CHAPTER 5
ORGANIC GEOCHEMISTRY

5.1. Background of Study

5.1.1. Introduction

Hydrocarbons are major constituents of petroleum and therefore, interest in petroleum generation, diagenesis, and utilisation have led to increase interest in hydrocarbon geochemistry. Many hydrocarbons in petroleum sediments and in various fossil fuels resemble compounds produced by biological system.

Organic geochemistry is now sufficiently well developed, that it can be a useful addition to the range of techniques available to the geologist. Analitical methodology (e.g. GC & GC-MS) for the determination of hydrocarbons in sediments is evolving at a rapid rate.

5.1.2. Hydrocarbon Compounds In Sediments

Hydrocarbons are generated as part of the diagenesis processes of sedimentary organic matter. Beginning from the growth of plants, their transport and burial to the diagenesis and metamorphism of their fossil remains. Land plants, algae, bacteria and other micro-organisms are the sources of organic matter in sediments. They may grow and accumulate in place, or be carried in from transported into a different sedimentary basin.

Local conditions such as climate, water salinity, nutrient availability, toxicity and grazing by animal control the make up of the plant community (Cooper, 1990). In sediments, these biochemicals are partially recycled, partially degraded and partially oxidised by micro-organisms. When algae are toxic to grazing animals, and
often present in rocks. Kerogen which produces hydrocarbons, is derived from (marine and fresh water), terrestrial and re-worked materials (Brooks, 1981).

5.1.4. Variety and Characteristics of Hydrocarbons

Two main elements namely hydrogen and carbon are needed to generate thousands of compounds known collectively as hydrocarbons (HC).

There are several different ways in which the hydrocarbons can be classified when dealing with carbonaceous sediments. Hydrocarbons are traditionally separated into those of low molecular weight with high volatility (< C14), and higher molecular weight with lower volatility (> C14). This study will focus primarily on the higher molecular weight hydrocarbons.

Hydrocarbons can also be classified as either saturated, unsaturated or aromatic. Saturated hydrocarbons are also referred to as paraffins or alkanes and although they are trace components of biological lipids, they are geochemically quite stable and are a major constituent of the organic matter of terrestrial sedimentary rocks. In order to be a useful biomarker, a compound must retain enough of its original biological parent structure.

The retention of carbon back bone of the alcohol phytol from chlorophyll-a, in the pristane and phytane are examples of the phenomenon which will be discussed further in the following section.
5.1.4.1 Saturated Hydrocarbons

N-alkanes are the dominant natural hydrocarbons in organic materials and most abundant in organisms. This compound class has been isolated from bacteria, phyto-plankton, zooplankton, benthic and pelagic algae, and from higher level organism of terrestrial and aquatic origin. The major alkane found in organism and sediments are isoprenoids, n-paraffins and steranes, which are structurally similar to biological acids and alcohols and in many instances may be derived from these biological precursors. On the other hand, the relatively high concentration of alkanes in sedimentary deposits, as compared to those found in organism is at least partially due to their low chemical and catabolic activity which results in a preferential preservation and consequent relative enrichment of these compounds in older deposits (Tissot and Welte, 1984).

Many of the compounds that are branched or cyclic alkanes are isoprenoids (can be broken down into C₃ isoprene type units) e.g. found in several marine organism including phytophankton, benthic algae and zooplanktonic, as well as in sediments. Pristane, the C₁₉ isoprenoid was suggested to have originated from diagenesis of the phythol side chain of chlorophyll-a under oxidising conditions (Powell and Mckirdy, 1973). However, because pristane is also associated with many different organism it is not a useful specific biomarker. It is more commonly used in association with the related structure phytane, which is more likely to from phytol under reducing conditions. Thus, pristane to phytane ratios are used as indicators of redox conditions in sediments (Cooper, 1990).
Cyclic alkane, also referred to as cycloalkanes or cyclic hydrocarbons are proving to be excellent biomarker, included in this class of compounds are a group of polycyclic hydrocarbons known as hopanes and steranes. These hydrocarbons have also proved to be useful geochemical indicators with respect to studies on the diagenesis of sediment extracts and biodegradation of crude oils.

5.2. Results

5.2.1. Petrography

Optically, vitrinite reflectance is a comparative measure of the intensity of incident light that is reflected from vitrinite surface to the intensity of light reflected back from a calibrated standard. A photometer was used to measure the reflectance intensity. In this study, the vitrinite reflectance is measured on spots of 2-3 nm diameter in monochromatic green light (546 nm) using oil immersion objectives. The percentage of light reflected from the measured vitrinite were electronically displayed via a computerised technique.

A total of 25 readings were made to calculate the mean reflectance in oil (% Ro). The $R_{\text{min}}$ and $R_{\text{max}}$ are also shown (see Appendix D).

Micropetrographic examination suggests a relatively high contribution of terrestrial materials within the total organic content of the rock. The major components of the organic matter are vitrinite, structureless grey particles and very high reflecting amorphous sapropel, other recognisable coal macerals are generally not abundant. The mean vitrinite reflectance values are given in Table 5.1.
The generally high values of the mean vitrinite reflectance (\(\%\ Ro\)) for all the samples studied is in the range of 1.02% - 1.13% indicating that these sediments have reached a higher level of thermal maturity. However, the (\(\%\ Ro\)) values of the Charu samples Ch\(_2\) and Ch\(_4\) are similar, both having \(\%\ Ro\) values of 1.13\%, whilst the Pa\(_1\), Sa\(_1\), Sa\(_4\), Per, Per\(_3\), Tr\(_1\), Tr\(_2\), Km\(_2\) and Km\(_3\) samples have recorded (\(\%\ Ro\)) values of 1.08, 1.10, 1.08, 1.10, 1.08, 1.07, 1.04, 1.02 respectively indicating again a high level of thermal maturity.

Table 5.1 Vitrinite reflectance values (\(\%\ Ro\)) for the studied sediments.

<table>
<thead>
<tr>
<th>Formation</th>
<th>Sample No</th>
<th>Lithology</th>
<th>(%\ Ro)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charu</td>
<td>Ch(_2)</td>
<td>Coaly shale</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>Ch(_4)</td>
<td>Coaly shale</td>
<td>1.13</td>
</tr>
<tr>
<td>Panching</td>
<td>Pa(_1)</td>
<td>Limestone</td>
<td>1.08</td>
</tr>
<tr>
<td>Sagor</td>
<td>Sa(_1)</td>
<td>Shale</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>Sa(_4)</td>
<td>Shale</td>
<td>1.08</td>
</tr>
<tr>
<td>Permian</td>
<td>Per(_2)</td>
<td>Shale</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>Per(_3)</td>
<td>Shale</td>
<td>1.08</td>
</tr>
<tr>
<td>Semantan</td>
<td>Tr(_1)</td>
<td>Shale</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>Tr(_2)</td>
<td>Shale</td>
<td>1.07</td>
</tr>
<tr>
<td>Kemaman</td>
<td>Km(_2)</td>
<td>Phyllite</td>
<td>1.04</td>
</tr>
<tr>
<td>Metasediments</td>
<td>Km(_9)</td>
<td>Slate</td>
<td>1.02</td>
</tr>
</tbody>
</table>
According to Teichmuller (1987), the rate of increase of vitrinite reflectance depends on the rank ranges as a function of chemical and physico structural changes. It is low at low rank lignite stage and increases in the stages of bituminous coal and anthracite.

5.2.2 Interpretation of Vitrinite Reflectance

The frequency distribution of reflectance readings for all samples is presented in histograms of Figures 5.1, 5.2, 5.3, 5.4, 5.5 and 5.6. In ideal case, as in most coals, such histograms are single peaked, in this study, however, the vitrinite reflectance of the studied samples show multipeaked histograms with a relatively wide scatter.

The attempt for gathering the histograms into population groups show that most samples having either two or three histogram peaks (bimodal or trimodal distribution), the exception being Kmeta sample which show only single histogram peak. The presence of broad range of distribution in the vitrinite reflectance data could be related to recycled organic matter which is very common in marine sediments as demonstrated by Van Gijzel, in Brooks, (1981). The other possibility could be due to measurement being mistakenly made on inertinite as at a high maturity level of >1.0 %, it is often difficult to distinguish between vitrinite and inertinite.

5.2.3 Fluorescence Microscopy

The application of fluorescence microscopic techniques to the study of dispersed sedimentary organic materials is appealing for many reasons, one being a useful tool for the direct examination of those macerals prone to the generation of liquid hydrocarbon (Senftle, et al., 1993). An excitation wavelength in the UV or blue
Figure 5.1A & B. Vitrinite reflectance histograms.
A) Sample CH₂; B) Sample CH₄
(Location Charu Fm. Pahang)
Figure 5.2A & B. Vitrinite reflectance histograms. A-sample Sa1, B-sample Sa4 (Location Bukit Pak Sagor).
Figure 5.3A & B. Vitrinite reflectance histograms.

A) Sample Per2; B) Sample Per3.

(Location: Jengka Pass)
Figure 5.4A & B. Vitrinite reflectance histograms.
A) Sample Tr1; B) Sample Tr2.
(Location: Semantan Fm)
Figure 5.5A & B. Vitrinite reflectance histograms.
A) Sample Km9 (slate); B) Sample Km2 (Phyllite)
(Location: Bt Tg Mat Amin, Chukai)
Figure 5.6. Vitrinite reflectance histogram of the Panching limestone (Pat).
( Location: Bt. Panching )
range of the spectrum is used to produce a fluorescence, which is generally restricted to the liptinitic components.

Photomicrographs showing maceral composition of whole rock samples from selected carbonaceous sediments used in this study are shown in Plates 5.1, 5.2, 5.3, 5.4, 5.5 and 5.6. All photos were taken under reflected light and oil immersions. Most of the organic remains are poorly preserved and of amorphous nature. The rocks are generally stained with bitumen. Under blue light excitation, yellow orange fluorescence of bitumen and some amorphous organic matter can be observed (Plates 5.2 - 5.5 - 5.6). Scanning electron micrograph (Plate 5.7) illustrate cellular structure of wood in sample from Bt. Tg. Mat Amin, Chukai.

5.2.4. Total Organic Carbon (TOC)

The total organic carbon data for six selected samples represent the different lithologies of the different formations is given in Table 5.2.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Lithology</th>
<th>LECO results wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pa1</td>
<td>Limestone</td>
<td>Trace</td>
</tr>
<tr>
<td>Sa4</td>
<td>Shale</td>
<td>0.26</td>
</tr>
<tr>
<td>Per1</td>
<td>Shale</td>
<td>1.34</td>
</tr>
<tr>
<td>Tr4</td>
<td>Shale</td>
<td>0.57</td>
</tr>
<tr>
<td>Ch1</td>
<td>Shale</td>
<td>1.34</td>
</tr>
<tr>
<td>Ch2</td>
<td>Coaly shale</td>
<td>4.76</td>
</tr>
<tr>
<td>Ch4</td>
<td>Coaly shale</td>
<td>9.55</td>
</tr>
</tbody>
</table>
a) Sample Per1 (Location: Jengka Pass)

b) Sample Ch4 (Location: Charu Fm.).

Plate 5.1 a & b. Photomicrographs showing dark brown bitumen staining occurring within a groundmass with fine grained, highly reflecting vitrinite particles, inertinite, quartz and clay matrix. Reflected white light; field width = 0.21 mm.
Plate 5.2. Photomicrograph showing yellow orange fluorescing bitumen staining. Same view as plate 5.1 b under blue light excitation; field width = 0.21 mm. Charu Formation, Pahang.
Plate 5.3a & b. Photomicrographs showing possible poorly preserved graphitized plant remains. Reflected white light; field width = 0.21 mm.
Plate 5.4. Photomicrograph showing a particle with distinct cellular structure of unknown identity. Reflected white light; field width = 0.21 mm.
Sample Km2 (Phyllite)
(Location: Bt. Tg. Mat Amin (Chukai))
Plate 5.5a & b. Photomicrographs showing amorphous organic matter. Reflected blue light; field width = 0.21 mm.
Plate 5.6a & b. Photomicrographs showing yellow orange fluorescing bitumen occurring within ground mass of unrecognisable macerals. Reflected blue light; field width $a = 0.65$ mm & $b = 0.21$ mm.
Plate 5.7. Scanning electron micrograph show cellular carbonaceous wood fragments preserved in sample Kms (Phyllite). Location: Bt. Tg. Mat Amin (Chukai).
Generally the total organic carbon content (Table 5.2) show a distinct variation between the abundance of organic matter present in the shales and coaly shales, compared to that in the limestone.

The Charu samples possess the highest TOC, followed by the Permian and Semantan samples, the Sagor samples read a very low TOC and the Panching limestone sample possesses only a trace amount of organic matter. However, the TOC content of the Charu samples Ch1, Ch2 and Ch3 are 1.34, 4.76 and 9.55 %, respectively, with an average of 5.22 %, the Permian sample (Per1) has recorded TOC content of 1.34 %, the Semantan sample (Tr4) has TOC content of 0.57, the Sagor sample (Sa4) displayed TOC content of 0.26 %, whilst the Panching limestone sample (Pa1) illustrated only trace TOC values. The organic richness in these samples is probably due to either to abundance of organic matter in the form of kerogen and/or to the presence of bitumen.

5.2.5. Normal Alkane and Acyclic Isoprenoids

The distribution of saturated hydrocarbons illustrated by capillary gas Chromatograms (Figures 5.6 – 5.11) of selected nine carbonaceous samples represent the different lithologies of the different formations. The GC fingerprints of the shales and coaly shales reveal a wide range of n-alkanes with carbon number that range from nC21 to nC31 or higher. A number of samples show dominant humps comprising unresolved complex hydrocarbon mixtures. The hump appearing generally at around nC22. The presence of hump is possibly an indication of biodegradation. The moderate molecular weight n-alkanes (nC10 – nC20) and acyclic isoprenoids, such as pristane and phytane, occur only in low concentration in all samples. The possible presence of C21 highly branched isoprenoid is noted in the limestone sample.
Figure 5.7. Gas chromatograms of saturated hydrocarbons.
A) Charu Fm. (Ch4); B) Panching limestone Fm. (Pa1)
Figure 5.8. Gas chromatograms of saturated hydrocarbons
A) Sample Ch1; B) Sample Ch2; Charu Fm
Figure 5.9. Gas chromatograms of saturated hydrocarbons
A) Sample Tr2; B) Sample Tr4; Semantan Fm.
Figure 5.10. Gas chromatograms of saturated hydrocarbons
A) Sample Sa2; B) Sample Sa4; Sagar Fm.
Figure 5.11 Gas chromatogram of saturated hydrocarbons. Sample Per1; Jengka Pass.
(Simoneit, Per. Comm., 1999) but could not be confirmed by mass spectra due to its low concentration. The Panching limestone sample (Fig. 5.7b) show a slight even n-alkane predominance and is dominated by nC$_{17}$ - nC$_{19}$ alkanes. These suggest a significant contribution of algal derived organic matter and lacks in higher plant material as suggested by a very low abundance of higher molecular weight n-alkanes (nC$_{20}$ to nC$_{31}$). The shale/coaly shale samples display a smooth homologous series within the higher molecular weight n – alkanes extend beyond nC$_{30}$ suggesting significant input of higher land plant organic matter into these sediments. The fingerprints also show apparent evidence of slight biodegradation (i.e. partially removal of n–alkanes relative to entire alkane distribution) for most of the samples, being more affected around nC$_{10}$ to nC$_{21}$. The Panching limestone sample is possibly most biodegraded as suggested by the presence of the highest hump of an unresolved complex compounds among the samples studied. The presence of biodegradation could be related to the mixing of oxygenated waters within these sediments due to prolong surface exposures which is a necessary condition for biodegradation to have taken place.

5.2.5.1. Pr/Ph ratio

The isoprenoid alkanes pristane (Pr) and phytane (Ph) are present in all of the samples studied, usually as the most major constituents of the isoprenoid alkanes.

Historically, the ratio of the pristane to phytane, has long been associated with the redox conditions of the depositional environment (Brooks and Smith, 1969; Powell and Mckridy, 1973). These early workers assumed that both pristane and phytane were derived from the phytal side chain of chlorophyll. More recently, it has been shown that pristane can be derived from α–tocopherol and phytane from the
bisphytanyl ethers which occur in archaeabacteria (Philp 1994). According to Cooper (1990), pristane and phytane are derived from the chlorophyll of higher plants, algae and photosynthetic bacteria and from archaebacteria.

The existence of various precursors therefore dictates that the Pr/Ph ratio should be used with care. All of the samples studied here display Pr/Ph ratios greater than 3.0 except for Pa1 (Table 5.5). The highest ratio occurs in the samples Sa2 and Ch1. The Ch2 and Ch4 samples show Pr/Ph ratios < 4, whilst the Ch1, Sa2 and Sa4 samples have Pr/Ph ratios > 4. The Panching limestone has a Pr/Ph ratio equal to 1.8. The high Pr/Ph ratios in the Charu and Sagor samples and the low Pr/Ph ratio of the Panching limestone, are more likely to be associated with the source of organic matter and less indicative of the extent of the anoxicity / oxicity of the depositional condition (discussed further in section 5.3.2).

5.2.5.2. Carbon Preference Index (CPI)

The CPI value is influenced by type of organic matter and by the maturity (Tissot and Welte 1984). High CPI values represent an odd carbon number preference over even and occur in response to the chemistry in higher plant of surface waxes (an important precursor of waxy components in sedimentary organic matter). Hydrocarbons thought to be derived from a coaly organic matter source contain carbon preference indices equal to or greater than one. Moldowan et al. (1985) concluded that an odd carbon preference is characteristic of oils derived from source rocks deposited in non marine depositional environments. In contrast, predominance of an even numbered n-alkane preference is commonly observed in bitumens and oils derived from carbonate evaporite rocks (Palacas et al., 1984). If the total even and
odd numbered paraffins are equally abundant the value of the (CPI) will be equal to one, as generally observed in high maturity samples (Tissot and Welte 1984).

In the studied samples a distinct odd over even predominance of higher molecular weight \( n \)-alkanes (C\textsubscript{25}-C\textsubscript{31}) is observed producing a CPI value of between 1.0 and 1.2 (Table 5.5). The GC fingerprints reveal a noticeable odd over even predominance with CPI values of 1.2, 1.1, 1.2 for Samples Ch\textsubscript{1}, Ch\textsubscript{2} and Ch\textsubscript{3} respectively. Samples Sa\textsubscript{2} and Sa\textsubscript{4} possess CPI values of 1.0. Samples Pa\textsubscript{1} has a CPI value of 1.2. Samples Per\textsubscript{1}, Tr\textsubscript{2} and Tr\textsubscript{4} have CPI values of 1.0. The CPI values of > 1.0 observed in most of the studied samples is believed to be influenced by the type of organic matter rather than thermal maturity as all samples are known to possess a high maturity of > 1.0 % Ro (Table 5.1), and to be discussed further in section 5.3.1.

5.2.6. **Gas Chromatography – Mass Spectrometry (GC – MS)**

Examples of tricyclic terpanes and pentacyclic triterpanes distributions of selected samples are given in Figures 5.12, 5.13, 5.14 and Figures 5.15, 5.16 & 5.17 for steranes. Peaks identification are given in Table 5.3 and 5.4.

5.2.6.1. **Tricyclic and Tetracyclic Terpanes (M/Z 191)**

The tricyclic terpanes are useful series of biomarkers for differentiating type of organic matter, maturity and depositional environments discussed in sections 5.3.1 – 5.3.3. Figures 5.12, 5.13 and 5.14 show typical distribution of the tricyclic and tetracyclic terpanes in a selection of samples studied here. Tricyclic and tetracyclic terpanes are present in high abundance in all of the samples analysed. The C\textsubscript{24} tetracyclic is the major component in most of these samples.
Figure 5.12A & B (M/Z 191) mass chromatograms showing the relative distribution of terpanes and triterpanes released from the Charu Formation. A) Sample Ch1, B) Sample Ch4.
Figure 5.13. M/Z 191 mass chromatograms showing the relative distribution of terpanes and triterpanes released from A) Panching limestone Fm. (Pa1) ; B) Sagor Fm. (Sa2)
Figure 5.14 M/Z 191 mass chromatograms showing the relative distribution of terpanes and triterpanes released from A) Permian Fm. (Perm); B) Semantan Fm. (Trn)
Figure 5.15A & B. Sterane (MIZ 217) distributions from rocks extracts of the Charu Fm.
A) Sample Ch1, ; B) Sample Ch4
Figure 5.16. Sterane (M/Z 217) distributions from rocks extracts of: A) The Panching limestone (P1); B) the Sagor Fm. (Sa2)
Figure 5.17. Sterane (M/Z 217) distributions from rocks extracts of: A) The Permian Fm. (Per1), B) The Semantan Fm. (Tr2)
Table 5.3 Identification for mass fragmentograms in M/Z 191

<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{23} tii</td>
<td>Tricyclic terpanes</td>
</tr>
<tr>
<td>C_{24} tin</td>
<td>Tricyclic terpanes</td>
</tr>
<tr>
<td>C_{25} tin</td>
<td>Tricyclic terpanes</td>
</tr>
<tr>
<td>C_{24} tetra</td>
<td>Tetracyclic terpanes</td>
</tr>
<tr>
<td>(Tm) (C_{27})</td>
<td>17 α(H) , - 22,29,30 - trisnorhopane</td>
</tr>
<tr>
<td>(Ts) (C_{27})</td>
<td>18 α(H), - 22,29,30 - trisnorneohopane</td>
</tr>
<tr>
<td>C_{29}</td>
<td>17 α(H), 21 β (H) norhopane</td>
</tr>
<tr>
<td>C_{29}Ts</td>
<td>18 α(H) – 30 - norneohopane</td>
</tr>
<tr>
<td>C_{30}</td>
<td>17 α(H), 21 β (H) hopane</td>
</tr>
<tr>
<td>C_{30}*m</td>
<td>17 β (H), 21 α (H) moretane</td>
</tr>
<tr>
<td>C_{31}S</td>
<td>17 α(H), 21 β (H)22S homohopane</td>
</tr>
<tr>
<td>C_{31}R</td>
<td>17 α(H), 21 β (H)22R homohopane</td>
</tr>
<tr>
<td>C_{32}S</td>
<td>17 α(H), 21 β (H)22S bishomohopane</td>
</tr>
<tr>
<td>C_{32}R</td>
<td>17 α(H), 21 β (H)22R bishomohopane</td>
</tr>
<tr>
<td>C_{33}S</td>
<td>17 α(H), 21 β (H)22S trishomohopane</td>
</tr>
<tr>
<td>C_{33}R</td>
<td>17 α(H), 21 β (H)22R trishomohopane</td>
</tr>
<tr>
<td>C_{34}S</td>
<td>17 α(H), 21 β (H)22S tetrakishomohopane</td>
</tr>
<tr>
<td>C_{34}R</td>
<td>17 α(H), 21 β (H)22R tetrakishomohopane</td>
</tr>
</tbody>
</table>

Table 5.4 Identification of peaks in M/Z 217

Steranes and diasteranes.

Di : C_{27} 13β (H), 17α – 20S diasteranes  
: C_{27} 13β (H), 17α – 20R diasteranes  
C_{27} : C_{27} 5α (H), 14α (H), 17α (H) – 20S & 20R steranes  
C_{28} : C_{28} 5α (H), 14α (H), 17α (H) – 20S & 20R steranes  
C_{29} : C_{29} 5α (H), 14α (H), 17α (H) – 20S & 20R steranes
Figure 5.18 Structures of commonly occurring biomarkers in the samples studied
5.2.6.2 Pentacyclic Terpanes

The distribution of hopanes within the Kuantan Group and Triassic carbonaceous sediments in this study were determined from the distribution in the m/z 191 ion chromatograms. Triterpenoids with hopane skeleton ( Figure 5.18 ) are ubiquitous in geological samples, indicating a widespread bacterial input ( Van Dorsselaer et al., 1974 ; Ensminger et al., 1974 ).

5.2.6.2.1. Hopane

The m/z 191 chromatograms for the selected samples show that the pattern of all samples belongs mostly to the 17α (H), 21β (H) hopanes series. The hopane series is ranging from C27 to C34 or more with the absence of the C28 homologue. The C30 regular hopane is the most predominance member of the series followed by C29 norhopane. The extended hopanes which occurs as stereo isomeric pairs, from C31 to C35, commonly display a staircase distribution pattern (i.e uniformly lower amount with increasing molecular weight ). The C31 and higher homologues occur as either 22S and 22R epimers. The commonly observed values of the 22S/22R epimers of C31, C32, C33 extended hopanes are within the range of 1.3 – 1.4, 1.2 – 1.4 and 1.3 – 1.5 respectively. Tm commonly exceeds Ts.

5.2.7. Steranes M/z 217

Steranes commonly found in mature sediments and crude oils are derived via diagenesis from sterols which are widely dispersed in plants and microrganism, with the C27 and C28 sterols most abundant in marine organism and the C29 sterols in higher plants ( Gonzalez - vila, 1995 ). The C27, C28 and C29 steranes occur as 20S and 20R epimers.
The m/z 217 (Figures 5.15, 5.16, 5.17) fragmentograms show similar sterane distribution for all the selected samples. The distribution is, however, likely to be masked by a number of contamination peaks of probable phthalate compound. The steranes are present at relatively lower concentrations compare to tricyclic, tetracyclic and pentacyclic terpanes. The distribution of the C_{27} : C_{28} : C_{29} steranes occur in approximately equal concentration. However samples such as Tr2 and Ch1 show that the C_{27} steranes are slightly more abundant than the C_{29} steranes probably indicating a predominance of a quatic microrganism compared to other samples.

The diasterane peaks are present only in minor or trace amounts in nearly all the studied samples. The panching limestone sample (Pa1) shows low concentrations of rearranged steranes/diasteranes relative to regular steranes and could be indication of an acidic carbonate depositional environments as suggested by Zumberger (1984). Rubinstein et al. (1975) proposed that the relative concentrations of the diasteranes reflect the presence of clay minerals and their ability to catalyse sterane rearrangement reactions. Sieskind et al. (1979) have shown that the diasteranes can form from precursor sterol substance through the acid – catalytic activity of clay. This possibly suggests the low abundance of diasteranes in these carbonaceous samples studied could be related to limited occurrence of acid – clay catalysed rearrangement of regular steranes.

5.3 Discussion

5.3.1 Maturity

Maturation of organic matter in sediments is a chemical change in which heat and pressure act during burial of sediments, causing many changes in the original organic matter of the sediments. Many varied parameters have been suggested and
used as possible indicators of organic maturity such as mean vitrinite reflectance (\%Ro), amount of extractable soluble organic matters, n-alkane preference index (CPI), and pentacyclic triterpanes isomers ratios (Douglas and Williams, 1981).

The geochemical maturity parameters of the studied samples are presented in Tables 5.5 and 5.6. The mean vitrinite reflectance (\%Ro) for all the studied samples is in the range of 1.02\% - 1.13\%, indicating that these sediments have reached a high level of thermal maturity of late oil window range.

It is well established that the carbon preference index (CPI) values are influenced by the type of organic matter and by the degree of maturity. Higher (CPI) values \( > 1.5 \) always refer to relatively immature samples, low (CPI) values do not necessary mean higher maturity, they can also mean a lack of higher n-alkane stemming from terrestrial input (Tissot and Welte, 1984). Bray and Evans (1961) quantified numerical values of the n-alkane distribution by defining a carbon preference index CPI and they found this value higher in immature sediments but near unity or just below in crude oils.

The slight odd-even predominance of n-alkane in these samples (CPI\textsubscript{25-23} : 1.0-1.2, Table 5.5) is consistent with their maturity range. The decrease in CPI values being an indication of the increase in thermal maturity, however, no correlation is observed with vitrinite reflectance data. In these studied samples, it is believed that the influence of type of organic matter, which is mostly of terrestrial origin, is more dominant than the thermal effect on the CPI values obtained.

Two maturity parameters based on hopane and sterane isomer ratio have been used to assess the maturity level of the oils by a number of workers. For example, Seifert and Moldovan (1980) used the epimerisation ratio of 22R to 22S of C\textsubscript{31} - 33
Table 5.5 Organic Geochemistry Data

<table>
<thead>
<tr>
<th>Formation</th>
<th>Age</th>
<th>Sample</th>
<th>Lithology</th>
<th>n-alkane max</th>
<th>Pr/Ph</th>
<th>Pr/nC17</th>
<th>Ph/nC18</th>
<th>nC27/nC17</th>
<th>CPI nC25-nC31</th>
<th>TOC %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semantan</td>
<td>Triassic</td>
<td>Tr2</td>
<td>Shale</td>
<td>C27</td>
<td>8.3</td>
<td>5.0</td>
<td>0.24</td>
<td>19</td>
<td>1.1</td>
<td>n.d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tr4</td>
<td>Shale</td>
<td>C27</td>
<td>3.3</td>
<td>3.3</td>
<td>0.19</td>
<td>16.7</td>
<td>1.1</td>
<td>0.57</td>
</tr>
<tr>
<td>Permian</td>
<td>Permian</td>
<td>Per1</td>
<td>Shale</td>
<td>C27</td>
<td>7.5</td>
<td>5.5</td>
<td>0.24</td>
<td>35</td>
<td>1.1</td>
<td>1.34</td>
</tr>
<tr>
<td>Sagor</td>
<td>Carboniferous</td>
<td>Sa2</td>
<td>Shale</td>
<td>C27</td>
<td>9.0</td>
<td>0.15</td>
<td>0.23</td>
<td>24.8</td>
<td>1.0</td>
<td>n.d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sa4</td>
<td>Shale</td>
<td>C27</td>
<td>6.5</td>
<td>8.0</td>
<td>0.23</td>
<td>39.7</td>
<td>1.0</td>
<td>0.26</td>
</tr>
<tr>
<td>Panching</td>
<td>Carboniferous</td>
<td>Pa1</td>
<td>Limestone</td>
<td>C18</td>
<td>1.8</td>
<td>0.2</td>
<td>0.20</td>
<td>0.85</td>
<td>1.2</td>
<td>trace</td>
</tr>
<tr>
<td>Charu</td>
<td>Carboniferous</td>
<td>Ch1</td>
<td>Shale</td>
<td>C28</td>
<td>9.0</td>
<td>0.04</td>
<td>0.17</td>
<td>3.2</td>
<td>1.2</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ch2</td>
<td>Coaly shale</td>
<td>C27</td>
<td>3.5</td>
<td>1.1</td>
<td>0.38</td>
<td>7.6</td>
<td>1.1</td>
<td>4.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ch4</td>
<td>Coaly shale</td>
<td>C27</td>
<td>3.6</td>
<td>2.4</td>
<td>0.28</td>
<td>28.8</td>
<td>1.2</td>
<td>9.55</td>
</tr>
</tbody>
</table>

Pr/Ph: Pristane/Phytane ratio, CPI: Carbon preference index (after Bray and Evans, 1961). TOC: total organic carbon (% wt); n.d: not determined; nC27/nC17: normal - C27/normal -C17; Pr/nC17: Pristane/normal C17; Ph/nC18: phytane/normal C18
Table 5.6 Biomarker parameters for selected rock extracts in the area of study

<table>
<thead>
<tr>
<th>Formation</th>
<th>Age</th>
<th>Sample</th>
<th>Lithology</th>
<th>Hopanes</th>
<th>Extended Hopanes</th>
<th>C24 tetra/C23 tri</th>
<th>C23 tri/C30 hop</th>
<th>C24 tetra/C30 hop</th>
<th>C2920S/20S+20R Steranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semantan</td>
<td>Triassic</td>
<td>Tr2</td>
<td>Shale</td>
<td>Ts/Tm 0.9 C29/C30 0.6 C32 0.59</td>
<td>C31 1.4 C32 1.4 C33 1.3</td>
<td>C24 1.6 C23 tri 0.3 C30 hop 0.4</td>
<td>C24 tetra/C30 hop 0.5</td>
<td>C2920S/20S+20R Steranes 0.6</td>
<td></td>
</tr>
<tr>
<td>Permian</td>
<td>Permian</td>
<td>Per1</td>
<td>Shale</td>
<td>Ts/Tm 0.9 C29/C30 0.6 C32 0.54</td>
<td>C31 1.3 C32 1.2 C33 1.4</td>
<td>C24 2.5 C23 tri 0.5 C30 hop 1.2</td>
<td>C24 tetra/C30 hop 0.6</td>
<td>C2920S/20S+20R Steranes 0.5</td>
<td></td>
</tr>
<tr>
<td>Sagor</td>
<td>Carboniferous</td>
<td>Sa2</td>
<td>Shale</td>
<td>Ts/Tm 0.8 C29/C30 0.7 C32 0.56</td>
<td>C31 1.3 C32 1.3 C33 1.4</td>
<td>C24 2.5 C23 tri 0.6 C30 hop 1.6</td>
<td>C24 tetra/C30 hop 0.6</td>
<td>C2920S/20S+20R Steranes 0.6</td>
<td></td>
</tr>
<tr>
<td>Panching</td>
<td>Carboniferous</td>
<td>Pa1</td>
<td>Limestone</td>
<td>Ts/Tm 0.9 C29/C30 0.7 C32 0.57</td>
<td>C31 1.4 C32 1.4 C33 1.4</td>
<td>C24 3.4 C23 tri 0.4 C30 hop 1.2</td>
<td>C24 tetra/C30 hop 0.6</td>
<td>C2920S/20S+20R Steranes 0.6</td>
<td></td>
</tr>
<tr>
<td>Charu</td>
<td>Carboniferous</td>
<td>Ch1</td>
<td>Shale</td>
<td>Ts/Tm 0.8 C29/C30 0.6 C32 0.56</td>
<td>C31 1.3 C32 1.4 C33 1.5</td>
<td>C24 1.9 C23 tri 0.3 C30 hop 0.5</td>
<td>C24 tetra/C30 hop 0.6</td>
<td>C2920S/20S+20R Steranes 0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ch4</td>
<td>Coaly shale</td>
<td>Ts/Tm 0.9 C29/C30 0.7 C32 0.59</td>
<td>C31 1.3 C32 1.3 C33 1.5</td>
<td>C24 2.8 C23 tri 0.8 C30 hop 2.3</td>
<td>C24 tetra/C30 hop 0.6</td>
<td>C2920S/20S+20R Steranes 0.5</td>
<td></td>
</tr>
</tbody>
</table>

Tm: 17α(H) - trisnorhopane; Ts: 18α(H) - trisnorisohopane; C29/C30: αβ norhopane/αβ C30 hopane; C24tetra/C23tri: C24 tetracyclic terpanes/C23 tricyclic terpanes; 22S/22S + 22R of C31-32-33 17α(H) homohopane ratio; C29 20S/20S + 20R sterane
extended hopane. The stereo isomeric ratio 22S/22R of the extended hopanes $C_{31} - C_{35}$ also have been used as maturity indicators (Ensminger, et al., 1974; Mackenzie et al., 1980). In general 22S/22R ratio < 1.2 are considered immature where ratios of about 1.3 or greater indicate the rock are within the oil generation window (Palacas et al., 1984). Data in Table 5.6 show all the samples have 22S/22R ratio of the extended hopane $C_{31} - 33$ within the oil maturation window range (1.3 – 1.5).

Extracts from samples of the Charu, Sagor and Panching limestone Permian and Semantan formations have a predominance of $T_m$. In addition they have high concentrations of $C_{29}$ Ts and relatively low concentration of $C_{30}$ moretane and the $C_{31}-C_{35}$ extended hopanes. The lower moretane concentration and elevated concentration of the Ts series reflect the high maturity of these sediments.

The 22S/22S+22R for $C_{32}$ hopane in all the samples studied is about 0.60 (i.e. close to the range of 0.56-0.59, Table 5.6). The 22S/22S+22R ratio has an equilibrium value of 0.60 and corresponds to the onset of hydrocarbon generation (Mackenzie 1984). The isomerisation of the $C_{29}$ steranes, as shown by the epimer ratio of 20S/20S+20R, range from 0.5 to 0.6, has typical of equilibrium values, thus supporting the vitrinite reflectance data.

This high maturity suggests the sediments have been buried to considerable depth, prior to being uplifted to their present position. Although of high maturity, the samples are still within the oil-window range, suggesting these samples have not been too severely effected by thermal metamorphism or active tectonic activities of the Eastern and Central Belt of Peninsular Malaysia.
5.3.2. Type of the organic matter

Gas chromatogram fingerprints of all the samples show abundant pristane and high pristane/phytane ratios which are characteristic of terrigenous materials. The most common application of these alkanes is to infer the source of the organic materials (Gonzalez-Vila, 1995).

The gas chromatograms of the saturated hydrocarbons for all the selected samples in this study display smooth homologus series of n-alkane extending beyond n-C_31, with a low odd/even predominance and with a higher relative concentration of long chain n-alkanes. The waxy appearance of these samples suggest a significant contribution of organic matter input of land plant origin.

A relatively lower abundance of n-alkanes is displayed by the Panching limestone sample. Most of the samples show evidence of slight biodegradation as suggested by the presence of an unresolved hump and the loss of the lower molecular weight n-alkanes in the shales/coaly shales of the Charu and Sagor, Permian and Semantan formations. The waxy appearance of these samples suggest significant input of higher land plant organic matter in these sediments. The Panching limestone samples is dominated by nC_17-nC_19 alkanes suggesting significant contributions of algal derived organic matter. The lack of higher land plant derived organic matter within the Panching limestone sample is suggested from the low concentration of higher molecular weight n-alkanes compared to the Charu, Sagor, Permian and Semantan sediments.

No distinct variation have been observed for the Ts/Tm ratios (Table 5.6). In general low values of this ratio are considered to be associated with higher land-plant organic matter. Among the samples studied here, this ratio may not be indicative of
Based on the above discussed parameters, although differences between the sediments within a particular formations could not be made, distinction can be made between the dominant type of organic matter that is present in the shale and coaly shale compared to the limestone. It can be said that the Charu, Sagor, Permian and Semantan formations seem to have received substantial amounts of land-derived organic matter that has been transported into a marine depositional setting, whilst the Panching limestone is dominated by algal-derived organic matter and lacks higher plant material.

5.3.3 Depositional Environment

High Pr/Ph ratios have generally been inferred to indicate that the organic matter has undergone some degree of oxidation and decarboxylation of the phytol side-chain of chlorophyll which leads to the formation of pristane. Under reducing conditions, phytane is more likely to be produced through hydrogenation and dehydration of phytol (Brooks et al., 1969). Organic matter derived predominantly from terrestrial plants would therefore be expected to show a high Pr/Ph ratio, however, organic matter derived predominantly from aquatic photosynthetic organism, such as algae, could also have a high Pr/Ph ratio if the water column were relatively well oxygenated (Clayton, 1993). Marine or open water sedimentation with high bacterial activity yields only relatively small amounts of pristane and phytane as a result gives low Pr/Ph (<2.0) and Pr/nC17 (<1.0) ratios, where as in peat swamp environments, with low aerobic bacterial activity, most of the phytol are converted to pristane with only small amounts of phytane. Thus, oils from source rocks deposited under peat swamp conditions will have a high Pr/Ph (>3.0) and Pr/nC17 (>1.0) ratios (Didyle et al., 1978, Ljimbach, 1975).
The Pr/Ph and Pr/nC\textsubscript{17} ratios for the studied samples (Table 5.5), show the Pr/Ph ratios of these carbonaceous samples varies from fairly low 1.8 to a fairly high 9.0, where as the Pr/nC\textsubscript{17} varies from very low 0.04 to moderately high 8.0, the exception being in the Panching limestone (Pa1) which show Pr/Ph and Pr/nC\textsubscript{17} ratios of 1.8 and 0.2 respectively. The high Pr/Ph > 3.0 and high Pr/nC\textsubscript{17} > 1.0 ratios indicating that the Ch\textsubscript{1}, Ch\textsubscript{2}, Ch\textsubscript{4}, Sa\textsubscript{4}, Per\textsubscript{1}, Tr\textsubscript{2} and Tr\textsubscript{4} samples were most probably deposited under oxidising condition. This is observed for all of the Sagor, Charu, Permian and the Semantan samples analysed except for Sa\textsubscript{2} and Ch\textsubscript{1} with relatively low Pr/nC\textsubscript{17} values. Although the Pr/Ph ratio values in the samples studied are most likely source influenced, the low values of Pr/Ph (< 2) in the Panching limestone (Pa1) sample may to a certain extent suggests an aquatic depositional environment under reducing condition.

The ratio of C\textsubscript{27} trisnorhopane (Tm), relative to C\textsubscript{27} trisnorneohopane (Ts), Tm/Ts, was first proposed as a maturity parameter by Seifert and Moldowan (1981). The Ts/Tm ratio can also serve as a facies parameter for related oils (Barkat, et al. 1997). Mello, et al (1988b) suggested that Ts/Tm values below (1.0) imply a lacustrine, saline, marine evaporite or marine carbonate depositional environment, whereas values above 1.0 indicate lacustrine fresh water or marine deltaic environment. Based on the Ts/Tm data in Table 5.6, all of the studied samples possess Ts/Tm ratios of < 1.0, therefore would be related to either lacustrine, saline or marine carbonate depositional environment. This is in agreement with the depositional environments postulated by workers such as Metacliffe, et al. (1980) who postulated the Charu formation was deposited in a shallow marine near shore environment, the Panching limestone formed in a warm shallow marine reefal
environments, and the Sagor formation was deposited in a relatively shallow marine environment. Goh (1973) postulated carbonaceous sediments that formed slate and phyllite in Chukai area were deposited in shallow water close to shore line, and according to Jaafar, (1976) and Yusof, (1984) Semantan Formation probably accumulated in relatively deeper marine environment.

The relative abundance of the C_{31}-C_{34} extended hopanes compared to the C_{30} hopane and C_{29} norhopane have been proposed to be typically associated with carbonate sedimentary environments (Palacas et al., 1984). However, a relatively high concentration of extended hopanes and C_{29} norhopanes was found in the rock extracts of the Charu, Sagor, Permian and Semantan formations, although the extracted samples were actually black shales and coaly shale, not carbonates. Enhanced concentrations of extended hopanes have been proposed to reflect the more anoxic marine nature of a depositional environment (Moldowan, 1988) as is probably the situation with the Charu, Sagor, Semantan and Permian organic rich sediments studied.

5.4 Conclusions

The results from this investigation of the selected Upper Paleozoic Kuantan Group carbonaceous sediments using petrography and organic geochemical data such as % Ro, CPI values, and measurement of the stereoisometric ratios (22S/22S+22R and 20S/20S+20R) of the extended hopane and steranes, indicate the sediments studied have reached a relatively high level of thermal maturity (late oil window maturity).

Features such as high Pr/Ph ratio (> 3.0) and high Pr/nC_{17} (> 1.0), strong predominance of high molecular weight n-alkane, low concentration of steranes, high
C24 tetra/C23 tricyclic ratio, and relatively high Ts/Tm ratio indicate that the Charu, Sagor, Permian and Semantan samples were derived from higher plant organic matter that was most probably deposited under oxidizing conditions.

The Panching limestone sample is dominated by nC17 – nC19 alkanes suggesting significant contribution of algal derived organic matter and lacks higher plant material. The high abundance of C24 tetracyclic terpanes could be associated with either higher land-plant, algae, or a microbial source. The Pr/Ph and Pr/nC17 ratios show distinct differences between the Panching limestone and the shales of the Charu, Sagor, Permian and Semantan formations, reflecting dissimilarities in depositional environmental conditions.

The distribution of tetracyclic, tricyclic terpanes and pentacyclic triterpanes show little variation between the studied samples, suggesting that all these biomarker extracts were derived from the same general type of organic matter namely land plant and were reworked into the marine sediments that subsequently formed the Charu, Sagor, Permian and Semantan formations. The presence of significant marine influence is suggested by the high abundance of tricyclic terpanes in all the samples studied.

The differences in depositional setting and resulting organic geochemical facies between the formations are further manifested by the relative abundance of the land derived macerals as observed petrographically.

Although of high maturity, the samples are still within the oil window maturity range, suggesting these samples have not been too severely effected by thermal metamorphism or the active tectonic activities of the Eastern and Central belts of Peninsular Malaysia.