The main aim of this chapter is to study the biomarkers i.e. the distribution of hopanoids and alkanes in bitumen extracts of coals and carbonaceous shales of Barail Group of Upper Assam to assess the maturity of potential petroleum source rocks in the studied area. The biomarker study also includes the assessments of depositional environment, organic sources and types in addition to thermal maturity. This chapter involves the detail analytical method of biomarker study.

6.1 Introduction

Biomarkers are being increasingly used to determine the geological history of a petroleum deposit and have application in the determination of thermal history, oil-source correlation and in recognition of altered oils. Sedimentary rocks record a wide variety of ancient environments and are hosts for the fossilized remains of the living creatures which populated those habitats. The bulk of biomass is, however, composed of microorganisms, comprising bacteria, algae and fungi. Most of these are without skeletal tissue and have little chance of preservation in a recognizable form, except in very favourable circumstances. Microbes may, however, leave a record of their presence through the modified but identifiable residues of the lipids which formed their cell membranes. Many higher plants also leave chemical residues which once constituted their cuticular waxes, resins, and essential oils. These molecules, which are mostly preserved in the form of hydrocarbons, are known as chemical fossils, or biomarkers.

Biomarkers are occurring in all organic-rich rocks and petroleum. They do not represent the remains of an individual organism in the same way as a shell or a bone but rather a 'brew' comprising the residue of an entire community. Such a mixture will include the relics from the original primary producers or photo-synthesizers, as well as the subsequent waves of grazing or heterotrophic organisms beginning with meiofauna, protozoans, fungi, and bacteria which use oxygen, followed by anaerobes such as
sulphate-reducing bacteria and finally by methanogens. If sunlight persists to depths where the waters become anaerobic then the photosynthetic bacteria may be important community members.

6.1.1 Biomarkers as thermal indicators

Some of the most significant recent advances in biomarker chemistry are in the use of the ratios of key molecules to determine the thermal history of sediment. Research into the formation and subsequent isomerization of aromatic compound classes such as methyl naphthalenes, methylphenanthrenes, and alkylbiphenyls has identified changes which are effected more by time than by temperature and vice versa. This then opens the possibility of quantifying both upper temperature limits and heating rates, data which in turn can be applied in basin modelling studies. A new source rock maturity indicator for marine sediments based on an HPLC analysis of porphyrins has recently been identified, allowing unequivocal recognition of the generation status of a particular source interval.

6.1.2 Biomarkers as palaeo-environmental and bio-stratigraphic indicators

Biomarkers are considered as an important indicator for palaeo-environmental reconstruction and hydrocarbon source potential. A recent study that the tracing of the origins of a homologous series of trimethylalkylbenzenes are found in certain source rocks to their source organism, Chlorobium sp., by a combination of their chemical structures and carbon isotope signatures. Chlorobium sp., or green sulphur bacteria, requires both low light and anoxic, sulphidem rich waters for growth, thus indicating a quiet, stratified marine water body for the depositional environment of the source rock. In another study, the distributions of $C_{30}$ 4-methyl sterane isomers, which are known to be produced by dinoflagellate algae, showed dramatic differences between marine source rocks and those occurring in sediments deposited in deep eutrophic lakes. The $C_{30}$ 4-methyl steranes described above appear to be largely confined to sediments of Mesozoic and Eocene age.
6.1.3 Previous work on biomarkers

Biomarkers are molecular compounds which can be extracted from crude oils, coals and all kinds of sedimentary rocks (Tissot and Welte, 1984). Biomarkers have numerous biological origins, and their occurrence can be related to a specific source, giving information of the type of fauna/flora present in the environment, or to depositional conditions, such as salinity or temperature (Peters and Moldowan, 1993). For these reasons, biomarkers are regularly used in palaeo-environmental studies (Olcott, 2007; Eglinton and Eglinton, 2008). Recent applications of biomarkers aim at tracing the evolution of life. In archean rocks, biomarkers give information on the timing and evolution of early forms of life (Brocks et al., 1999, 2005; Eigenbrode et al., 2008), while in more recent rocks and sediments, biomarkers help determining taxonomic relationships between taxa (Arouri et al., 2000; Talyzina et al., 2000). In the last decades, chemotaxonomic applications have been particularly developed for the study of flora associated with amber and coal deposits mostly of Mesozoic to recent age (Simoneit et al., 1986; Otto et al., 1997; Stefanova et al., 2005).

Mathur et al. (2000) studied oils from Lakadong and Langpar reservoirs from the Upper Assam Basin, using whole oil gas chromatography. Their study has shown that these oils are waxy with a predominance of n-alkanes in the carbon number range of 21–35 with maxima at C_{29}. Thus, Lakadong and Langpar oils in the Upper Assam Basin derive from terrigenous organic matter (Hedberg, 1968; Tissot and Welte, 1984). Mathur and Das (2013) carried out a study on the origin and maturity of Lakadong and Langpar oils in the basin using selected ion monitoring GC–MS analysis of biomarkers. They showed that these oils have high oleanane and low sterane contents. Further, C_{29} steranes are predominant amongst C_{27}, C_{28} and C_{29} steranes. An oil to source rock correlation study by (Goswami et al., 2005) in the western part of the basin showed that oils from the Bokabil (Early to Middle Miocene) and Sylhet (Middle to Late Eocene) formations are derived from terrigenous organic matter.
6.2 Experimental Procedure

6.2.1 Extraction method

For biomarker analyses, rock fragments were extracted with dichloromethane (DCM) during 24 hr in the refrigerator, in order to remove possible contamination on the sample surface. After this first extraction, the rock fragments were crushed to enable extraction of the lipids preserved inside the rock. Approximately 30 g of pulverized samples were extracted with a mixture of methanol (MeOH) and dichloromethane (DCM) (1/2, v/v) for 24 h with extensive stirring. This second extract was dried by means of roto-evaporation and partly resolubilized in cyclohexane. The cyclohexane-soluble fraction (maltenes) was further separated by column chromatography.

The apolar fraction was recovered from the maltenes by elution with cyclohexane on an activated silica column. Subsequent elution with a mixture of cyclohexane - DCM (2/1, v/v) recovered the aromatic fraction after which the polar fraction was recovered by elution with a mixture DCM – MeOH (2/1, v/v).

6.2.2 Procedure for analysis of biomarkers using GC-MS

The GC-MS is calibrated prior to analysis of the samples. Two different types of calibration are carried out; mass calibration of the mass spectrometer and retention time calibration of the gas chromatograph. Mass calibration is carried out to ensure that the mass spectrometer traps the ions of correct mass, i.e. when mass spectrometer has been set to detect ions of mass 191, it should detect only ions of mass 191 ± 0.5 and not beyond. This will ensure that only the fragments corresponding to the parent molecule that needs to be measured are detected. The mass spectrometer has an in-built calibration and tuning procedure. The calibration is carried out using a standard compound perfluorotributylamine (PFTBA). The PFTBA is automatically injected into the mass spectrometer and fragmented into ions of known masses during the mass calibration procedure. The lens voltage and current of the various lenses is adjusted during the tuning process to get the maximum response at the correct mass. The retention time calibration for the gas chromatograph is carried out after the mass calibration of the mass spectrometer. A standard solution of C\textsubscript{30} hopane is injected into gas chromatograph under the same analytical conditions (described below) as those
used for sample analysis and the retention time for the standard compound is determined.

The following analytical conditions of the gas chromatograph-mass spectrometer were maintained.

### 6.2.3 Gas Chromatograph – Mass Spectrometer conditions

**Oven**

<table>
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<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td>Initial Temperature</td>
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</tr>
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<td>Oven Ramp Rate</td>
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<tr>
<td>Final Temperature</td>
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<tr>
<td>Hold Time</td>
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</tbody>
</table>

**Injector**

- Temperature: 300ºC
- Mode: Split

**Carrier gas**

- Gas: Helium
- Flow Rate: 1 ml/min
- Slit ratio: 1:10

**Transfer line**

- Temperature: 300ºC

**Mass Spectrometer conditions**

- Electron Energy: 70eV
- Source Temperature: 200ºC

**m/z ratio to be mentioned**

<table>
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</tr>
</thead>
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<td>0.05</td>
</tr>
<tr>
<td>218</td>
<td>1</td>
<td>0.05</td>
</tr>
</tbody>
</table>
6.3 Composition of generated hydrocarbons

Hydrocarbons are a complex mixture of both organic and inorganic compounds. During the entire hydrocarbon generation process both oil and gas are generated. Hydrocarbons can be subdivided into four broad classes of compounds based on their polarity (Tissot and Welte, 1984).

6.3.1 Saturated hydrocarbons

The saturated hydrocarbons are compounds of carbon and hydrogen which do not contain any double bond between two carbon atoms. Based on the structures, saturated hydrocarbons can be grouped into two categories, i.e., i) Acyclics (either straight chain compounds or branched chain compounds) and ii) Cyclics (closed chain compounds). As these compounds neither have double bonds nor any atom other than hydrogen and carbon, these compounds are completely non-polar.

6.3.2 Aromatic hydrocarbons

Aromatic hydrocarbons are compounds of carbon and hydrogen that have at least one aromatic ring present in its atomic structure. Aromatic compounds are slightly polar due to the presence of double bonds, e.g. Benzene, Toluene, Xylene, Naphthalene etc.

6.3.3 Resins

Resins are non-hydrocarbon component of hydrocarbons which consist of large aromatic rings with a number of hetero atoms like nitrogen, sulphur and oxygen present in its atomic structures. Resins have higher polarity than aromatic compounds.

6.3.4 Asphaltenes

Asphaltenes have very complex structure which consist of a number of aromatic rings and also have hetero atoms like nitrogen, sulphur and oxygen. The asphaltenes fractions of hydrocarbons which are insoluble in non-polar solvents like n-pentane, n-hexane or n-heptane.

The saturated and aromatic hydrocarbons contain large molecules that called biomarkers. These biomarker compounds are used to determine the origin, maturity and biodegradation of sediments. The biomarker compounds are described below in detail.
6.4 Biomarker Compounds

Biomarkers or biological markers are present in minute quantities in saturated and aromatic hydrocarbons. They are also called the geochemical fossils, discussed above. Although they are organic compounds and their basic structure allows them to be undoubtedly related to parent compounds i.e. natural products of living organisms. Thus, biomarkers are geolipids derived from biolipids either without any transformation or with minor rearrangements which do not significantly affect the carbon skeleton. They are specific of well defined categories of living organisms indicative of environment of deposition. For example, pristane and phytane are derived from porphyrins, present in chlorophyll. Pristane (Pr or IP19) and phytane (Ph or IP20) are two of the most widely used compounds in geochemistry. The most usual source of pristane and phytane is the phytol side chain in chlorophylls (the main pigments that harvest the energy from sunlight terrestrial and aquatic plants). Under reducing conditions the phytol (C$_{20}$) is converted into phytane (C$_{20}$), but under oxidizing conditions, oxidation to an acid followed by decarboxylation is more likely, eventually resulting in pristine (C$_{19}$). The pristane/phytane ratio can be used as measure of the amount of oxygen present (i.e. the redox potential) of the depositional environment of a sediment (Didyk et al., 1978)

Steroids and triterpenoids are derived mainly from the cell membranes of microorganisms. The steroid family is characterized by a tetracyclic carbon skeleton. The precursors are sterols which are found mainly in the cell membranes of planktonic organisms. Their decay in sediments produces hydrocarbons such as steranes having the same tetracyclic carbon skeleton. Steranes having carbon number 27, 28, 29 and 30 are most important in petroleum geochemistry. C$_{29}$ sterane is derived from terrestrial organic matter. The main source of C$_{27}$ steranes is cholesterol, which is ubiquitous in eukaryotes, but tends to be in greater relative abundance in animals, so enhanced zooplankton contributions to sedimentary organic matter may be characterized by enhanced C$_{27}$ sterane abundance. C$_{30}$ steranes are derived from marine algae and are thus diagnostic of marine depositional environment. Triterpenoids belonging to hopane family are characterized by a pentacyclic carbon skeleton. Their precursors are molecules which form part of the cell membranes of prokaryote organisms (bacteria, bluealgae). The precursors of C$_{30}$ hopane are bacteriohopanepolyols (C$_{35}$ components)
and diplopterol (C\textsubscript{30}) which are abundant in the cell membranes of many bacteria (Peters \textit{et al.}, 2005).

### 6.5 Biomarkers as indicators of geological environment

Biomarker or geochemical fossils provide information about the organisms contributing to the organic matter of sediments (Tissot and Welte, 1984). The three main types of organic matter that can be differentiated using biomarkers are:

#### 6.5.1 Biomarkers present in marine organic matter

In marine organic matter, phytoplankton is the major contributor with some contribution from zooplankton and benthic algae. The principal biogenic molecules are

- n-alkanes of medium molecular weight range i.e. C\textsubscript{12}-C\textsubscript{20}
- predominance of C\textsubscript{15} and C\textsubscript{17} n-alkanes
- C\textsubscript{15}-C\textsubscript{20} isoprenoids
- abundant steroids, particularly, C\textsubscript{27}sterane

#### 6.5.2 Biomarkers present in the continental organic matter

The continental organic matter is mainly made up of the debris of higher plants incorporated in deltaic or other mainly land derived sediments. Biogenic hydrocarbons include mostly odd n-alkanes of high molecular weight (C\textsubscript{25}-C\textsubscript{33}), and hopanes. When steranes are present, C\textsubscript{29} steranes are most abundant and sterane / hopane ratio is usually low to very low. Isoprenoids are moderately abundant dominated by pristane. Pristane / phytane ratio may reach from 4 to 10.

#### 6.5.3 Biomarkers present in microbial organic matter

Microbial organic matter is abundant in some lacustrine or paralic environment where plant material is heavily degraded during alternating periods of subaerial microbial activity and water flooding. The related organic matter is rich in lipids that may be either the remains of the degraded plant material, or may be reworked or synthesized by micro organisms. Biogenetic hydrocarbons are dominated by long chain n- and iso-alkanes, sometimes extending up to C\textsubscript{40} or C\textsubscript{50}, without any appreciable predominance. Isoprenoids and cyclic hydrocarbons are scarce, except hopane which are synthesized by prokaryotes. Thus, biomarkers can be used to identify the main organic contributor,
whether or not they are autochthonous. For example, organic matter of terrestrial origin may is contained in sediment laid down in the marine environment. Terrestrial organic matter deposited in deltas, in marine brackish or non-marine environments can be identified as terrestrial origin.

6.5.4 Biomarkers parameters used as indicators of geological depositional environment

Biomarker parameters that are commonly used as indicators of geological depositional environment are as follows:

i) **Pristane/phytane ratio (Pr/Ph):** The pristane to phytane ratio (Pr/Ph) has been used as an indicator of redox conditions during sedimentary diagenesis (Didyk *et al.*, 1978). This usage is based on the fact that the major sources of sedimentary organic matter are phytoplankton and terrestrial plants, and so photosynthetic pigments are potentially important substrates for diagenetic processes. Phytol forms part of the structure of most of the major primary photosynthetic pigments, chlorophylls, and is generally released from the tetrapyrrole unit of chlorophylls at a very early stage of diagenesis. Thereafter, the phytol can be considered to be determined mainly by redox potential. Under reducing conditions, phytane is produced and under oxidizing conditions, pristane is produced. Therefore, Pr/Ph > 3 is for terrestrial oils (oxidizing conditions) and < 1 for marine oils (anoxic conditions).

ii) **Pristane/n-C_{17} (pr/n-C\textsubscript{17}) and Phytane/n-C_{18} ratio (ph/n-C\textsubscript{18}):** To determine the type of source rock from which the hydrocarbon have generated as well as the maturity of the source rocks at the time of generation, the ratios between pristane / n- C\textsubscript{17} and phytane / n-C\textsubscript{18} are used. A high pristane/n- C\textsubscript{17} ratio and low phytane/n-C\textsubscript{18} ratio correspond to hydrocarbon generated from terrestrial organic matter deposited under oxic environment. Whereas a low pristane/n-C\textsubscript{17} ratio and high phytane/n-C\textsubscript{18} corresponds to hydrocarbon generated from organic matter deposited anoxic or reducing environment. If both the ratios are high, it implies that either the hydrocarbon is biodegraded or has generated from immature source rock. However, if both the ratios are low, than the oil has generated from mature source rocks (Shanmugam, 1985).
iii) **Oleanane Index (Olean Index):** Oleanane is considered as indicator of terrestrial plant, deriving from angiosperms (flowering plants). During the Late Cretaceous to Eocene period, Angiosperms became predominant and therefore, source rocks of Jurassic age and older than that, and their associated organic matter, do not contain oleanane. Thus, the ratio Oleanane Index (18α + 18β Oleanane / C₃₀ hopane) is a source and age parameter, but it is also related to maturity of the source rock (Ekweozor and Telnaes, 1990; Ekweozor and Udo, 1988; Peters *et al*., 2005).

iv) **Bicadinane/hopane ratio (Bicad/hop):** Bicadinanes originate from the “dammar” resins exuded by tropical angiosperms. In land plants, Bicadinanes are common in Surma Basin in northeast Bangladesh (Alam and Pearson, 1990). Presence of bicadinanes in the hydrocarbon indicates that the source rocks are derived from terrestrial organic matter.

v) **Steranes / hopane ratio (St29/Tt30):** The ratio of steranes to hopanes indicates the relative contributions of eukaryotes (mainly algae and higher plants) and bacteria (Moldowan *et al*., 1985). The steroid/hopanoid contributions to sediments can vary widely depending upon the communities of organisms present and the degree of concentration of lipids consequent upon degradation of the organic detritus. Hence quite large variations in the sterane/hopane ratio can be observed for sediments from similar environments. However, high sterane concentrations together with high sterane/hopane ratios are distinctive of marine sediments where phytoplankton is most dominant. Conversely, low absolute sterane concentrations and low sterane/hopane ratios are characteristic of organic matter deposited in fresh water coal-swamp environments (Peters *et al*., 2005).

vi) **Distribution of C₃₁-C₃₅ homohopanes:** Distribution of C₃₁ to C₃₅ extended hopanes (homohopanes) can be used to infer redox conditions during deposition of the source rock. Higher concentrations of C₃₅ homohopane imply anoxic condition of deposition as in the marine depositional environment (Peters *et al*., 2005).

vii) **C₃₅/C₃₄ hopane (Hop₃₅/₃₄):** In the reducing environment, C₃₅ hopane is most dominant whereas in oxidizing environment, the C₃₅ hopane is oxidized to C₃₀.
carboxylic acid and further to C_{31} hopane. Therefore, a high C_{35}/C_{34} hopane is suggestive of anoxic marine or hypersaline environment (Peters and Moldowan, 1991).

\textbf{viii) Diasteranes ratio (Diast\%):} The abundance of diasteranes related to steranes in hydrocarbons indicate the presence of clay minerals in the source rock. Therefore, carbonate-sourced hydrocarbons can generally be distinguished from clastic sources by their low diasterane/sterane ratio (Mello \textit{et al.}, 1988). The diasterane/sterane ratio is also a maturity indicator indicating low value for low maturity hydrocarbons (Seifert and Moldowan, 1978).

\textbf{ix) C_{27} to C_{29} steranes:} To access the source and depositional environments, Ternary plots of the C_{27}-C_{29} distributions are considered (Moldowan \textit{et al.}, 1985). The main source of cholestane (C_{27}) is cholesterol, which is ubiquitous in eukaryotes, but tends to be in greater relative abundance in animals, so zooplankton contributions can sometimes be inferred. It is also indicate that, a relative increase in C_{28} and decrease in C_{29} steranes in marine sourced hydrocarbons. Predominance of C_{29} steranes is the indicative of Coals and Type-III kerogens (Peters \textit{et al.}, 2005)

\textbf{x) C_{29}/C_{30} hopanes (Hop_{29/30}):} The ratio is primarily controlled by source and depositional environment organic matters (Peters \textit{et al.}, 2005).

\textbf{xi) C_{23} tricyclic terpanes (t23/T30H) and C_{24} tetracyclic terpanes (Tetra/Hop):} C_{23} tricyclic terpanes (t23) and C_{24} tetracyclic terpanes (Tetra) are very useful as a source parameter. C_{24} tetracyclic terpane is abundant in hydrocarbons derived from carbonate or evaporatic source rocks. C_{23} tricyclic terpanes are wide spread in lacustrine and marine source rocks (De Grande \textit{et al.}, 1993; Philp and Gilbert, 1986). These ratios also increase with maturity.

\textbf{xii) C_{30} diahopane / C_{29} Ts ratio:} C_{30} diahopane which originates due to bacterial input to sedimentary basins containing clays deposited under oxic to suboxic environmental conditions. Since many terrigenous rocks are deposited under oxic to suboxic conditions are clay rich and shows high values of C_{30} diahopane / C_{29} Ts is an indicator of oxic to suboxic environment of deposition (de Grande \textit{et al.}, 1993; Philp and Gilbert, 1986).
xi)  

**C30 Diahopane / hopane ratio:** The diahopane occurs widely in organic matter derived from kerogens deposited in oxic to suboxic conditions, including coals (Moldowan *et al*., 1991; Philp and Gilbert, 1986). A high diahopane / hopane ratio indicates that the hydrocarbons originated from terrestrial organic matter.

### 6.5.5 Biomarkers as indicators of thermal maturation

The biomarkers study is also useful to determine the maturity of the source rock at which the hydrocarbon has been expelled. Certain molecules with a biogenic structure, are not known, as such, in living organisms. For example, living organisms only synthesize n-alkanes having odd number of carbon atoms (odd n-alkanes). However, during diagenesis and catagenesis, n-alkanes having even number of carbon atoms (even n-alkanes) are generated. Therefore, during catagenesis odd n-alkanes are progressively diluted due to thermal maturation. Odd over even predominance can be measured using a parameter called carbon preference index (CPI), which can be used as an indicator of maturity (Tissot and Welte, 1984).

Similarly, living organisms synthesize only (17β, 21β) H-hopane or ββ hopane or (17β, 21 α) H-hopane or βα hopane. However, (17α, 21β) H-hopane or αβ hopane is also present in crude oils. The αβ hopane is generated by subsequent isomerization of ββ or βα hopane. Thus, the ratio ββ / βα–hopane is used as maturity parameter (Peters *et al*., 2005).

Another thermal related change that occurs in C31 to C35 hopanes is the isomerization C22 position. The biologically produced hopane has a 22R configuration that is gradually converted to a mixture of 22S and 22R during catagenesis (Schoell *et al*., 1983). Similarly, in C27 to C29 steranes, the 20R isomer is produced biologically which converts to 20S progressively. Hence, the ratio 20S/(20S+20R) C27 to C29 steranes can be used a maturity parameter (Seifert and Moldowan, 1986).

### 6.5.6 Biomarker parameters used as indicators of thermal maturation

Biomarker maturity parameters that are commonly used are

i)  

**Sterane maturity parameters (St29S/S+R and St29I/I+R):** C29 20S/(S+R) sterane (St29S/S+R) is a useful maturity parameter used in combination with another maturity parameter i.e. C29 iso / (iso + regular) sterane (St29I/I+R). The parameter is based on epimerization of C-20 position of C29 sterane. C29 iso / (iso
+ regular) steranes when use along with C\textsubscript{29} 20S/ (S+R) is a very useful parameter for determining maturity in the immature to peak mature range. The ratio C\textsubscript{29} 20S/(S+R) sterane varies from 0 (immature stage) to a maximum value of 0.55 (early mature stage) whereas C\textsubscript{29} iso / (iso + regular) sterane varies from a very low value at immature stage to 0.70 in the peak mature stage (Seifert and Moldowan, 1986).

\textbf{ii) } \textit{C\textsubscript{32} 22S S/(S+R) hopanes (Hop32 S/S+R): } The 22R isomer of C\textsubscript{32} hopane is present in immature hydrocarbons. With increase in maturity, the 22R isomer gets converted to 22S isomer. So, C\textsubscript{32} 22S/(22(S+R) is a very consistent maturity parameter that varies from 0 (immature stage) to 0.60 (early mature stage) (Schoell \textit{et al.}, 1983).

\textbf{iii) } \textit{Ts/Tm: } The ratio, Ts/(Ts+Tm) is used as a maturity parameter, however, it is also influenced by the source characteristics. The C\textsubscript{27} hopane i.e. C\textsubscript{27} 17\alpha-\textit{trisnorhopane} or Tm is less stable than C\textsubscript{27} 18\alpha-\textit{trisnorhopane} or Ts. It is most reliable as thermal maturity indicator when evaluating hydrocarbon from a consistent organic facies source. The value of this ratio varies from low in immature range to 1.0 in late hydrocarbon generation stage (Moldowan \textit{et al.}, 1986)

\textbf{iv) } \textit{Hopane / Moretane (Hop/Mor): } Moretane is thermally less stable than hopane. During heating, moretane gets converted to hopane and thus, the ratio Hopane / (Hopane + Moretane) mostly used as a maturity parameter. The value of this ratio varies from very low values in the immature range to 0.95 in the early mature range (Seifert and Moldowan, 1980)

\textbf{v) } \textit{29Ts/29Tm: } The ratio 29Ts/29Tm is defined as the abundance of the C\textsubscript{29} neohopane, commonly called C\textsubscript{29}Ts relative to the C\textsubscript{29} regular hopane. The ratio measures the relative abundance of the neohopane to the regular hopane. (Cornford \textit{et al.}, 1988; Hughes \textit{et al.}, 1985).

\textbf{vi) } \textit{Diahopane / normoretane (Dia/NorM): } The ratio Diahopane / Normoretane is a important maturity parameter that can reveal the possible presence of mixtures of early charge (containing normoretane) and late charge (containing diahopane) hydrocarbons (Cornford \textit{et al.}, 1988).
6.6 Experimental Results and discussions

8 numbers of representative samples of both coal and carbonaceous shale from different wells of the study area were considered for biomarker analysis. A combination of GC and GC-MS data were used to characterize the organic matter, source and environment of deposition of the well core samples. From the extraction, the dominance (%) of hydrocarbons i.e. saturates, aromatics, resins and asphaltenes has been determined and reported in Table 6.1. The saturates / aromatics ratio (sats/arom) are also reported in Table 6.1. GC traces of aliphatic hydrocarbons of the rock extracts show the presence in high abundances of the n-alkanes, ranging from about n-C_{12} up to n-C_{35} reported in Table 6.1. However, the low molecular weight (MW) hydrocarbons (especially those below n-C_{20}) are severely depleted, particularly in samples A-1 and G-3 (Table 6.1). The loss of low molecular weight hydrocarbons is most probable due to weathering effects of the samples. The GC-MS traces (m/z 191 and m/z 217) of the extracts are given in Figures 6.1(A, B), Figures 6.2, Figures 6.3 and Figures 6.4.
Figure 6.1(A,B) Mass Chromatography of Barail coal/ carbonaceous shale of Upper Assam Basin showing Hopanes.

Figure 6.2 m/z 217 mass Chromatogram of Barail coal/ carbonaceous shale of Upper Assam Basin showing steranes
Figure 6.3 m/z 85 Chromatogram of Barail coal/ carbonaceous shale extract of Upper Assam. The sample contain a negligible or a very low proportion of aliphatic chains>C_{18} which is of lower thermal maturity.

Figure 6.4 m/z 218 mass Chromatogram of Barail coal/ Carbonaceous shale of Upper Assam Basin showing Iso-steranes
Table 6.1 Extraction and n-alkanes data of Barail coal and carbonaceous shale

<table>
<thead>
<tr>
<th>Samples</th>
<th>Saturates (%)</th>
<th>Aromatics (%)</th>
<th>Resins (%)</th>
<th>Asphaltenes (%)</th>
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<th>C_{16-18}</th>
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<td>--</td>
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<td>0.14</td>
<td>0.04</td>
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<td>G-3</td>
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<td>1.4</td>
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<td>7.1</td>
<td>50.4</td>
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<td>0.10</td>
<td>0.22</td>
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<td>45.8</td>
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<td>0.11</td>
<td>0.25</td>
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<td>3.2</td>
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<td>1.5</td>
<td>0.08</td>
<td>0.15</td>
<td>0.03</td>
<td>0.26</td>
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</tbody>
</table>

6.6.1 Biomarkers as source and environment of deposition

Biomarker ratios like pristane / phytane (Pr/Ph), Pr / n-C_{17} and Ph/ n-C_{18} have been determined using gas chromatographic analysis (Table 6.2). As has been discussed earlier, phytol, which is a part of chlorophyll present in all photosynthetic plants, is released at very early stage of diagenesis. Phytane is produced under reducing conditions, whereas pristane is produced under oxidizing conditions. Therefore, Pr/Ph ratio > 3 for terrestrial origin (oxidizing conditions) and < 1 for marine origin (anoxic conditions) (Shanmugam, 1985; Didyk et al., 1978; Peters et al., 2005). The Pristane (Pr) indicate most dominant peak in the GC traces and all the extracts of both coal and carbonaceous shale shows very high pristane and phytane (Pr/ Ph) ratio with values ranging from 5.5 to 9.2. Since Pr/Ph ratio > 3 for almost all the extracts (Table 6.2), it can be concluded that the organic matter deposited under terrestrial conditions. The very high Pr/Ph ratio in addition with the higher molecular weight n-alkanes and predominance of odd over even carbon number, suggests that the extracts contain high abundances of land plant organic matter.

The ratios Pr / n- C_{17} and Ph / n-C_{18} are considered for determination of the type as well as the maturity of the source rocks at the time of hydrocarbon generation. In the present study both the Pr / n- C_{17} (0.9-1.5) and Ph / n-C_{18} (0.9-2.1) ratios are high which implies that either the organic matters are biodegraded or has generated from...
immature source rock. A plot of Pr / n- C\textsubscript{17} and Ph/ n-C\textsubscript{18} (Figure. 6.5) organic matter have generated from terrestrial organic matter.

Table 6.2 Source and maturity parameters (Pristane and Phytane)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pr/Ph</th>
<th>Pr/n-C\textsubscript{17}</th>
<th>Ph/n-C\textsubscript{18}</th>
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</thead>
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</tr>
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<td>A-1</td>
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<td>G-1</td>
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<td>0.9</td>
</tr>
<tr>
<td>G-2</td>
<td>5.5</td>
<td>0.9</td>
<td>1.4</td>
</tr>
<tr>
<td>G-3</td>
<td>9.2</td>
<td>1.5</td>
<td>2.1</td>
</tr>
<tr>
<td>CH-1</td>
<td>8.1</td>
<td>1.1</td>
<td>2.0</td>
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<tr>
<td>R-1</td>
<td>7.9</td>
<td>1.2</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Figure 6.5 Plot of pr / n-C\textsubscript{17} and ph / n-C\textsubscript{18} ratios Barail coal and carbonaceous shale (after Shanmugam, 1985)

The triterpane distributions (m/z 191) indicate the presence of both hopane and non-hopanoid biomarkers. The hopanes range from C\textsubscript{27}-C\textsubscript{33} with very low abundances of extended hopanes. The low abundances of the extended hopanes related to the Pr/Ph ratio suggests that the organic matter was deposited in a coastal plain or deltaic setting (Mathur, 2013).
The ratio of steranes to hopanes reflects the relative abundance of eukaryotes (mainly algae and higher plants) and bacteria. High sterane/hopane ratios are typical of marine sediments, in which phytoplankton contributions dominate (Moldowan et al., 1985). Low sterane/hopane ratios are characteristic of sediments deposited in freshwater coal-swamp environments (Peters et al., 2005; Tissot and Welte, 1984). The Barail coal and carbonaceous shale extracts show low steranes to hopanes ratio (<1) (Table 6.3), indicating that the organic matters are derived from source rocks deposited under terrestrial environment.

The ratio between long carbon chain hopanes i.e. $C_{31} - C_{35}$ to short carbon chain hopanes ($C_{27}-C_{30}$) is measured by the ratio HomoHops. Generally, in bitumens from highly reducing environments, the long chain components seem to dominate (Peters et al., 2005). Under oxidizing environment, the $C_{35}$ precursors tend to be oxidized to the $C_{32}$ carboxylic acid, which is often a dominant component in peats and soils (Quirk et al., 1984). This acid can undergo decarboxylation to yield $C_{31}$ hopanes which generally dominate in the bitumens of immature coals. In the present study, the homohopane ratio of all the extract shows the value less than 1 (Table 6.3).

The $C_{27}$ hopanes, Tm ($C_{27} 18\alpha$ (H)-22, 29, 30-trisnorhopane) is present in much higher proportions with respect to Ts ($C_{27} 17\alpha$(H)-22,29,30-trisnorhopane), suggesting the extracts containing high abundances of land plant organic matter. The non-hopanoids, which are mainly derived from land plant materials, is also present including oleananes (O) and triterpenoids (x). The non-hopanoids are present in the extract of both coal and carbonaceous shales (O/$C_{30}$H ranges from 0.24-0.85) (Table 6.3). The organic matters derived mostly from terrestrial plants were indicated by the presence of oleananes (Philp and Gilbert, 1986; Riva et al., 1988). It also been suggested that oleanane formation is not favourable in acidic environment such coal swamps, therefore less of the compounds such as those with oleanane skeletons were preserved (Sosrowidjojo et al., 1994; Murray et al., 1997). The low proportions of the oleananes in the coal samples are usually related to the depositional environmental conditions under which the organic matter was deposited. However, the high degree of bacterial reworking that occurs in some peat forming environments could produce higher quantities of bacterial-derived compounds i.e. hopanes which diluted the oleananes (Wan Hasiah and Abolins, 1998).
The $18\alpha + 18\beta$ Oleanane / $C_{30}$ hopane ratio also known as Oleanane Index is an important source indicator, affected by angiosperm (flowering plants) contribution to the source rock (Ekweozor et al., 1979). Since all the extracts of the present study are rich in Oleanane, (Table 6.3), it can be concluded that organic matters of the coal and carbonaceous shale of study area are derived from terrestrial source rocks having significant higher plant input.

The bicadinanes or resin derived compounds, are absent in all the extracts of both coal and carbonaceous shales. Polycadinenes are the main source of bicadinanes, biopolymers present in dammar resin which are produced from trees of the *Dipterocarpaceae* family (Van Aarssen et al., 1990).

A higher proportion of $C_{35}/C_{34}$ hopane is revealing the anoxic marine or hypersaline environment whereas low proportion of $C_{35}/C_{34}$ hopane is indicative of oxidizing or terrestrial environment (Peters and Moldowan, 1991; Sieskind et al., 1979; ten Haven et al., 1988). In the present study, the $C_{35} / (C_{35} + C_{34})$ hopane ratio is quite low (0.33-0.55) for all the extracts of both Barail coal and carbonaceous shales (Table 6.3), indicates that the organic matters are derived from source rocks deposited under terrestrial environment.

The sterane traces (m/z 217) of the Barail coal and carbonaceous shale extracts are dominated by the regular steranes, particularly the 20R steranes. A high abundance of $C_{29}$-steranes, ranging from about 64.5-76.2% compared to $C_{27}$-steranes (3.7-15.7%) and $C_{28}$-steranes (16.5-24.3%) indicating higher proportion of land plant organic matter (Table 6.4). Diasteranes are also present in all of the extracts mostly $C_{29}$ in higher amount (>55%) (Table 6.4). The disteranes present higher in the carbonaceous shale ($C_{29}$ diasteranes/regular steranes 0.67-0.85%); whereas low in the coals ($C_{29}$ diasteranes/regular steranes 0.40-0.72%). This is due to the formation of diasteranes is considered to be form clay-catalyzed conversion of diasteranes (Rubinstein et al., 1975; Salleh et al., 2008). As in case of coal which contains lower clay content as the conversion is limited compared to shales.

The distributions of $C_{27}-C_{29}$ steranes shown by the Ternary plots of are useful for correlation of organic matter types and to determine the source input and depositional environments for organic matter. Predominance of $C_{29}$ steranes indicates coal and type-III kerogen (Moldowan et al., 1985; Peters et al., 2000). From the ternary
plot in the present study reveals that most of the hydrocarbons have derived from organic matter or kerogen deposited under deltaic to terrigenous environment (Figure 6.6; Table 6.4). The ternary plot also showing the relative abundances of C$_{27}$-C$_{29}$ reg. steranes and C$_{27}$-C$_{29}$ diasteranes of the extracts of coal and carbonaceous shale core samples are shown in Figure 6.7 and Table 6.4 respectively.

**Figure 6.6** Distribution of C$_{27}$, C$_{28}$ and C$_{29}$ steranes (%) for Barail coal and carbonaceous shale (after Moldowan *et al.*, 1985)
C₂₃ tricyclic terpanes (t23) and C₂₄ tetracyclic terpanes (Tetra) are very useful for correlation purposes and as a source parameter. The tricyclic terpanes which are generally related with algal matter (Aquino Neto et al., 1992) and represent marine and lacustrine oil are absent in these extract of terrigenous coal and carbonaceous shales.

6.6.2 Maturity based on biomarker distributions

In the present study, a number of biomarker maturity parameters used for the assessment of the level of thermal maturity of the extracts (Table 6.5). With increasing thermal maturation, more and more n-alkanes are generated compared to isoprenoid compounds like pristane and phytane (Shanmugam, 1985) Therefore, with increasing maturity, pr / n-C₁₇ and ph / n-C₁₈ decrease. A plot of pr / n-C₁₇ and ph / n-C₁₈ shows that the extracts of Barail coal and carbonaceous shale represent the immature zone (Figure 6.6, Table 6.2).

The biologically produced hopane has a 22R configuration that is gradually converted to a mixture of 22S and 22R during catagenesis. The ratio 22S/(22S+22R) epimer ratio of C₃₁-C₃₃ hopanes, therefore, increases from zero to an equilibrium values of approximately 0.6 by the top of the oil window (0.6% Ro) (Peters et al., 2005; Seifert and Moldowan, 1980). Most of the extract of the coal and shale of Barail Group have C₃₁
and C32 S/(S+R) Hopane are 0.40-0.59 and 0.42-0.58 respectively suggesting the hydrocarbons were generated from source rock at immature level.

C29 iso / (iso + regular) steranes along with C29 20S/ (S+R) is a very useful parameter for determining maturity of the source rock i.e. in the immature to peak mature range. The ratio C29 20S/(S+R) sterane varies from 0.44-0.81, indicates immature stage whereas C29 iso / (iso + regular) sterane varies from a very low value (0.18-0.49) also indicates immature stage (Peters et al., 2005; Seifert and Moldowan, 1986). Sterane maturity parameters of all the extract (Table 6.4) shows very low maturity that corresponds to immature source rock.

The ratio Ts/Tm (0.13-0.30) reported in Table 6.5, is used as a maturity indicator, because Ts or C27 18α-trisnorhopane exhibits greater thermal stability than Tm or C27 17α-trisnorhopane. The value of this ratio varies from low in immature range to 1.0 in late hydrocarbon generation stage (Moldowan et al., 1986; Peters et al., 2005). The ratio 29Ts/29Tm (0.04-0.23) (Table 6.5), which is increase with thermal maturity, is defined as the abundance of the C29 neohopane, commonly called C29Ts relative to the C29 regular hopane (Cornford et al., 1988; Hughes et al., 1985). The plot of Ts/Tm to 29Ts/Tm of the extracts of both coal and carbonaceous shale indicate immature nature of the source.
### Table 6.3 Biomarker source parameters (Hopanes)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lithology</th>
<th>Tm/ Ts</th>
<th>O/ C_{30}H</th>
<th>C_{30}H/ C_{30}M</th>
<th>C_{29}TmH/ C_{29}H+ C_{29}M</th>
<th>C_{30}H/ C_{30}H+ C_{30}M</th>
<th>C_{30} H /C_{29}Ts</th>
<th>Homo Hop</th>
<th>C_{31} S/ C_{31} (S+R)</th>
<th>C_{32} S/ C_{32} (S+R)</th>
<th>C_{33} H/ (C_{33}H + C_{33}M)</th>
<th>C_{33} S/ (C_{33}H + C_{33}M)</th>
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<tbody>
<tr>
<td>L-1</td>
<td>Coal</td>
<td>3.64</td>
<td>0.61</td>
<td>0.42</td>
<td>0.88</td>
<td>0.80</td>
<td>9.91</td>
<td>0.82</td>
<td>0.42</td>
<td>0.57</td>
<td>0.55</td>
<td>1.22</td>
</tr>
<tr>
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<td>0.88</td>
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<td>0.91</td>
<td>26.85</td>
<td>0.81</td>
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<td>0.42</td>
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<td>0.87</td>
<td>0.87</td>
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<td>0.85</td>
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### Table 6.4 Biomarker source parameters (Steranes)

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<th>Sample</th>
<th>Lithology</th>
<th>Diasterane %</th>
<th>C_{29}Dia/ C_{29}Reg</th>
<th>St C_{29} S/ (S+R)</th>
<th>St C_{29} I/ (I+R)</th>
<th>Reg. Sterane Distribution (%)</th>
<th>Diasteranes Distribution (%)</th>
</tr>
</thead>
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<td>C_{27}</td>
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<td>Ts/Ts+Tm</td>
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Table 6.5 Biomarker maturity parameters