7.1. Plots of the % elemental composition of the kerogen for the element that matches the hetero atom in each of the compounds i.e. %S vs DBT; %O vs DBF and %N vs C is shown in Fig. 7.7. The plots indicate clear relationship that increase in %age of S, O, N increases the concentrations of DBT, DBF, C, respectively. The results suggest a probable relationship between the solid state abundance of the hetero atom in the kerogen and the organic compound formed from it after reaction with BP (or a related precursor).

Abundant BP has been reported in kerogen bound structures [221] and similarly BP acids and alcohols have been found in abundance in kerogen degradation study from Moroccon Timahdit oil shale [222]. Insertion and chemical reaction of heteroatomic species with biological precursors has been observed in various stages of sedimentary OM [65,77-79]. These results showed that insertion reactions are going on in sedimentary environments where kerogen surface heteroatoms and methylene species reacted with BPs to synthesize heterocyclics aromatic hydrocarbons and F respectively.
**Fig. 7.6**  Relationship of reactant (BP)-product (DBT, DBF and F) for Kohat Basin sediments (data given in Table 7.1).
Fig. 7.7 Relationship between compounds in SOM and the N, S, and O concentration of kerogen from each sample (data given in Table 7.1).
7.2.2.2 Methylated homologous of heterocyclics and Fs

In order to facilitate easy recognition of heterocyclic compounds with substituents on similar positions in the carbon ring system to the BP structural systems Table 7.2 has been included to show these relationships for both methyl and dimethyl compounds.

The representative mass chromatograms in Fig. 7.8 obtained from the aromatic fraction of Kohat Basin sediment (Depth, 4345 m) show the relative abundances of MBPs, MDBT, MDBFs, MCs and MFs. The thermal maturity of the sample is immature to early oil generation window as indicated by C\textsubscript{32} hopane and C\textsubscript{29} sterane isomerization ratios (0.43 and 0.43, respectively) and T\textsubscript{max} value (431 °C). The most abundant methyl substituted isomers from DBTs (4-MDBT), DBFs (4-MDBF), Cs (1-MC) and Fs (1-MF) show structure association with most abundant methylbiphenyl (3-MBP). Similarly the least abundant methyl substituted isomers from each compound class i.e. 1-MDBT, 1-MDBF, 4-MC, and 4-MF show structure association with least abundant MBP isomer i.e. 2- (Fig. 7.8; Table 7.2). The compounds related with BP in a reactant-product sense are indicated by symbols in Fig. 7.8. It is noteworthy that the relative abundance results for methyl isomers of the BP reactant and the products indicate that the hetero atomic elements (S, O, N) and methylene insertion occurred into MBPs in sediments to produce corresponding methyl homologous of DBT, DBF, C and F, respectively. Keumi et al. [223] reported the positional reactivity for DBF with different species and showed that the reactivity of position 4 is minimum as less as 5% of all possible four substitution positions in DBF (1, 2, 3 and 4). In contrast, the 4-MDBF is the most abundant isomer from MDBFs in sediments (Fig. 7.8b) indicates MDBFs are formed from MBPs by insertion of O species. While there is some evidence for methylation of the aromatic rings during these surface catalysed reactions the majority of methyl heterocycles are derived from the methyl substituted BPs rather than by methylation of the parent heterocyclic compounds.
Table 7.2  Ring position relationships between BP and related heterocyclic compounds and Fs.

![Diagram](image_url)

<table>
<thead>
<tr>
<th>BPs</th>
<th>DBTs &amp; DBFs</th>
<th>Cs &amp; Fs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>4; 2</td>
<td>1; 3</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>2,2'</td>
<td>1,9</td>
<td>4,5</td>
</tr>
<tr>
<td>2,3'</td>
<td>1,8; 1,6*</td>
<td>3,5; 1,5*</td>
</tr>
<tr>
<td>2,5</td>
<td>1,4</td>
<td>1,4</td>
</tr>
<tr>
<td>2,4</td>
<td>1,3</td>
<td>2,4</td>
</tr>
<tr>
<td>2,4'</td>
<td>1,7</td>
<td>2,5</td>
</tr>
<tr>
<td>2,3</td>
<td>1,2</td>
<td>3,4</td>
</tr>
<tr>
<td>3,5</td>
<td>2,4</td>
<td>1,3</td>
</tr>
<tr>
<td>3,3'</td>
<td>4,6; 2,8; 2,6*</td>
<td>1,8; 3,6; 1,6*</td>
</tr>
<tr>
<td>3,4'</td>
<td>3,6; 2,7</td>
<td>1,7; 2,6</td>
</tr>
<tr>
<td>4,4'</td>
<td>3,7</td>
<td>2,7</td>
</tr>
<tr>
<td>3,4</td>
<td>2,3; 3,4</td>
<td>1,2; 2,3</td>
</tr>
</tbody>
</table>

*: after rotation of phenyl ring along single bond
Fig. 7.8 Representative ion chromatograms show relative distributions of MDBTs (m/z: 198), MDBFs (m/z: 182), MBPs (m/z: 168), MCs (m/z: 181) and MFs (m/z: 180) from the Kohat Basin, Pakistan sediment (Depth, 4345 m). Symbols relate precursor-product compounds.
These relationships between methyl substituted BPs and methyl homologous of DBT, DBF, C and F are also a feature of crude oils. Distribution of these compounds in the crude oils from two different basins of the world (Pakistan and Australia) is also reported (Fig. 7.9) along with sediments to illustrate the global features of carbon catalyses formation of heterocyclic aromatics hydrocarbons.

**Quantitative Relationship between MBPs and MDBTs in Sediments**

The quantitative measurements were performed for MBPs and MDBTs isomers from Kohat Basin sediments and reported in Table 7.3. The absolute abundance relationship between the corresponding individual isomers of MBPs and MDBTs in sediments is shown in Fig. 7.10a. The concentration of associated isomers of MBPs is plotted against associated MDBTs isomers. It is observed that the concentration of corresponding isomers increase together. The most abundant 4-MDBT concentration increases with increase in concentration of 3-MBP. Similarly, the least abundant 1-MDBT concentration showed similar increase in abundance with 2-MBP. The good straight line relationships \( R^2 \), 0.98 indicate that the MDBTs showed product precursor link to the MBPs in sediments. Moreover, the ratios between methyl substituted BP and DBT to the parent compounds from the suite of sediment and crude oils are shown in Table 7.3 and is shown in Fig. 7.10b. It is interesting to observe that both ratios showed an excellent linkage between their values. Where MBPs/BP ratio increases the MDBTs/DBT ratio decreases and vice versa. It shows that the methyl substituted DBT isomers are formed from methyl substituted BP isomers rather than methyl substitution of parent compounds i.e. DBT and BP respectively. Similarly, the MBPs/BP and MDBTs/DBT ratios for crude oils (Table 7.3) are also in same of range of sediments.

The significant abundance of DBTs in sediments from range of low to medium maturity [4] and the relative distribution of MDBTs vary with OM type. The results from Kohat Basin sediments are consistence that the geosynthesis of MDBTs occurred by surface reactions where bonded S still present on the kerogen surface.
Fig. 7.9 Distributions of MBPs and methyl homologues of DBF, C and F in crude oils from two different basins. a) Chaknaurang, Upper Indus Basin, Pakistan; b) Barrow, Carnarvon Basin, NW Australia. MBPs (m/z 168), MFs (m/z 180), MDBFs (m/z 182) and MCs (m/z 181). Symbols relate precursor-product compounds.
Table 7.3 Concentration and compound ratios of sediments and crude Oils

<table>
<thead>
<tr>
<th>Samples</th>
<th>Concentration (µg/g TOC)</th>
<th>Compound ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Depth (m)</td>
<td>2- MBP</td>
</tr>
<tr>
<td>S3</td>
<td>4345-70</td>
<td>0.38</td>
</tr>
<tr>
<td>S4</td>
<td>4410-40</td>
<td>0.03</td>
</tr>
<tr>
<td>S5</td>
<td>4510-12</td>
<td>0.00</td>
</tr>
<tr>
<td>S6</td>
<td>4534-60</td>
<td>0.02</td>
</tr>
<tr>
<td>S8</td>
<td>4680-82</td>
<td>0.05</td>
</tr>
<tr>
<td>S9</td>
<td>4690-92</td>
<td>0.10</td>
</tr>
<tr>
<td>S10</td>
<td>4710-12</td>
<td>0.97</td>
</tr>
<tr>
<td>S11</td>
<td>4741-42</td>
<td>0.00</td>
</tr>
<tr>
<td>S12</td>
<td>4834-50</td>
<td>0.02</td>
</tr>
<tr>
<td>S13</td>
<td>4860-62</td>
<td>0.00</td>
</tr>
<tr>
<td>S14</td>
<td>4940-42</td>
<td>0.00</td>
</tr>
<tr>
<td>P19</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>P20</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>P21</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>P22</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

-: not determined
Fig. 7.10 Relationship between MBPs and MDBTs in Kohat Basin sediments. a) absolute concentration plot shows association between individual isomers of MBPs and MDBTs. b) plot shows ratio of MBPs and MDBTs to the parent BP and DBT in sediment samples.
7.2.2.3 Dimethyl homologous of heterocyclics and Fs

The product-precursor relationship can also be extended to the compounds with two methyl substituents. This approach is however limited by availability of GC-MS data to enable reliable identification of isomers. Data is available for DMBPs and DMCs [49,224] however no data is available for DMFs or DMDBFs although I have been able to obtain an authentic sample of 1,7-DMF. The relationships between DMBP isomers and isomers of DMDBT, DMC and DMF are described from sediments and crude oils in following sections.

a) DMBPs vs DMDBTs

Dimethyl homologues of DBT and BP have been showed a structure relationship in natural sedimentary OM and comparison of substitution pattern between BP and DBT structural system is shown in Table 7.2.

The relative distributions of DMBPs and DMDBTs in representative sediment sample are shown in Fig. 7.11. The two most abundant DMBP isomers 3,4'- and 3,3'- have the corresponding structural DMDBT isomers 3,6- and 4,6- as the most abundant. At a lower level of relative abundance the 3,5- and 3,4-DMBP isomers have a similar lower relative abundance pair of DMDBT isomers namely 2,4- and 3,4-. It is interesting that the set of DMBPs with a substituents in position 2 have a corresponding set of DMDBT isomers with substituents in position 1 (Table 7.2). Although a number of the DMDBT isomers with this substitution pattern showed co-elution it is apparent that the abundance of this group relative to the 4,6- and 3,6- isomers are in a similar proportion to the set of 2- substituted biphenyls relative to the 3- substituted biphenyls (Fig. 7.11).

It is interesting that the two most abundant DMBP isomers namely 3,3'- and 3,4'- could form two DMDBT isomer additional to the high abundance 3,6- and 4,6- DMDBT isomers discussed above. These are 2,8- and 2,7- isomers, neither isomer has been reported in geochemical samples [181,225] and probably reflects a strong preference for substitution of the sulfur reactive species at ring position
Fig. 7.11  Relative distribution of DMBPs and DMDBTs in Kohat Basin sediments (depth, 4680 m). Numbers on peaks indicate dimethyl substituted isomers of BP and DBT (Table 7.2). Symbols relate precursor-product compounds.
adjacent to the methyl substituents. In 3,3′-DMBP isomer the phenyl ring rotation across the single bond followed by sulfur insertion is the probable source for the 2,6-DMDBT isomer.

These relationships between methyl and dimethyl substituted BPs and DBTs is a common feature of crude oils. Fig. 7.12 shows the distribution of these compounds in the crude oils from Pakistan and Australia. Again the symbols indicate relationships between BP isomers and the product DBT isomers derived from them. While the peak patterns are a little different to those from the sediment extract (Fig. 7.8 and 7.11) the relative abundances of isomers indicates a reactant-product relationship consistent with that discussed above for the sediment samples.

b) DMBPs vs DMCs and DMFs

DMCs and DMFs have been showed a structure relationship with DMBPs in natural sedimentary OM and comparison of substitution pattern between C, F and BP structural system is shown in Table 7.2. The relationships between DMBP isomers and isomers of DMC and DMF apparent in the chromatograms shown in Fig. 7.13 for a sediment extract from the Kohat Basin, Pakistan and the Griffin crude oil from Australia.

In both samples the two most abundant DMBP isomers 3,3′- and 3,4′- have 1,8- and 1,7- DMCs as the two most abundant DMC isomers (refer to Table 7.2. for comparison of related substitution patterns in BP and the heterocyclic compounds). Again this relationship is consistent with a carbon catalysed derivation of the DMCs from DMBPs. Some preference for the position of substitution into the BP ring system is indicated by the relative abundances of reaction products. 1,6-DMC is the next most abundant isomer. It is a co-product from 3,3′-DMBP and, like 2,6-DMC the co-product from 3,4′-DMBP, it has a lower abundance than the alternative product with a methyl at position 1 indicating the preference for substitution of the hetero atom adjacent to a methyl substituent. This is again the case for preferential formation of 1,2-DMC rather than 2,3-DMC from 3,4-DMBP.
Fig. 7.12  Relative distributions of methyl and dimethyl biphenyls and dibenzothiophenes in crude oils from two different basins. a) Mela-1, Kohat Basin, Pakistan, b) Wanaea, Carnarvon Basin, Australia. MBPs (m/z 168), DMBPs (m/z 182), MDBTs (m/z 198) and DMDBTs (m/z 212). Symbols relate precursor-product compounds.
Fig. 7.13 Relative distribution of DMBPs (m/z: 182), DMCs (m/z: 195) and DMFs (m/z: 194) in the Kohat Basin sediment (Depth, 4940 m) and the Carnarvon Basin Griffin crude oil. Numbers on peaks indicate dimethyl substituted isomers. Symbols show precursor-product relationships (Table 3).
In the case of DMFs only the 1,7- isomer has been identified using an authentic sample. The other peak assignments have been made assuming that the effect of changing the position of ring substitution of methyl groups on Cs has the same effect on retention time as that for DBFs and can be used to predict the retention time of the DMF isomers relative to the 1,7-DMF reference compound. Again the relationships in relative abundance of these isomers to those of DMBP support the proposed formation relationship.

The relative abundance of DMFs showed two sets of dimethyl isomers where one set showed tentatively identified 1,8-, 1,3- and 1,6- isomers including 1,7- isomer identified using authentic standard while second set show lower abundance collectively mark as X (Fig. 7.13). It can be seen that the 1,7- and 1,8-DMF isomers from both sediment and oil sample indicate higher abundance show a structure association with most abundant DMBP isomer, 3,4′- and 3,3′-. However, it is noteworthy that the small relative abundance difference between 3,4′-DMBP isomer with 3,3′-DMBP isomer in sediment sample could be related to the similar relative abundance difference of corresponding structure associated dimethyl isomers of F, i.e. 1,7- and 1,8- respectively (Fig. 7.13). While in case of oil sample this observation is reversed where 3,3′-DMBP isomer is relatively higher than 3,4′-DMBP isomer showed same difference in relative abundance of corresponding dimethyl isomers of F i.e. 1,8-DMF isomer is higher than 1,7-DMF isomer (Fig. 7.13). Similarly, next abundant 1,3-DMF showed structure and relative abundance relationship with next abundant DMBPs isomer, 3,4′-. The relative abundance of second set of dimethyl isomers of F indicated by X could be related to the dimethyl isomers of BP having lower abundance i.e. 3,4-, 4,4′- (c.f. Table 7.2).

The relative abundance results between structure associated isomer of DMBPs with DMCs and DMFs revealed that the hetero-atomic element (N) and methylene insertion occurred into DMBPs in sediments and crude oils to produce corresponding dimethyl homologous of C and F, respectively.
7.2.3 Paleoredox Conditions and Heterocyclics Formation

Fig. 7.14 displays the abundances of DBT, DBF, C and BP, Pr/Ph and $\delta^{34}$S with depth for the Kohat Basin sediments. Since all the aromatic components tend to show similar abundance profiles with depth suggests to indicate a common precursor. Given that both the Carnarvon Basin crude oil and Kohat Basin sediments contain Type III kerogen (terrestrial-derived OM) the most likely natural product precursor for BP is thus suggested to be lignin phenol. A similar observation was made by Fenton et al. [215]. Lignin is a co-polymer comprised of phenyl–propenyl alcohols [226] and it is likely that these phenolic compounds could be the precursor for BP, and BP is thus intermediate source of DBT, DBF, C and F. However, other natural product precursor(s) can not be fully excluded for BP precursor. $\delta^{34}$S of pyrite in the Kohat Basin samples support changes in the paleoredox conditions of the water column. $\delta^{34}$S vary from –6.5 to -31.1 ‰. The $\delta^{34}$S results (-17.9 to -31.1 ‰) are mostly in the range of expected for periodic fluctuating dysoxic/euxinic depositional conditions [121,215]. These trends reflect the variations in the isotopic composition of seawater sulfate and imply a change in the sulfur cycle and a relative increase in the fraction of sulfur buried as pyrite. The sample with a $\delta^{34}$S of -6.5 ‰ is where C shows a maximum concentration and this result can not be explained. The exact source of the N present in C is unknown, but the availability of a specific N source is key here. The other aromatic compounds, BP, DBT and DBF, show a similar abundance profile with depth as observed by Fenton et al [215]. The redox conditions during this period of time (based on $\delta^{34}$S of pyrite and Pr/Ph) would favour the formation of DBF, DBT from BP. Anoxic/euxinic conditions are periodic, therefore it is not unexpected to observe similar abundance profiles of DBT, DBF and BP with depth. The samples will reflect an average of the seasonal redox conditions spanning several millions of years.
Fig 7.14. $\delta^{34}\text{S}(\text{‰})$ of pyrite against concentrations of DBT, DBF, BP, C and Pr/Ph with depth in Kohat Basin sediments Pakistan.
CONCLUSIONS

DBT, DBF, C and F have been shown to form by reactions of BP with surface active S, O, N and methylene species on carbon surfaces when heated at 300 °C.

Evidence that similar reactions occur in sediments was shown by enhanced formation of the heterocyclic compounds relative to biphenyls when the appropriate hetero element was present in the kerogen. More specific evidence for a reactant-product relationship between BPs and heterocyclics (and Fs) was obtained from a comparison of the methylated compounds in sediments and crude oil. Methyl substituted BPs (both mono and dimethyl) were shown to have an isomer abundance profile similar to that predicted for methylated heterocyclics (and Fs).

A similar abundances of DBT, DBF and BP, together with Pr/Ph and δ^{34}S of pyrite for the Kohat Basin sediments of various depths suggest that these compounds share a similar precursor. Given that the Kohat Basin sediments contain Type III kerogen, the most likely natural product precursor is lignin phenol. Phenol coupling can lead to BP, the intermediate precursor for DBT, DBF, C and F. δ^{34}S of pyrite of the sediments vary from –6.5 to -31.1 ‰, reflecting periodic fluctuations in the redox (anoxic/euxinic) depositional conditions.
REFERENCES


159


Hughes, W.B., Holba, A.G., Dzou, L.I., 1995. The ratio of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment.
and lithology of petroleum source rocks. Geochimica et Cosmochimica Acta 59, 3581-3598.


[183]. Alexander, R., Bastow, T.B., Kagi, R.I., Singh, R.K., 1992b. Identification of 1,2,2,5-tetramethyltetralin and 1,2,2,5,6-pentamethyltetralin as racemates in petroleum, Journal of the Chemical Society: Chemical Communications 23, 1712–1714.

from different palaeogeographical locations. Organic Geochemistry 32, 1195-1210.


Appendix

Isoprenoids

1. 2,6-diemethyundecane
2. nor-Farnesane
3. Farnesane
4. 2,6,10-trimethyltridecane
5. nor-Pristane
6. Pristane
7. Phytane

8. Tricyclic terpanes (Cheilanthanes)
9. C₂₄, 17,21-secohopane (Tetracyclic terpanes)
Hopanes

X = H; 30-norhopane (C_{29} hopane)
= CH_{3}; C_{30} hopane
= C_{2}H_{5}; C_{31} homohopane
= C_{3}H_{7}; C_{32} bishomohopane
= C_{4}H_{9}; C_{33} trishomohopane
= C_{5}H_{11}; C_{34} tetrakishomohopane
= C_{6}H_{13}; C_{35} pentakishomohopane

S and R isomers at C_{22},
17\alpha(H),21\beta(H) shown

Y = H; C_{29} moretane
= CH_{3}; C_{30} moretane
= C_{2}H_{5}; C_{31} moretane

17\beta(H),21\alpha(H) shown

C_{27}
17\alpha(H)-22,29,30-trisnorhopane (Tm)

C_{27}
18\alpha(H)-22,29,30-trisnorneohopane (Ts)

C_{30}, 17\alpha(H)-diahopane

C_{29}, 18\alpha(H)-30-norneohopane (C_{29}Ts)
Steranes and diasteranes

R = H; C_{27}-sterane, \textbf{a}  
= \text{CH}_3; C_{28}-sterane, \textbf{b}  
= \text{C}_2\text{H}_5; C_{29}-sterane, \textbf{c}  
S and R isomers at C_{20},  
5\alpha(H),14\alpha(H),17\alpha(H)

R = H; C_{27}-sterane, \textbf{d}  
= \text{CH}_3; C_{28}-sterane, \textbf{e}  
= \text{C}_2\text{H}_5; C_{29}-sterane, \textbf{f}  
14\beta(H),17\beta(H)

Diasteranes

R = H; C_{27}, \textbf{a}  
= \text{CH}_3; C_{28}, \textbf{b}  
= \text{C}_2\text{H}_5; C_{29} \textbf{c}  
S and R isomers at C_{20},  
13\beta(H),17\alpha(H)

Adamantane

Diamantane

Triaromatic steroids (TA)

C_{19} TA; \hspace{1em} X=H, Y=H, \textbf{a}  
C_{20} TA ; \hspace{1em} X=\text{CH}_3, Y=H \textbf{b}  
C_{21} TA ; \hspace{1em} X=\text{CH}_3, Y=\text{CH}_3 \textbf{c}  
C_{22} TA ; \hspace{1em} X= \text{CH}_3, Y=\text{C}_2\text{H}_5 \textbf{d}  
C_{25} TA ; \hspace{1em} X=\text{CH}_3, Y=\text{C}_5\text{H}_{11} \textbf{e}  
C_{26} TA ; \hspace{1em} X=\text{CH}_3, Y=\text{C}_6\text{H}_{13} \textbf{f}  
C_{27} TA ; \hspace{1em} X=\text{CH}_3, Y=\text{C}_7\text{H}_{15} \textbf{g}  
C_{28} TA ; \hspace{1em} X=\text{CH}_3, Y=\text{C}_8\text{H}_{17} \textbf{h}  

172
Retene XXI

Biphenyl XXII

Naphthalene XXIII Phenanthrene XXIV

Dibenzofuran XXV

Carbazole XXVI

Dibenzothiophene XXVII

Fluorene XXVIII

---

173