GEOCHEMICAL EVALUATION OF SOURCE ROCKS OF PALEOCENE AGE, KOHAT SUB-BASIN, PAKISTAN

By

Jazeb Sohail

01-262201-013

Department of Earth and Environmental Sciences

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A thesis submitted in fulfillment of the requirements for the award of the degree of Masters of Science (Geology)

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Approval of Examination

Scholar's Name: **Jazeb Sohail,** Registration No. **01-262201-013,** Program of Study: **Master of Science in Geology,** Thesis Title: **Geochemical Evaluation of Source Rocks of Paleocene Age, Kohat sub-basin, Pakistan**

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DEDICATION

With all the love and admiration this work is unequivocally dedicated to my family, I desire to pay my sincerest thanks to my father**, Sohail Anwer** and mother, **Rabia Sohail**, for their prodigious support. I would not be me without their endless concern.

Furthermore, my heart wishes to appreciate my siblings **Hammad Sohail** and **Eman Sohail** for their tenacious efforts during my research. My whole hearted appreciation for **Shawal Zeb** whose encouragement made me struggle for the optimal results throughout the study.

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ABSTRACT

Kohat basin is present in the northwest extension of Indus basin KPK, Pakistan. It is the main hydrocarbon producing basin of the province. It has numerous petroleum plays in production and potential categories from Cambrian to Miocene. Detailed geochemical analyses of well cutting of Tolanj-01 were carried out to understand the Paleocene (Patala, Lockhart and Hangu Formation) potential in the basin. The geochemical analysis included total organic carbon (TOC), rock Eval pyrolysis (RE) and organic petrography (vitrinite reflectance). These results were used to evaluate organic richness, thermal maturity, kerogen type, hydrocarbons type and environment of deposition were determined. Well cuttings of Hangu Formations (0.08-1.8) shows poor to Good, Lockhart limestone (0.05-0.5) poor to fair and Patala Formation (0.8-0.19) shows poor to fair TOC content. The present kerogen appears to be Type III. Thermal maturity of the extracts shows high thermal maturity and mature oil zone. GP is generally poor but some of Lockhart limestone and Hangu Formation shows Fair potential. Vitrinite reflectance of all these formations exist in oil window. Ro values are in the range of 0.82 to 0.95 %. Pr/Ph values are greater than 1 which indicates the presence of sub-oxic environment of deposition. $Pr/n\text{-}C_{17}$ versus $Ph/n\text{-}C_{18}$ shows that the extracts falls in the category of mixed organic matter deposited in transitional depositional settings. $C_{19}TCT/C_{19}TCT+C_{23}TCT$ ratio, $C_{24}TeCT/ C_{24}TeCT+ C_{23}TCT$ ratio indicate source as marine. Ternary diagram shows as higher plant input for Lockhart and Hangu Formation while Patala shows higher marine input. CPI, 2-MP and 3-MP show higher thermal maturity. $Pr/n\text{-}C_{17}$ versus $Ph/n\text{-}C_{18,}$ shows higher thermal maturity. Moretane index, extracts fall in thermally mature window. Ts/Ts+Tm ratio shows more thermal maturity. Steranes value shows extracts as mature and fall in oil window.

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LIST OF ABBREVIATIONS

Ga	Billions of years
CPI	Carbon preference Index
DCM	Dichloromethane
HDIP	Hydrocarbon Development Institute of Pakistan
MKT	Main Karakorum Thrust
MBT	Main Boundary Thrust
MMT	Main Mantle Thrust
Ma	Millions of years
MPI	Methylphenanthrene Index
SRT	Salt Range Thrust
GCMS	Gas Chromatography Mass Spectrometry
FID	Flame Ionization Detector
TLM	Transmitted Light Microscopy
RLM	Reflected Light Microscopy
H	Hopane
HH	Homohopane
HCs	Hydrocarbons
HCl	Hydrochloric acid
HI	Hydrogen Index
NSO	Nitrogen Sulphur Oxygen
OEP	Odd to Even Predominance
OGDCL	Oil and Gas Development Company Limited
POL	Pakistan Oilfield Limited
PPL	Pakistan Petroleum Limited
Ro/Vr	Vitrinite Reflectance
S	Steranes
TAR	Terrigenous aquatic ratio
TCT	Tricyclic Terpanes
TecT	Tetracyclic Terpanes
OI	Oxygen Index
Vs	versus

CHAPTER 1

INTRODUCTION

1.1   General Statement

The products obtained from petroleum and petroleum itself is essential and as well as important and used for the source of energy. Development in technology and advancement demand for fossil fuels has increased which leads to an increasing trend of petroleum exploration ever. In present time the economy is being controlled by the amount of energy utilized or by energy sector. The economic stability and political stability of the country depend upon these energy sectors. The exploration and availability of hydrocarbons is directly related to the development, prosperity and nation building of the country (Alger, 1980). The energy demand is rising rapidly and will grow by 41% from 2012 to 2035 (BP Energy Outlook, 2020). The increasing population and growing industries especially automobiles play a major role in this saga. There is more and more demand for fossils fuel as the needs increasing day by day. Even though there is a significant decrease in oil prices from the past few years due to the financial crisis and unstable world market. Continuous researches has to be done for the exploration of fossil fuels to meet the future needs of oil and natural gas.

It is essential to understand the economic significance of the petroleum system in which organic matter is accumulated transformed, matured and migrated into the reservoir in sufficient geologic time, proper burial depth and temperature pressure conditions and economic viability changes with the change in quality, quantity and the type of petroleum present. In the exploration of oil, the main interest is identification of porous and permeable formations commonly known as source or reservoir rock. Primary stage in fossil fuel exploration process is geochemical evaluation of source rock. It provides idea about organic matter, thermal maturity, environment of deposition, age, kerogen type and production potential of source rock (Lafargue et al, 1998).

There is a great potential of hydrocarbons in Pakistan, Kohat Basin has emerged as a profitable hydrocarbon bearing province of the country. This area automatically receives attention for the exploitation of oil and gas due to the exploitation in a potwar plateau for oil and gas reserves. Features such as diapiric Structures, oil seeps and shale

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oil in the Kohat Plateau is the reasons which make it attractive for further Investigation and exploitation. The exploration has started several decades ago but thick Siwaliks restrict the development of oil fields in the basin. Recently discoveries in the last 15 years of oil fields like Nashpa and Mela increased the reserves of hydrocarbon in Pakistan. In early days of exploration, the main focus was reservoir and its properties but now the focus is shifted towards the source rock and the origin of hydrocarbons. In Pakistan due to lack of technology and resources unconventional reservoir are not being explored. This research will help the oil companies for future ventures for the exploration of unconventional reservoir (Meissner et al., 1974; Shah, 1977; Kadri, I.B., 1995).

In past most of the evaluation was done by the help of surface geology which is less reliable. Further the advancement in geophysics, seismic studies help the geologists to predict more about the subsurface possibilities. Recently the importance of geochemistry is understood widely around the globe and it helps in understanding and exploring the origin of hydrocarbon and petroleum plays. Paleocene age rocks are considered as a source rock which has a potential of generation in Kohat sub-basin and potwar sub basin (Kadri, I.B., 1995).

This research focuses to find out the Geochemical Evaluation of Source Rocks of Paleocene age, Tolanj-01 well, Kushal Garh Block, Kohat Sub-Basin. Literature review shows nothing about this study project previously reported in this Block.

1.2 Paleocene Source Rock of the World

Paleocene age formations are considered as one of the major hydrocarbon producing formation worldwide. They possess fair to good potential as a source rock. About 2.8% of the world's productions of hydrocarbon are from Paleocene Age formations (Ulmashek and Klemme, 1990). (Table. 1.1)

Table. 1.1 Source rocks stratigraphic distribution Worldwide (Ulmashek and Klemme, 1990).

Era	Period		Distribution
CENOZOIC	Tertiary	Quaternary	
		Pliocene	
		Miocene	Upper Tertiary 12.5%
		Oligocene	
		Eocene	U Cretaceous – Lw Tertiary 2.8%
		Paleocene	
MESOZOIC		Cretaceous	Aptian-Turonian 29% / Lower Cretaceous 2.6%
		Jurassic	Upper Jurassic 25%
		Triassic	M Jurassic to U Permian 1.2 %
PALEOZOIC		Permian	Penn.-U Permian 8%
		Carboniferous	M-U Miss. 0.4%
		Devonian	U Devonian - U Miss. 8% / L - M Devonian 0.3 %
		Silurian	Silurian 9%
		Ordovician	Cambro-Ordovician 1 %
		Cambrian	
PRECAMBRIAN		U Proterozoic	U Proterozoic 0.2 %

Oil — Gas

1.3 Exploration History of the Study Area

Upper Indus basin has undergone an extensive hydrocarbon exploration for more than a century. The Kohat Plateau area was explored by Several other companies, including APEC, POL, OGDCL, PPL and MOL. In 1866, one of the earliest well drilled was Kundal well near to seepage in Mianwali. Most of the exploration was in the vicinity of Potwar sub-basin. In 1977-78, Texas Gulf drilled a well name Karak-1 in Kohat sub-basin. That well did not reach its target depth and left abandoned due to the thick Siwaliks at 4459m. Assumption was made that the reservoir is so deep in this

region because of thick Siwaliks. In the Kohat plateau three wells were drilled in 1990 to 1993 by Amoco Pakistan Exploration Company (APEC) which are Tolanj-01, Kahi-01 and Sumari-01 (Nadeem and Raza, 2012).

First discovery of oil made a breakthrough in Kohat region by OGDCL at Chanda (Shakardara Structures) from Jurrassic age (Datta formation) and was named as Chanda oil field. First well was drilled in 1999 and started its production in 2004. In 2002, MOL in Tal Block discovered gas in the Kohat region. Mela oil field was discovered by the OGDCL in September 2006.This is a joint venture field and all three wells were drilled at this field are currently producing.

The discoveries of the fields like Manzalai (12 Wells), Makori (2 Wells), Nashpa (4 Wells), Chanda (3 Wells) and Mela (3 Wells) collectively producing around 32000 bbl/day of oil and 60 MMSCFD of gas per day. All these producing fields has made the Kohat sub-basin a profitable hydrocarbon bearing basin of Pakistan (Athar et al., 2012).

Dry or abandoned well of the region are Tolanj, kahi, Sumari, Shekhan, Sahib gul, Nakband and Latamber (Fig. 1.2).
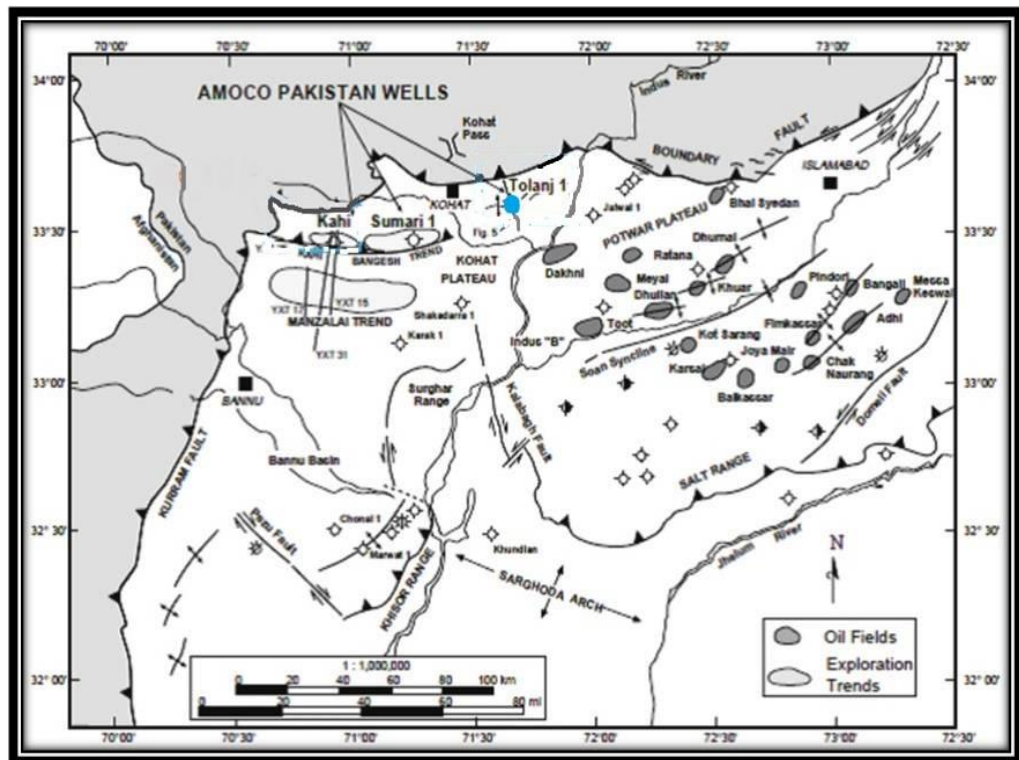
Figure 1.1 Map shows the exploration in Kohat Sub Basin with Study Well marked with Blue dot (Pivnik and Sercombe, 1993).

1.4 Previous Literature

Previous research in Kohat-Potwar Basin in North Pakistan identifies a numerous source rocks which has potential for hydrocarbons, which includes the Salt Range Formation (Precambrian), the Dandot, Sardhai and Chidru Formations (Permian) and Lockhart limestone and Patala Formations (Paleocene), (Raza,1973; Quadri and Quadri, 1996; Fazeelat, T.et al, 2010). TOC content range is from 0.5 to less than 3.5 %. It is considered that the Hydrocarbons are generated from the source rocks with Types II and III kerogen (Shah et al., 1977; Wandrey et al., 2004).

1.4.1 Hangu Formation

The term Hangu Shale and Sandstone used for Paleocene rock unit in Kohat sub-basin was introduced by Davies (1930a) and in 1973 Stratigraphic Committee of Pakistan formulized it as Hangu Formation. Fort Lockhart with Latitude 33° 33' 40" N and Longitude 71° 03' E is nominated as type section of the formation. The Dhak Pass with Latitude 32° 40' N Longitude 71° 44' E is a Principal Reference section at in the Salt Ranges Hangu Formation. It contains sandstone and grey shale which is interbedded in upper part of Kohat area. The sandstone has different colors, such as white, light grey and reddish brown. At some places it is dark brown and fine to coarse grained (Meissner et al., 1974; Shah, 1977).

Hangu Formation bare fair to good TOC content in the southern part of the Upper Indus Basin and is relatively mature. As oil source rock formation shows good potential. The formations in the Kohat area has higher TOC content and more mature (VR. 1.0), as oil source rock has good potential (Kadri, I.B., 1995).

1.4.2 Lockhart Limestone

The word "Lockhart Limestone" mostly used for the Paleocene age limestone of the Kohat sub-basin was introduced by Davies (1930a) and Stratigraphic Committee of Pakistan has extended the usage of this term to indistinguishable units in other portions of the Kohat-Potwar basin and Hazara basin. The type section of locality is Fort Lockhart in the Samana Range. Lockhart Limestone composed of medium bedded nodules which are grey to light grey, grey marl is of minor amount and calcareous shale in the lower part is bluish grey of Salt Range and Trans Indus Ranges. While in Kohat area it is comprise of medium to thick-bedded, massive, rubbly, brecciated and color is

grey to medium grey. The lower part has dark color scheme of grey to bluish grey and also flaggy (Meissner et al., 1974; Shah, 1977).

In Hazara basin and Kala Chitta area, the limestone contains intercalations of shale and marl. It is dark grey to black in color. Generally, it is well developed throughout in Kohat-Potwar basin and gives bituminous odor on fresh surface. The limestone overlies Hangu Formation and underlies Patala Formation. The limestone carries plentiful fossils and micro fossils mainly foraminifers, corals, echinoids, mollusks and algae etc. On the basis of those micro-fossils cluster dated as Paleocene age and Lockhart Limestone name has been allocated (Shah, 1977).

In the Hazara basin Lockhart Limestone has oil generation potential and is slightly bituminous. However, in Eastern Potwar, Lockhart Limestone to some extent is recognized, as source rocks for superior quality oil. This source rock is very rich in organic matter and also shows maturity (Kadri, I.B., 1995).

1.4.3   Patala Formation

The name Patala for the Patala Shale was named by Davis and Penfold and latter systemized by the Stratigraphic Committee of Pakistan. This formation stretched and elongated to a great extent in the Kohat-Potwar and Hazara basin. It shows fair exposure in the Salt Range. The Patala Formation is mostly composed of marl and shale with sandstone and limestone. The shale is carbonaceous and calcareous, selenite and contain marcasite nodules and dark greenish grey. There is some variation from place to place in the formation lithologically. The upper portion comprise of yellowish brown and calcareous sandstone in Patala Formation. Economic worth of Coal seams is present at some areas like Dandot area. In Kohat area it is carbonaceous with intercalate argillaceous limestone beds and dark grey shale. The shale is inter bedded nodular limestone and greenish brown in color in Hazara basin. While in the Kala Chitta Range, formation is distinguished as thin inter beds of limestone of light brown color and grey marl. Patala Formation thickness varies from one place to another in Kohat-Potwar basins. Patala Formation conformably overlies the Lockhart Limestone. It holds abundant foraminifera, ostracods and mollusks and is highly fossiliferous formation. Late Paleocene age has been assigned for this formation except for Hazara area, where it is recorded as Early Eocene (Meissner et al., 1974; Shah, 1977).

In the southern part of the Upper Indus Basin, Patala shale is considered as a major source rock which is relatively mature and have shown fair to good TOC content.

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The TOC content ranges from 0.5-3.5%. As oil source rock formation has good potential. The formation has higher TOC content in Kohat area and shows maturity (VR. 1.0) (Kadri, I.B., 1995).

In northeastern Kohat Patala Formation is very thick and recorded as 1057 meters in Tolanj-1 well. The color of shale in this formation is dark grey to black. In north-eastern Salt range has a well-developed section of Patala Formation. However, Coal beds in Central and Eastern Salt Range which is within Patala Formation are also very important and have very high bitumen extract and contain high genetic potential (Kadri, I.B., 1995).

1.5   Problem Statement

Extensive research has been carried out on different aspects like surface geology, biostratigraphy, sedimentology, hydrocarbon prospect interpretation via petrophysical analysis, seismic studies and reservoir evaluation of Paleocene age formations in Kohat sub basin (Meissner et al., 1974; Shah, 1977; Kadri, I.B., 1995; Raza,1973; Quadri and Quadri, 1996). Comparatively very small research has been done on source rock evaluation of Paleocene age formations in Kohat Sub-Basin.

This work will help to better understand the source rocks of Paleocene age rocks in Tolanj-01 and knowledge of petroleum prospect in the area for an interest of scientific and economic reasons.

1.6   Objectives of Research Work

The source potential of Paleocene age rocks can be done by detail geochemical analysis and biomarkers determination. This study has aimed for the achievement of the following objectives.

1.   Geochemical characterization of Paleocene formations to evaluate their organic richness, thermal maturity, type of kerogen/source input and expected type of hydrocarbons generated.

2.   Biomarker study for determination of environment of deposition, organic input, biodegradation and thermal maturity.

1.7   Data Required

For the evaluation of the source rock potential of Paleocene age formations, the Paleocene age formation well cuttings of Tolanj-01 well, Kushal Garh Block, Kohat Sub-Basin are required from Hydrocarbon Development Institute of Pakistan (HDIP) and will be analyzed in geochemical lab for analysis.

1.8   Methodology

For the evaluation of the source rock potential of Paleocene age formations the methodology adopted was acquiring the Paleocene age formation well cuttings of Tolanj-01 well, Kushal Garh Block, Kohat sub-basin, from Hydrocarbon Development Institute of Pakistan (HDIP) and analyzed in geochemical laboratory for analysis. The laboratory-work includes various analyses TOC, Rock Eval Pyrolysis, VR, GC and GCMS. The investigation of geochemical data will assist to recognize source rock potential of the Paleocene Formation (Fig. 1.2).
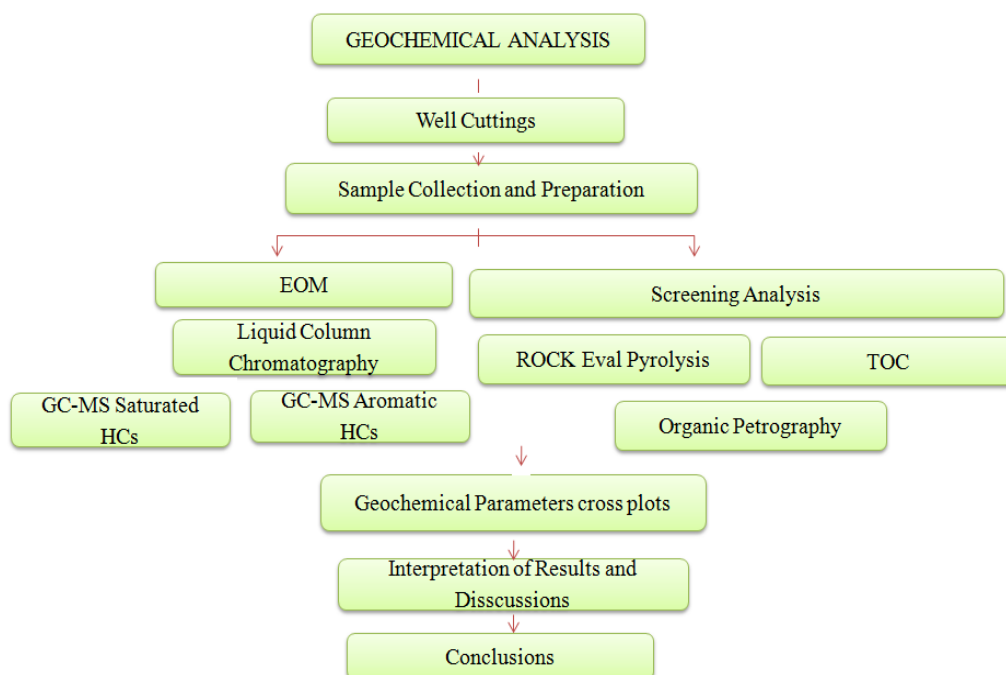
Figure 1.2 Methodology adopted for Geochemical Analysis.

1.9 Evaluation of source rock

A unit of rock, that generates oil and gas for commercial accumulations. Petroleum rocks are of marine and terrestrial origin. Marine source rocks are comprising of dead plankton, algae, microorganisms and deposited in marine environment. Terrestrial source rocks are comprising of woody plant material, algae etc. and deposited in lakes, lagoons and deltaic basins (Fred and Dasgupta,2013).

In both conditions, the mixture of organic substance should be buried with no oxygen around and should be buried in low energy environment because due to high energy environment organic material decompose or dissolve and disturb its accumulation in the basin (Fred and Dasgupta,2013).

Potential source rocks that has a capacity to generate petroleum commercially but has not yet done due to insufficient Thermal Maturation. Active source rocks that has the process of generating petroleum, cannot occur at the surface because it requires depth to generate petroleum. Inactive source rocks are the rocks that was once active but stopped generating petroleum or become spent, usually associated with area of overburden removal. Common source rocks are Shale and limestone.

The laboratory-work includes various analytical techniques and analyses which includes the source rock screening techniques, like Total Organic Carbon (TOC) analysis, Rock Eval Pyrolysis and organic Petrography (VR). Other techniques for extractable organic matter (EOM) like Solid-Liquid Chromatographic separation of fractions, Gas chromatography (GC-FID)/Whole Oil chromatography and Gas chromatography-mass spectrometry (GC-MS). The analysis of such type of geochemical data will assist to recognize source rock potential.

The determination of TOC indicates the organic matter richness both insoluble organic matter (kerogen) and soluble organic matter (bitumen). It measures the percentage of carbon in organic matter and does not quantify the potential source rock (Baker Hughes, 1999).

Next step for the sample is a standard analysis, Rock Eval Pyrolysis for determining source rock used to evaluate the amount of kerogen which can transform freely and estimate the remaining kerogen which can be extracted later at higher temperatures. This process can evaluate important variables and also provide supplementary information according to the hydrocarbons present in the source rock (Bjørlykke, 2010).

Organic petrography is based upon the laboratory analysis of samples (vitrinite reflectance microscope) to undergo the best possible analysis of sample. The organic petrography service delivers information about rock type, associated organic matter, thermal maturity and hydrocarbon generation zone. It is basically the study of macerals which is naturally present in the sedimentary rocks. These macerals are organic, occurs with organic matter which is slightly dispersed and are present in oil shales and coals as well.

Source rock is subjected to further geochemical analysis, Extractable organic matter (EOM) if it fulfills the criteria after the screening tool analysis. The criteria include TOC value greater than 0.5%, T_{max} greater than 430°C, GP valve greater than two, Vr value greater than 0.6 and kerogen type should not be Type-IV. The rock sample mentioned in above criteria are taken for further geochemical analysis. EOM is further separated into fractions like saturated compounds, aromatic compounds and NSOs by the process of column chromatography.

1.10   Research and Location of Study Area

The research area is a well named Tolanj-01which was drilled by AMOCO (APEC) in 1991. Kohat Area is bounded by Main Boundary Thrust (MBT) to the North and by Trans Indus Ranges to the South. Kohat Plateau merges to the southwest with the Bannu Basin. The eastern limit of Kohat Plateau marks by River Indus which distinguished it from the Potwar plateau and in the west the Kohat plateau is restricted by NNE-SSW oriented Kurram fault.

The study area Tolanj-01 well is located in Upper Indus basin, Kushal Garh Block, Kohat District, KPK, Pakistan. Tolanj-01 well lies approximately 150 km SW of Islamabad. It is easily accessible through M1 and M2 Motorway and N-80 Highway. It is about 20 km of Dakhni Oil and Gas Field in south east, 20 km from Shekhan-01 in the North West. The latitude (33° 33′ 42″) and longitude (71° 42′ 50″) of the study area and Tolanj-01 well is shown in location map (Fig. 1.3).
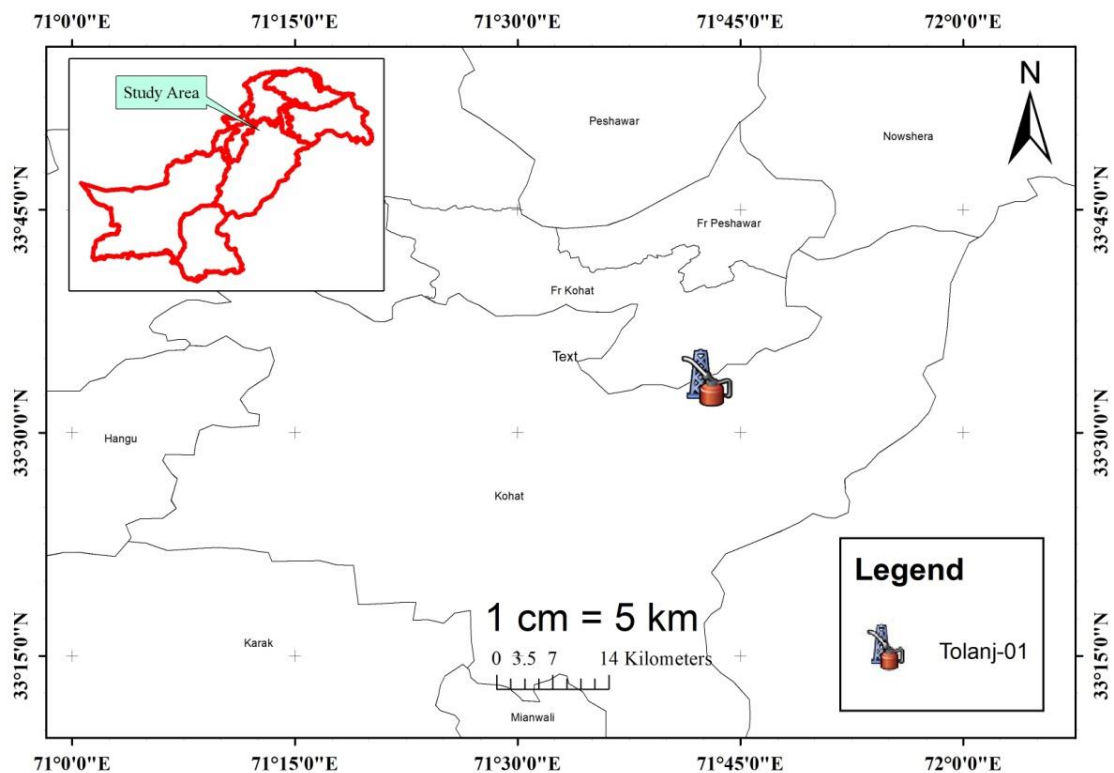
Figure 1.3 Inset Map showing Location of the Study Area Kohat district, Pakistan and Location of Tolanj-01 well (Map generated in ARCGIS).

CHAPTER 2

REGIONAL GEOLOGY, TECTONICS AND STRATIGRAPHY

2.1   Regional Geological Settings

The occurrence of super-continental cycles causes the large and small fragments of earth to combine and get separated. The first supercontinent usually named as Ur (3.0Ga) which is followed by Kenorland (2.7-2.5 Ga) then Columbia (1.9-1.8 Ga) further followed by Rodinia (1.1 Ga) then Gondawana (0.54 Ga) and at last Pangea (0.25 Ga) (Santosh et al, 2009).

Not all supercontinent is documented/reported; data regarding Gondwana and Pangea are available in geological record. In Early Permian to Carboniferous Pangea begin to break down and result in formation of different tectonic plates and Neo-Tethys Ocean (Scotese et al, 1979; Condie, 1984).

Indian plate was newly formed started its voyage and drifted toward North. The vast Indian ocean of Southern Hemisphere resulted in shrinkage of Neo-Tethys Ocean (Tapponnier et al. 1986).

Indian and Eurasian plate collision during Eocene time caused the closure of Neo-Tethys Ocean (Tahir Kheli et al. 1979a).

On the basis of tectonics, orogeny and lithology, Pakistan is divided into Tethyan Domain and Gondwanian Domain. The land collided with Indian plate constitutes of Tethyan domain which is Eurasian plate and Afghan block. The northward movement Indian plate and Kohistan-Ladakh arc is Gondwanian domain (Kazmi and Jan, 1997).

There are three lithospheric plates in Pakistan i.e. Indian-Australian plate, Arabian plate and Eurasian plate. Interaction between these plate margins were occurred during different ages which resulted in formation of different tectonic regimes, unique tectonic outlines and different geologic features which can be seen like Shyok and Indus sutures which show features related to Subduction, Chamman fault represent transform plate boundary, active trench arc system in Makran, volcanic and island arc system in Chaghi (Kazmi and Jan, 1997).

Indian plate thrusting under Eurasian plate occurred and still continued with time. This moment caused many thrust faults and structures in Northern Pakistan

influenced by pre-collisional and syn-collisional effects. Major faults names are MKT, MMT, MBT and SRT, divides northern Pakistan into Karakoram Block, Kohistan-Ladakh Arc, Foreland Fold-Thrust Belts and Punjab Foredeep (Gee, 1945; Yeats et al., 1984; Lillie et al., 1987 and Kazmi and Jan, 1997).

The tectonics of the country depends on two main convergent plate boundaries. One is the Northeast (NE) active collisional zone and second is Southwest (SW) Subduction zone, both the convergent zones connected by Chamman Transform Fault and displace in North to South (Kadri I.B., 1995).

The magnificent mountain ranges are formed due the collisional tectonics. Himalayas is the most famous for highest mountain ranges of the world. Pakistan is a home for many tallest mountain ranges like Himalaya, Hindukush and Karakorum. Rock sequences from Pre-Cambrian to Recent can be studied in these ranges (Kazmi and Jan, 1997).

2.2   Regional Tectonic Settings of Indus Basin

Pakistan marks many diverse basins geographically. There are two main basin known as sedimentary basins which are Indus basin and Baluchistan basin. They developed in separate geological time and bonded together in Cretaceous-Paleocene age. Pashin basin also named s Kakar-Khorasan basin which has been recently discovered have it own geological history for its development. It was formed by the interaction between Indian and Eurasian plates and the plate were classified as Median basin (Raza et al., 1989).

The Indus basin comprises of the eastern part of Pakistan which cover the area of Punjab, Sindth and Kyber Paktunkwa. It is the largest and most studied sedimentary basin. It is classified into two sub basins which are Upper Indus basin and lower Indus basin. Lower Indus basin is additionally divided into two basins, which are Central Indus basin and Southern Indus basin. Sargodha high divides the Indus basin into Upper Indus basin and Central Indus basin and Jacobabad high separate the Central Indus basin from Southern Indus basin. The upper Indus basin is additionally subdivided by Jhelum fault and Indus River into Potwar basin and Kohat basin (Kazmi and Abbasi, 2008; Raza et al., 1989).

The Indus basin extends about 1600km from NE-SW. It covers greater part of the eastern side in Pakistan. It covers area of about 300,000km$_2$ in which the upper Indus basin has the area about 50,000km$_2$ and the lower Indus basin has the area of

about 250,000km$_2$.As there is a compressional regime in the upper Indus basin so it comprises of many mountains where as lower Indus basin, this regime changes into extensional regime. Due to extensional regime, plain area is encountered (Shah, 2009).
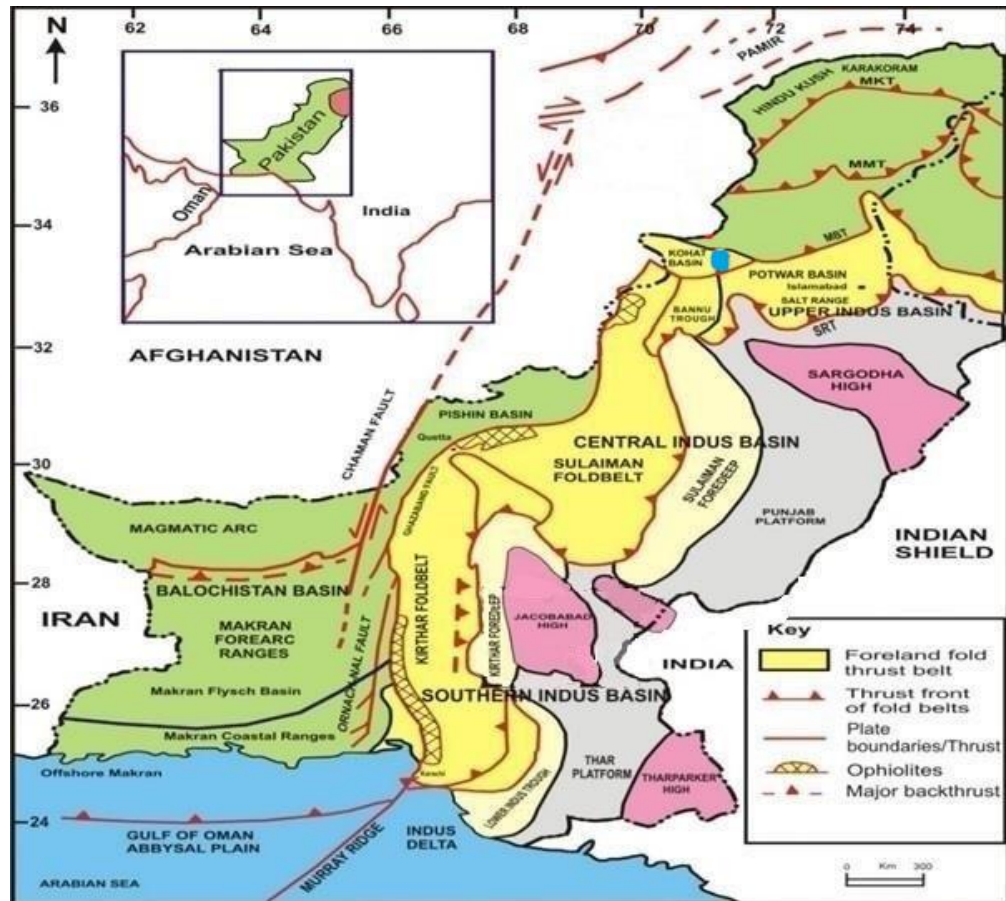
Figure 2.1 Tectonic Setting and Sedimentary Basin of Pakistan, Study Area shown with Blue dot (Aziz and Khan, 2003).

2.3   Regional Tectonic Settings of Kohat Sub-basin

Kohat-Potwar basin is present in northern Pakistan, located between latitude 32° and 34° N and longitude 70° and 74° E. The Kohat Area in bounded by MBT to the North and by Trans Indus Ranges to the South. The Kohat Plateau merges to the southwest with the Bannu Basin. The River Indus points the eastern limit of Kohat Plateau which distinguished it from the Potwar plateau and in West the Kohat plateau is restricted by NNE-SSW oriented Kurram fault.

The surface and subsurface outcrops of the area below the lower Eocene is less damaged and misshaped as compared to the Eocene. The South and Southeastern area of Kohat have less tight and damage structures compared to the North and Northwestern

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areas due to rational pursuit. The whole Kohat-Potwar region is composed of Imbricate Wrench Faults which are steep at Kohat and gentle in Potwar region.

This basin has rocks from Eocene to Pliocene age rocks, below those Paleocene and Mesozoic rocks are present. Southern side comprise of Miocene to Pliocene strata which is thrusting southward along with the direction of Bandarbarra and Karak Thrust on Bannu Depression, Pliocene to Pleistocene sequences at western side and Potwar plateau is present at Eastern side. Southern side of Kohat-Potwar basin, an area possesses sediment ranges from Paleozoic to Recent which is relatively flatter with dips of monoclines in North direction (Searle et al.1996).

A regional type of detachment surface of Precambrian sequence

Figure 2.2 Map shows, Regional Tectonic Setting of Kohat Basin with Study Well marked with Blue dot (Pivnik and Sercombe, 1993).

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2.4   Stratigraphy of Kohat Sub-basin

Burial record of Kohat-Potwar fold and thrust belts occurred in Precambrian age by sediments deposition in Salt Range Formation and Jhelum Group (Table 2.1). Upper Cambrian, Ordovician, Silurian, Devonian or Carboniferous starta are absent in this basin because of non-deposition and/or erosion (Shah, 1977).

Jurrasic sequence of the area overlies the Cretaceous sequence and it gets deposited on continental margin which is shallow and gently dipping in the northward direction. The sequence contains the carbonates sequence to be precise marl and grades towards the larger grains size rocks i.e. sandstones with some interbedded shale. A repetition of this cycle can be seen several times then it is changed into thick marls which belong to Upper Jurrasic age sequence overlain them and then followed by oolitic limestone which belong to Samana Suk formation which consist of dark colored cross bedded packestones to wackestones and calcareous sands (Ahmad, 2003).

Samana Suk Limestone's deposition was tailed by the unconformity (times of non-deposition) and little erosion. The Formation has ferruginous upper surface, indurated, burrowed and superficially weathered which shows the presence of hard ground. This indicates that exposure was sub-aqueous instead of sub-aerial. Another sequence of Chichali to Lumshiwal also present on the upper part of this hard ground. At the end of the Cretaceous aged sequences, another shale to sandstone sequence is present which is hard, non-fossiliferous, cliff like limestone of Kawagarh Formation. Color of the limestone toward the uppermost part graded as reddish, greyish and greenish color shale (Ali et al, 2010).

Paleocene sequences are not exposed in the area due to non-uniformity of the sequence. In the northern side two lithologies sandstone and limestone are present which is considered as equivalent to the Paleocene age Formations (Ahmad et al., 1999).

Laterally there is an immense heterogeneity in the Lockhart Limestone. The lithology is medium bedded to thick bedded at the place of type locality of Lockhart Limestone which is fort lockhart in Samana peak. These packestone to wackestone sequence contain abundant fossil fragments. In very few intra-formational conglomerates and layers of lenses with micritic matrix are present in this section. The transition zone between the Lockhart Limestone and Hangu Formation have two-meter thickness of brownish to blackish Marls which have shallow ramp or shallow platform type of environment of deposition. Hangu Formation is overlain by the black shale

considered as Panoba anticline which contains other lithologies, like beds of limestone and marl and breccias of black limestone. This black shale towards northern side in Kotal Pass, contained limestone changed into the conglomerates, sandstones and the breccias(cherty). At the western side in the Darsamand aniticline, this Late Cretaceous age sequence is tailed by breccia which is calcareous, dark in color and then followed by the thick shales having breccias (chert) and sandstone (quartzite) (Sameeni et al., 2009).

The Panoba Shale overlies the Lockhart Limestone which has different exposures in the area. This Formation has the shale of greenish grey color and lenses of sandstone with interbedded conglomerates and gypsiferous lamellae. This provides a shallow depth detachment zone which is the main reason for the deeper and the shallower structures in the area. After the Panoba Shales, there is a lateral change in the facies first into the red clays of Mami Khel, dark to white in color beds of Jatta Gypsum and Bahadur Khel Salt of pink color. This above order is reversed due to the Manzalai anticline and acts as detachment surface on the shallower level Like the Panoba Shale and give rise to the increase in structural complexity of the area but this complexity is at the shallower levels only. All these facies are shallow restricted marine facies and followed by carbonates dominated facies and also known as the Kohat group. These onsets the lower carbonates' layer of Shehkhan Limestone and Kuldana Formation's Clays overlie this limestone and the platform type or environment of deposition limestone overlies all of the former with is fossiliferous (nummulites) (Paracha et al., 2004a).

Kohat Limestone acts as a regional marker in the entire area because of its hardness and resistant nature. There is a major unconformity at the top or after the Kohat Limestone's in the area and after that is tailed by different lithologies like sandstones and clays which belong to the age of Miocene to Pliocene. The younger sequence has very less potential so they are not of high importance. Sandstone dominated Formations Kamlial followed by Chinji and then Nagri Formation mainly consists of Red clays and the basal conglomerates. Southern block contains younger formations as well (Ali, 2010).

Table 2.1 Generalized Stratigraphic column of the Kohat Sub-Basin (Fatmi & AN, 1973; Meissner et al,1974 & 1975; Kadri, 1995).

QUAT	PLEIS		Lithology
	PLIO-CENE	Siwalik Group	
	MIOCENE	Rawalpindi Group	
TERTIARY	EOCENE	Chorgali Fm	
		Sakesar Lst	
		Nammal Fm	
	PALEOCENE	Patala Fm	
		Lockhart Fm	
		Hangu Fm	
CRETACEOUS	E	Lumshiwal Fm	
		Chichali Fm	
	L		
JURASSIC	M	Samana Suk Fm	
		Shinawri Fm	
	E	Datta Fm	
TRIASSIC	L	Kingriali Fm	
	M	Tredian Fm	
	E	Mianwali Fm	
PERMIAN	LATE	Chhidru Fm	
		Wargal Fm	
		Amb Fm	
	EARLY	Sardhai Fm	
		Warccha Fm	
		Dandot Fm	
		Tobra Fm	
CAMBRIAN		Baghanwala Fm	
		Jutana Fm	
		Kussak Fm	
		Khewra Sandstone	
PRE-CAMBRIAN		Salt Range Fm	

2.5 Geology and Tectonics of the Study Area

This area lies in the Kushal Garh Block which is located in Kohat Sub-Basin. This area falls in Himalayan Karakorum fold and thrust belt known as frontal deformation zone. This fold and thrust belt is good indicator of NS shortening in area.
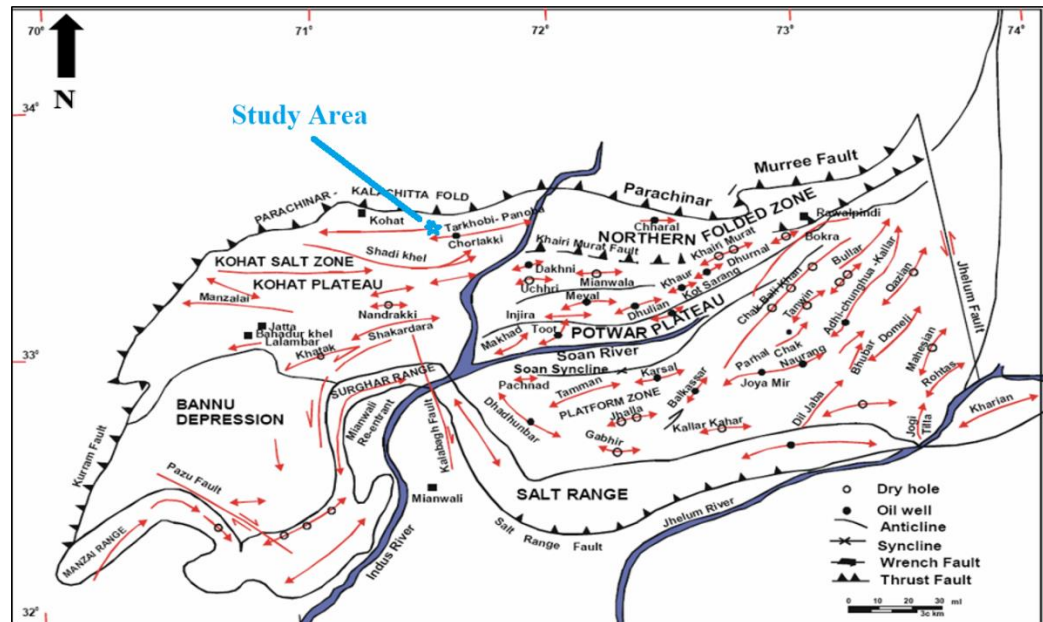
Figure 2.3 Genealized structure of Kohat-Potwar Basin (modified from Kazmi and Rana 1982; Khan and others 1986; Law and others 1998).

2.6 Borehole Stratigraphy

Tolanj-01 was drilled to 9816ft in the Eocene Kohat formation at the surface to the Jurassic Samanasuk Formation at total depth (TD). Different formations encountered during drilling are depicted below with their formation name, age, formation tops and thickness (Table 2.2).

The borehole stratigraphy is almost similar to the generalized stratigraphy of Kohat sub basin. The Paleocene age formation in Tolanj-01 well starts from 4510-8850ft with a thickness of 3882ft which comprises of Patala Formation 3470ft, Lockhart Limestone 420ft, Hangu Formation 450ft.

Table 2.2 Borehole Stratigraphy of Tolanj-01 Well.

Age	Formation	Formation Top (ft)	Thickness (ft)
EOCENE	KOHAT	0	385
	MAMI KHEL	385	245
	SHEKHAN	630	245
	MAMI KHEL	875	655
	SHEKHAN	1530	1780
	MAMI KHEL	3310	234
	SHEKHAN	3544	516
	PANOBA	4060	450
PALEOCENE	PATALA	4510	3470
	LOCKHART	7980	420
	HANGU	8400	450
CRETACEOUS	DARSAMAND	8850	296
EARLY CRETACEOUS	LUMSHIWAL	9116	513
JURASSIC	CHICHALI	9629	187
JURASSIC	SAMANA SUK	9816	1

2.7   Petroleum play of Kohat Sub-Basin

Petroleum system is described as a natural system consist all the geological processes and elements which is of utmost importance and required for hydrocarbon generation and accumulation. (Magoon and Dow, 1994)

Petroleum system forms in sedimentary basin, there are so many areas on the earth where subsidence occur and allow the sediments to accumulate as thick sedimentary sequences. Hydrocarbons generation process takes millions of years that start with the burial of animals and plant remains in sedimentary layers, portion of that material breakdown by bacterial decomposition and by chemical reactions. Heat and pressure because of burial transforms the sedimentary layers into different types of rocks like limestone, sandstone and shale, according to the abundance of sediments present of same composition. Heat and pressure also transforms the organic matter (plants and animals) into hydrocarbon or petroleum. Pores and connecting pores in the

rock allows the petroleum to accumulate or escape from the rock. A permeable rock holds the petroleum like a sponge, and low permeable rocks overlying act as a trap for petroleum (Don Hallet,2002).

The petroleum system is present wherever the required elements, suitable environment and processes are present. Petroleum is chemically a complex mixture of organic compound containing hydrogen and Carbon and nitrogen, oxygen and Sulphur as impurities. Petroleum is physically present widely in the earth surface as solid, semi-solid, liquid and gas. Naturally occurred complex of hydrocarbons distributed in sedimentary rocks in earth crust, first used by Agricola in 1546. Strictly means hydrocarbons occur in liquid form but the term petroleum should be used for the physically present and widely spread solid, semisolid liquid and gas members of this series (Magoon and Dow, 1994).

Elements of petroleum system, Petroleum geologists are mainly concerned to evaluate the geologic elements and geological processes. The geological elements needed are Source, Reservoir, Seal and overburden. The Geological processes needed are Traps, Generation of petroleum, Migration, Accumulation of Petroleum and Preservation of petroleum. It is very important that all the elements and processes occur at the right place and at the right time for the accumulation of petroleum (Magoon and Beaumont,2003).

Kohat Sub-Basin and fold belt is a prolific hydrocarbon basin and have many proven petroleum systems. The tectonic settings in the basin make it very good storage for hydrocarbon which can be explored and produced easily. Source and reservoir rocks are present in this region in Mesozoic-Paleogene. Evaporites thick layer and interbedded shale are present in this region and have a good quality sealing potential (Khan et al., 1986).

2.7.1 Source Rocks

A unit of rock, that generates oil and gas, for commercial accumulations. Common source rocks are Shale and limestone. Infra Cambrian Salt Range Formation displays good TOC and very good hydrogen index (H.I) values indicative of type II organic matter, Organic rich shales of Mianwali and Carbonates of Kingriali Formations (Triassic), Datta Formation (Jurassic) and Chichali (Cretaceous) considered as potential source rocks in the area. Patala shales (Palaeocene) are proven source in Upper Indus Basin. Maturity modelling suggests that the Palaeocene and older source

rocks have oil to condensate maturity level in the area. Main source potential lies in Datta (Excellent TOC values, type II/III kerogen), Chichali and Lumshiwal Formations which have been proven to yield in the surrounding wells. In Eastern part of Potwar, the Patala Formation and Lockhart Limestone are confirmed and demonstrated as source rocks for high quality oil (Kadri, I.B., 1995).

2.7.2   Reservoir Rocks

Porous and permeable rock unit holds the petroleum reserves. Porosity for storage and Permeability for the pore connectivity which will show, how easily the petroleum will flow out of the rock. Common reservoirs are sandstone, carbonates and fractured reservoirs.

Clastics and carbonates of Palaeocene, clastics of Lower Cretaceous and Jurassic are confirmed reservoirs in the basin. These are known to be the potential reservoir targets in the block area. Kingriali Formation is confirmed reservoir in Chanda Field. Carbonates of the Kingriali and Tredian Formations of Triassic age have very good porosity values in Chanda Deep1. The Datta Formation is a proven reservoir in the Manzalai, Makori and Chanda Field. Very good porosity values in the Datta Formation have been reported in Chanda-1 and Chanda Deep-1 wells (Jaswal et al., 1997).

2.7.3   Seal Rocks

A rock with lower permeability which prevents the escape of petroleum from the reservoir rock. The pore pressure must be greater than the buoyancy, on the Hydrocarbons in the seal rock, which is circulating in the reservoir. Most common seals are Evaporites, Chalks and Mudrocks.

Two types of seal-rocks i.e. regional and intra-formational can seal Mesozoic-Palaeocene reservoirs. The Upper Paleocene/Lower Eocene shale has good characteristics of an effective seal. Shales and carbonates of Cretaceous and Jurassic can also provide an effective sealing mechanism for the underlying Datta (Jurassic) reservoir. Paleozoic sequences have intra-formational shales which can act as seals in the block area. Interbedded shales and claystone of Mianwali, Tredian and Kingriali Formations of Triassic age and Datta Formation may also act as seals. The shales of the Chichali and Patala can also play as seal at bottom and top for the Lumshiwal Formation (Wandrey et al., 2004).

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2.7.4 Maturation

The Transformation of organic matter into petroleum is due to temperature, pressure and overburden. Rate of maturation depend upon time, temperature and pressure.

2.7.5 Migration

Migration is the permanent movement of petroleum from a pore, from where they originated. Migrations have two types. Primary migration: source rock to first porous and permeable refuge, i.e. carrier beds. Secondary migration: movement within the porous reservoir or from one reservoir to other.

2.7.6 Traps

It is a structural or stratigraphic property and feature which ensure the juxtaposition of reservoir and seal so that the hydrocarbon remain trapped and prevent escape or loss.

The potential traps in area are related to the major shortening episodes to the final collision of the Himalayas. These include anticlinal features and thrust bound wedges which were developed in Neogene-Quaternary time by thrust fault and propagation from north to south. Both Structural and combination traps are possible to exist in the area (KPOGCL, 2015).

2.7.7 Timing

Timing is a very critical factor in petroleum system. It is stated that the formation of trap must be before the migration of petroleum.

2.7.8 Overburden Pressure

An utmost important element in petroleum system, mostly succession of sedimentary rocks lies above on geological elements. Thermal degradation and maturation are determined by the overburden rock. Source rock temperature depend upon the thermal conductivity of the overburden rock, heat flow, ground surface temperature and thickness of the succession. Helps in the maturation of the petroleum in source rock (Magoon and Beaumont,2003).

CHAPTER 3

METHODOLOGY

3.1   Methodology

Methodology which was selected to perform geochemical analysis in this research consists of well cuttings as a sample from a study area. Geochemical analysis of well cuttings for Tolanj-01 well was performed in HDIP. (Fig. 1.2)

3.1.1   Data Required

The Well cuttings data was needed to perform the study of Tolanj-01 well Latitude (33° 33′ 42″), Longitude (71° 42′ 50″) for analyzing the potential source rock, organic matter maturity and biomarker analysis. Fifty-six (56) samples of well cuttings were acquired from HDIP for geochemical analysis.

Table 3.1 Sample Description of Target Well.

	Depth Interval (ft)	No. of Samples
Patala Formation	4705-7950	26
Lockhart Limestone	8015-8390	12
Hangu Formation	8400-8750	18

3.1.2   Laboratory Work

The laboratory work is carried to analyze the source rock characteristics of the Paleocene age Formations. The laboratory-work includes various analytical techniques and analyses which include the source rock screening techniques like total organic carbon analysis (TOC), rock eval pyrolysis and organic petrography (VR). Other techniques for extractable organic matter (EOM) like Solid-Liquid chromatographic separation of fractions, gas chromatography (GC-FID)/Whole Oil chromatography and gas chromatography-mass spectrometry(GC-MS). This analysis will assist for recognition of source rock potential of Paleocene Formations. Laboratory work flow is summarized as follows.

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3.1.3 Sample Preparation

Sample is prepared for various geochemical analyses. Sample preparation includes washing, pulverization (crushing and grinding), polishing, contamination removals, drying and de-asphalting.

The sample went through decontamination process before it is to be analyzed for the removal of any sort of contamination. The samples are being washed by water and dried at 40 ˚C in oven. Then the dried sample is crushed and milled in a ceramic made pestle and metal mortar. Pestle and mortar should be cleaned properly with hot water, methanol (CH3OH), dichloromethane (DCM) or other solution before crushing and grinding the sample. Dehydration and de-asphalting is done on samples and those powdered samples are stored in a tagged transparent zipper bag for further geochemical analysis and screening.

3.2 Screening Analysis

Screening Analysis of the source rock calculate the total organic carbon (TOC) and Rock-Eval Pyrolysis variables. It provides the free hydrocarbons (S_1), quantity of remaining potential in source rock (S_2) and estimate for maturity of source rock (Tmax). Evaluation of such data provides information about the kerogen type and source rock maturity.

3.2.1 Total Organic Carbon (TOC)

Total organic carbon is important screening tools. TOC value is used to be acquire from the oxidation of organic material and measuring the Co_2 produced in the way of control combustion. TOC consist of organic carbon present in a rock sample which includes bitumen and kerogen. For TOC calculations (100-150mg) grinded sample is weighed in ceramic crucible designed to withstand high temperature by using electrical balance. Inorganic carbon must be removed from the samples before it is used for TOC determination in LECO CS-300, by exposing the samples with 5-10% hydrochloric acid (HCL) drop wise till all the effervescence from the sample has disappeared. This removes the moisture from these samples. The effervescence elimination indicates the removal of all inorganic carbon and the organic carbon left behind in a sample. Then the sample is placed in oven at a temperature of 40°C overnight for the removal of any water content left behind in sample. The sample is

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now ready for analysis in Leco CS-300 TOC analyzer. This analyzer comprises of two parts, induction furnace and detector (Fig. 3.1).

Figure 3.1 Equipment used for TOC determination (LECO CS-300).

The sample is placed in the induction furnace for combustion. An iron chip as a catalyst is added to accelerate the process. Temperature range for iron chips is 1300-1400 °C and standard temperature is applied for the conversation of organic matter into gases (Leco manual for CS-300, 1996). Sulphur and Carbon in the samples are converted into Carbon dioxide (CO_2), carbon monoxide (CO) and sulfur dioxide (SO_2) respectively. CO is converted into CO2 by pallets catalyst. Both the sulfur and carbon content is detected by Infra-Red (IR) detectors in TOC analyzer separately because Sulphur is greater in size then carbon IR cells. All these calculations are done by built-in software. To avoid any error in analysis and to determine exact values of total carbon Leco standards are used for instrument calibration by known carbon and sulfur content as sample Pr-1 (Carbon= 0.205±0.0004, Sulphur= 0.101±0.0009). To minimize the error in sample preparation and analysis procedures Pr-1 sample is analyzed after every 9-10 samples. The amount of CO_2 produced from the sample is directly related to the organic matter present in sample. The amount of the organic carbon in sample is the direct measure of its organic richness. The carbon content of source rock is proportional

to the amount of CO_2 released. sedimentary rock must have Sufficient amount of organic matter. The source rock in the petroleum play has at least minimum value 0.5% in case of shale and 0.25% in case of carbonates which is then admired as a potential source rock which can generate hydrocarbon and will be studied further. TOC for good source rock at petroliferous area is 1.37% for shale, 0.5% for carbonates and 0.25% for calcareous shale.

Table 3.2 TOC standards for assessing organic richness of source rocks (Peters and Casa, 1994).

% TOC for Shale	% TOC for Carbonates	Descriptive Terms
0--0.5	0—0.2	Poor
0.5--1	0.2—0.5	Fair
1--2	0.5—1.0	Good
2--4	1—2	Very Good
>4	>2	Excellent

Elemental analysis on the bases of TOC, kerogen types on the basis of their chemical composition. Chart can be plotted against hydrogen and oxygen index to show the type of kerogen.

Table 3.3 Kerogen types on the basis of their chemical composition (Clifford Walters, 2007) (Peters and Casa, 1994).

Temperature	Type	Description
0-50	Type 4	Inertinite (barren)
50-200	Type 3	Vitrinite(Terrestrialplants(Gas)
200-300	Mix Type 2 and 3	Mix (Vitrinite/Exinite) (Terrestrial/Marine)
300-600	Type 2	Exinite (Planktons, Plants, algae, pollens, spores) (oil/gas)
Greater than 600	Type 1	Alginite (Algal material) (oil/light oil)
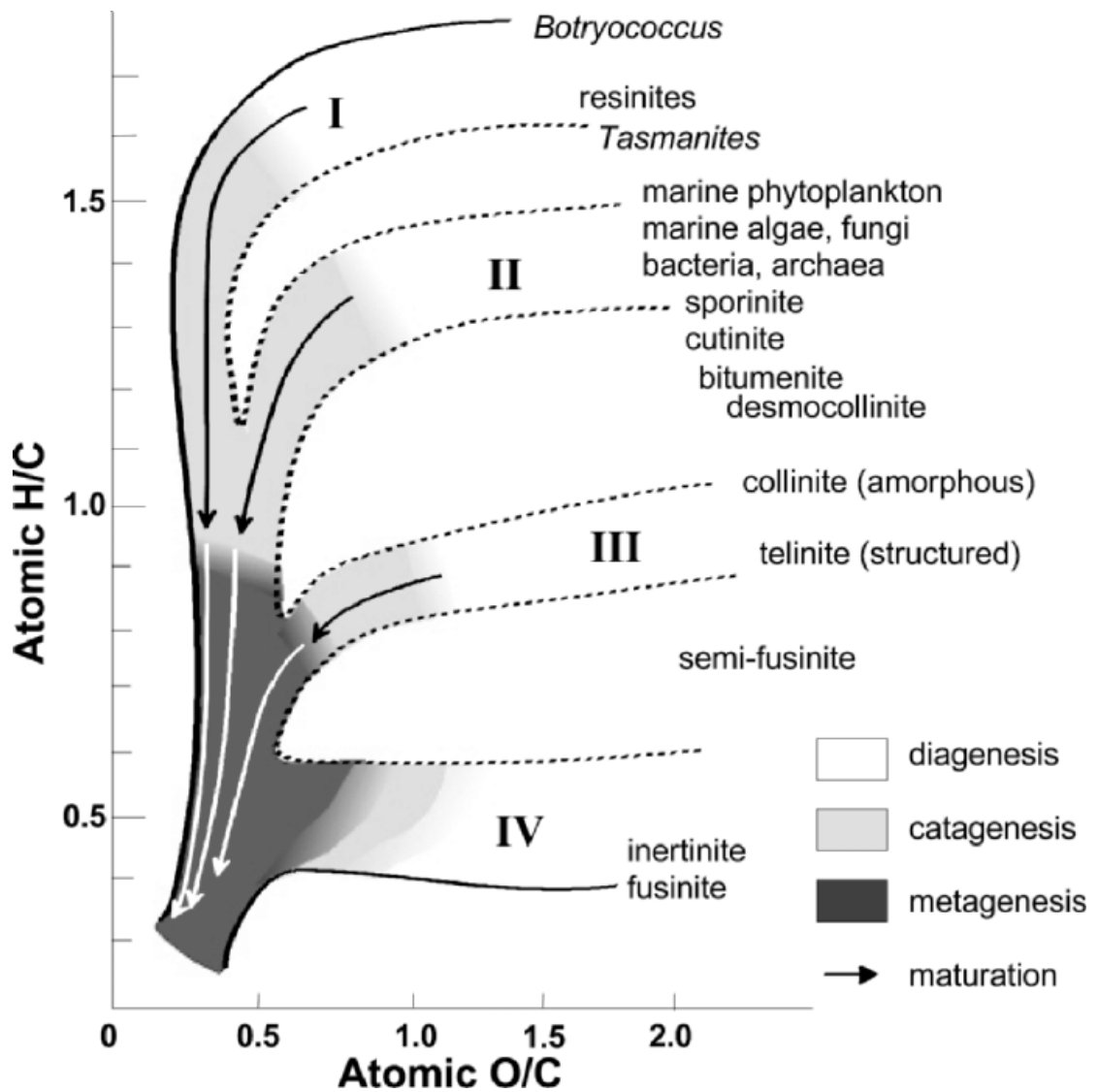
Figure 3.2 Van Krevelen Type Diagram (Clifford Walters, 2007).

When all other oxidized then transfer into Type 4. All samples have to be run twice to increase the precision in results. TOC does not reflect or investigate the current potential yield of a source rock. For the current potential yield, Rock-Eval Pyrolysis is performed.

3.2.2 Rock Eval Pyrolysis

Samples with fair TOC were run on Rock-Eval 6 for pyrolysis after TOC analysis to investigate the current potential yield. This process further analyzes organic matter's thermal maturity, types of kerogen and the potential of source rock. Combined with the total organic carbon (TOC) measurement, this is the most cost effective and rapid screening method for large number of samples. TOC value would be irrespective of depth. Present TOC value is less than original one.

All the samples having TOC greater than 0.5 are directed to rock eval pyrolysis study. Approximately 60 to 65 mg is weighed Pulverized sample in rock eval crucibles.

This instrument consists of pyrolysis chamber, oxidation chamber which contains FID and IR detectors. It contains hydrogen and nitrogen generators, air compressor, CO_2 purifier assembly and computer software (ROCK-EVAL 6 Turbo) along with the main instrument. In total 25 samples can be analyzed at a time. All samples have to be run twice to increase the precision in results. The French institute of petroleum (IFP) standard is used as standard and test repeated after every 9-10 samples (Fig. 3.3).

Figure 3.3 Showing Rock Eval-6 used for pyrolysis.

Samples are heated to 300 °C and remain there for some time, constant and consistent temperature gradient.

(i)   Free Hydrocarbon that have been already generated are volatilized and measured at 300°C for 3 minutes (mg HC/g R). Free State hydrocarbon is volatized and sensed by flame ionization detecter (FID) as S_1 peak.

(ii)   The temperature is then increased from 300 to 550-650°C at a rate of 25°C per minute (mg HC/g R). T_{max} is maximum evolution of S_2 hydrocarbon by cracking of kerogen. T_{max} depends on several other factors like the kerogen's maturity and nature of kerogen. Thermal cracking of all remaining kerogen takes place and hydrocarbon generated are volatilized and measured as S_2 peak. T_{max} should be greater than 435°C for mature source rock samples.

(iii) Similarly, S_3 peak are for hydrogen index, when kerogen is thermally crack at temperature between 300-390°C organic carbon-dioxide evolve and detected at FID and record S_3 peak (mg CO_2/g Rock).

(iv) S_4 for carbon or dead carbon (Residual matter), oxidation proceeds at 580˚C for 12 mints.

All these preceding parameters given by instrument itself while for further characterization; several other parameters can be calculated by using different formulas.

(i)   Hydrogen index (HI), HI = S_2/TOC x 100, an indication of gas or oil potential, Relative hydrogen content (0.1g HC/g; TOC).

(ii)   Oxygen Index (OI), OI = S_3/TOC x 100, Relative oxygen content (0.1g CO2/g; TOC).

(iii) Production Index, PI = S_2/S_1 +S_2, Measure of hydrocarbon retention, production index increase with maturation.

(iv)   Genetic Potential (GP), GP = S_1 + S_2, values used for the classification of source rock as either poor or good source rock. The values less than 2 fall in poor source rock.

(v) S_2/S_3 used to tell kerogen type when TOC is not available.

Table 3.4 Tmax Description (Peters and Casa, 1994).

T $_{max}$	Description
Less than 435	Immature
435-490	Mature(oil window)
470-490	Wet Gas/Condensates
490-550	Dry Gas
Greater than 550	Graphite

Table 3.5 Production Index Description (Peters and Casa, 1994).

Production index	Description
Less than 0.10	Immature
0.10-0.30	Oil Generation
Greater than 0.30	Gas, Oil Cracking
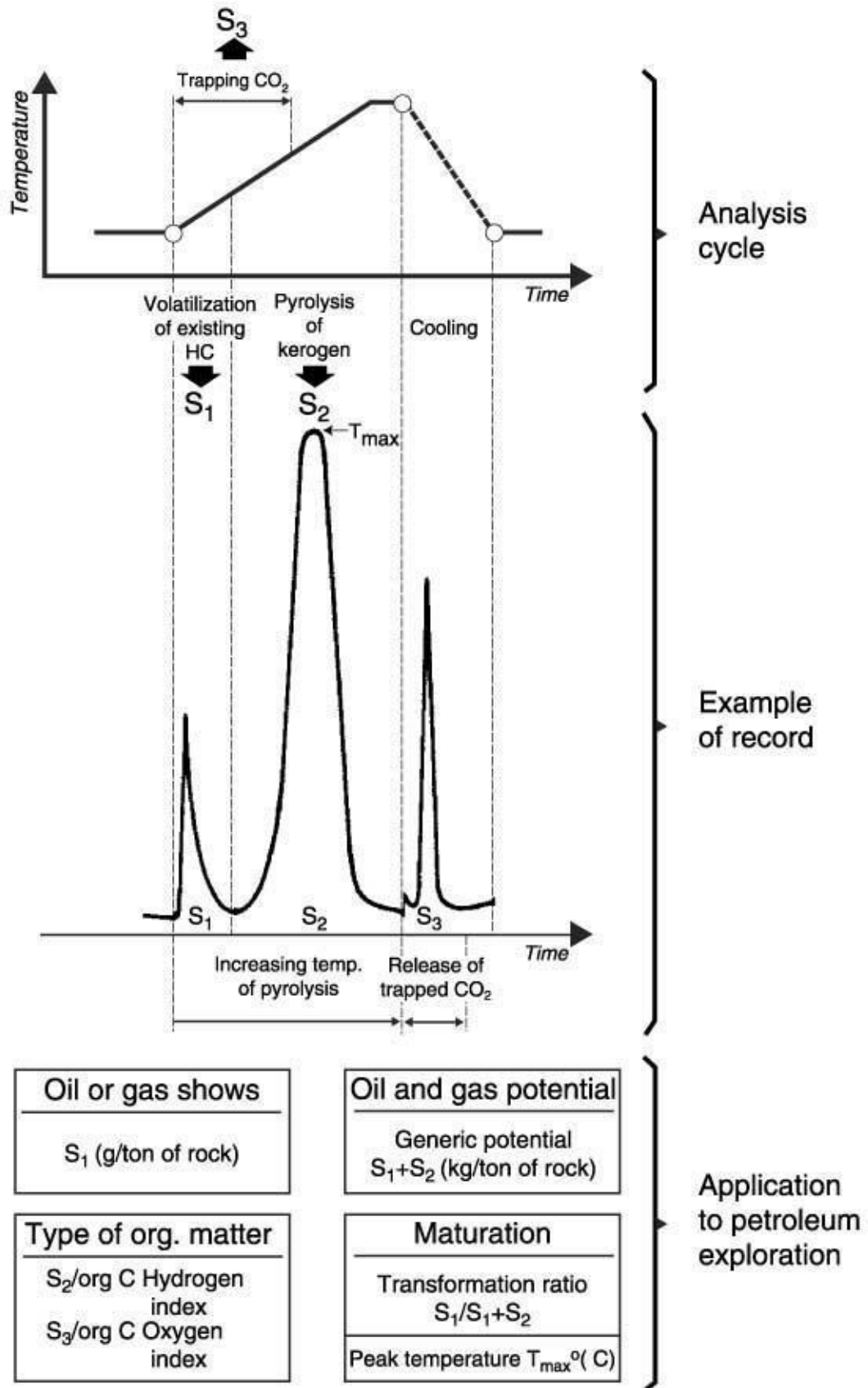
Figure 3.4 Diagram representing different parameters obtained from Rock Eval-6 (Lafargue, 1998).

3.2.3 Organic Petrography (Vitrinite Reflectance)

Organic petrography is based upon the laboratory analysis of samples (vitrinite reflectance microscope) to undergo the best possible analysis of sample. The organic petrography service delivers information about rock type, associated organic matter, thermal maturity and hydrocarbon generation zone. It is basically a study of macerals which naturally present in the sedimentary rocks. These macerals are organic, occurs with organic matter which is slightly dispersed and are present in oil shales and coals as well.

There are two types of microscopy in this study, TLM and RLM. Both these microscopies contain mount and thin section but the basic difference between these microscopies is polishing of thin section and mount. RLM thin section or mount should be polished whereas TLM mount or thin section used is not polished.
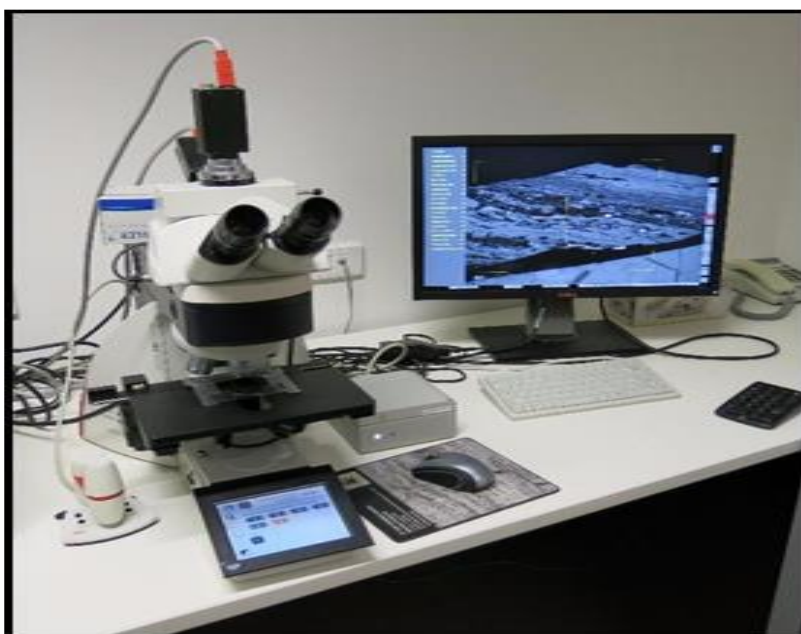
Figure 3.5 Reflectance Microscope used for Maceral Analysis (Carl. Zeiss Axio Imager Z1M).

First step is quality assurance, the sample is prepared in compliance with the standard practice method ASIM 02797, calibration of the instrument photometer and amplify the reflection standards before and after analysis of each sample. The crushed sample2mm-0.8mm in 8-10 grams is mounted or set up in a liquid polystyrene resin which is then allowed to harden. Then ground the sample with finer carborundum paper and polish it with finer alumina powders. Then by using a photometric microscope

samples are then observed under reflected light with reference to optical standards. Then by using oil immersion objectives and a green filter with a peak transmission of 546nm the samples are examined in white & blue light. The values are measured and recorded as a percentage of light reflected. Changes are thought to be significant in reflectance values greater than Vr 0.1%. Reflectance measurements above Vr 0.5% are reliable particularly; below this value other parameters are used. The reflectance changes aimlessly or haphazardly in immature rocks with increasing maturity. Different macerals have different values of vitrinite reflectance which indicate different thermal maturity stages. Macerals are of three types, Liptinite is present in oil shales, Virinite in coal and Inertinite in reworked mineral (no potential of source). Data correction as per standard test (minimum 20 measurements), Data is revived by field experts and organic geochemists. Repetition of the experiment ensures the consistency and statistically relevant data.

Organic petrography utilizes two main ideas which are type and rank, organic matter type tells about nature, richness and variety whereas rank tells about thermal maturity. It explains about how the oil shale and coal are changed with the passage of time under different temperature pressure conditions. Vitrinite reflectance value is the reflection of thermal maturity of the rock sample under evaluation.

Table 3.6 Vitrinite Reflectance, Tmax and Description (Peters and Casa, 1994).

R_o	T_{max}	Description
0.6%	Less than 435	Immature
1.3%	435-490	Mature(oil window)
1.9%	470-490	Wet Gas/Condensates
4%	490-550	Dry Gas
Greater than 4%	Greater than 550	Graphite

3.3   Extractable Organic Matter (EOM)

Source rock is subjected to further geochemical analysis, Extractable organic matter (EOM) if it fulfills the criteria after the screening tool analysis. The criteria include TOC value greater than 0.5%, T_{max} greater than 430°C, GP value greater than 2, Vr value greater than 0.6 and kerogen type should not be Type-IV. The rock sample fall in above mentioned criteria are taken for further geochemical analysis.

In petroleum source rocks and reservoir rocks the extractable organic matter (EOM) is defined as bitumen and also known as Bitumen extraction. Over geologic time and on exposure to high regional temperatures, bitumen is transformed into pyro-bitumen. Due to thermal reaction insoluble carbon-rich residue left behind and lighter oil and gas products separated. Laboratory, experiments on oil shales and petroleum source rocks produces gaseous and liquid products by decomposition of insoluble organic matter. The fluid left behind is characterize as bitumen, further thermal exposure, it continues to evolve and dis-proportionate into pyro-bitumen and Hydrocarbons. Bitumen is organic and it is dissolvable in other organic solvents. For EOM extraction, powdered sample is taken of (50 to80 grams) in crucible or thimble made of glass. It is sealed with glass wool and put in the extractor. Condenser is placed at the head of extractor. A 250ml mixture of organic solvent (mixture of DCM and methanol, ratio 70 to 30) in a reservoir flask placed in hot water bath which have a temperature range of 50 to 55°C. When the temperature of apparatus rises solvents evaporates and pass through the condenser and percolates into the rock sample. This percolation will extract the extractable organic matter from the sample. The material inorganic in nature will stay and organic solvent will go with solvent. The condenser will help to cool the circulation system. The solution is evaporated in the Rotary vapor under vacuum to remove excess solvent after all the percolation of the organic matter from the sample.

EOM is left behind as an end product and ratio of EOM to TOC which determine that whether the sample will undergo further detailed geochemical analysis or not. If the ratio is greater than 500ppm then the sample will undergo further analysis and if it is less from 500ppm, then that sample will not be used for further analysis.

Figure 3.6 Fractionation of different chemical compounds, a) Soxhlet and b) Column Chromatography.

3.3.1 Solid-Liquid Chromatographic separation of fractions

EOM is further separated into fractions like saturated compounds, aromatic compounds and NSOs by the process of column chromatography.

Solid Liquid Chromatography is currently the dominate type of chromatography. This technique is acquired for the separation of proteins, nucleic acids, or small molecules from complex mixtures in which the mobile phase is a liquid and solid stationary phase. It is also used for analytical applications. The major mechanism of retention in Liquid Chromatography is adsorption and the adsorbents are silica and alumina. It can be applied to the separation of different compounds that are soluble in a liquid phase. It is also useful in the separation of biological compounds and inorganic compounds. Column chromatography is a technique is a method used for isolation of a single chemical compounds from mixtures. Compounds movement in the column at different rates allows them to get separated into different fractions which can range from micrograms up to kilograms. It can be done by using gravity to move or compressed gas to push the solvent from the column. Column chromatography main advantage is its low cost and stationary phase used in the process can be replaced to prevent contamination.

Column chromatography is performed in the glass column, filled with silica slurry and alumina. A mixture of EOM and n-hexane (30ml) is made and added to the glass column with syringes. Dissolution occurs and the saturated fractions are collected in the beaker or glass dish. Dichloromethane (DCM)is added to the glass column to

36

separate the aromatics fractions. The above process is done again, Dissolution occurs and the aromatic fractions are collected in the beaker or glass dish. Mixture of methanol and ethyl acetate is added to the column and same process is repeated to separate the NSOs compounds. After the separation of all the three fractions, they are weighed to generate a correlation between different samples on the basis of different parameters like organic matter, origin, composition and thermal maturity.
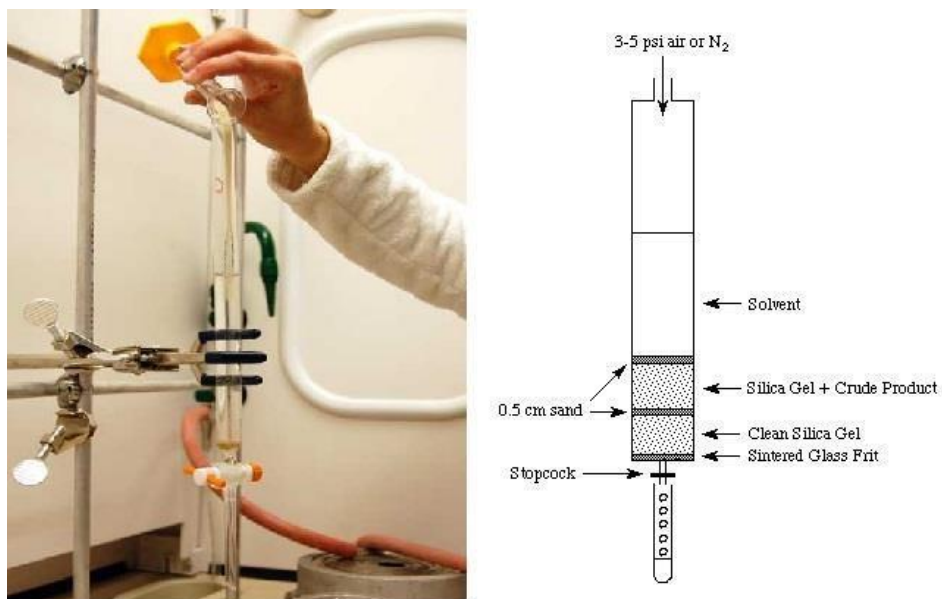
Figure 3.7 Column Chromatography used for separation of Saturated, Aromatics and NSOs fractions.

3.3.2 Gas Chromatography (GC-FID)

Gas Chromatography is a powerful instrument utilize for identification and separation of volatile compounds from a mixture. The instrument is used in oil industry and for academic purposes as well. A gas chromatograph equipped with a data station and integrator is used for Analyses. The capillary column is used for analysis of hydrocarbon. The injection with micro syringes is made to the column via injector. The heating start at a temperature of 40 ºC for1.5 minute then it increases up to 300 ºC at a rate of 4 ºC per minute. Compounds that are injected turn into gaseous state due to heat mixed with mobile phase (helium) and move along the column. Column lining has high boiling point so it acts as a stationary phase and adsorbs with column. All the components get separated one by one as there boiling point reaches and move toward the detector recorded on the chromatogram. Chromatogram is a graph between retention time (time taken by a compound) and intensity of compound present in column.

Flame ionization detector (FID) is used to detect compound in gas chromatography. It is very sensitive and detect even minute amount of concentration but limited to those components which has ability to burn.

3.3.3   Gas Chromatography-Mass Spectrometry (GC-MS)

This technique is used for compounds like steroids and terpenoids which are usually present in trace quantity. All the process from injection to results on chromatogram is same as GC but the difference between GC-FID and GC-MS lies in detectors. GC-MS use Mass spectrometer, single ion detector (SIM) and multiple ion detector (MID) as a detector.

Figure 3.8 Gas Chromatograph mass spectrometer(GC-MS).

3.4   Biomarkers Identification

The resultant chromatograms of GC-MS are used for identification of biomarkers. The different parameters like thermal maturity, origin of organic matter, kerogen type, age and environment of deposition are identified on the basis of these biomarkers which are identified from the chromatograms. These biomarkers delineate a complete picture of source rock potential and also explain correlations between source to oil and oil to oil. Result in identification of origin of oil, similarities and dissimilarities between different families of oil in same or different fields.

Some biomarkers used for identification of different parameters thermal maturity, origin of organic matter, kerogen type, age and environment of deposition (Table 3.7 and Table 3.8).

Table 3.7 Steranes Identification from m/z 217 and 218 Chromatograms.

STERANES

Code	Compound	Empirical formula	Target ions
S20	C20 5α(H),14α(H),17α(H)sterane	C20H34	217, 218
S21	C21 5α(H),14α(H),17 β (H)-sterane	C20H36	217, 218
S22	C22 5α(H),14α(H),17 β (H)-sterane	C20H38	217, 218
DIA27S	C27 20S − 13β(H),17α(H)diasterane	C27 H48	217, 218, 259
DIA27R	C27 20R − 13β(H),17α(H)diasterane	C27 H48	217, 218, 259
DIA27S2	C27 20S− 13β(H),17α(H)diasterane	C27 H48	217, 218, 259
DIA2R2	C27 20R − 13β(H),17α(H)diasterane	C27 H48	217, 218, 259
DIA28S	C28 20S − 13β(H),17α(H)diasterane	C28H50	217, 218, 259
DIA28R	C28 20R − 13β(H),17α(H)diasterane	C28H50	217, 218, 259
DIA29S	C29 20S − 13β(H),17α(H)diasterane	C29H52	217, 218, 259
DIA29R	C29 20R − 13α(H),1 β(H)-diasterane	C29H52	217, 218, 259
C27S	C27 20S − 5α(H),14α(H),17α(H)cholestane	C27H48	217, 218
C27ββR	C27 20R − 5α(H),14β(H),17β(H)cholestane	C27H48	217, 218
C27ββS	C27 20S − 5α(H),14β(H),17β(H)cholestane	C27H48	217, 218
C27R	C27 20R − 5α(H),14α(H),17α(H)cholestane	C27H48	217, 218
C28S	C28 20S − 5α(H),14α(H),17α(H)ergostane	C28H50	217, 218
C28ββR	C28 20R − 5α(H),14β(H),17β(H)ergostane	C28H50	217, 218
C28ββS	C28 20S − 5α(H),14β(H),17β(H)ergostane	C28H50	217, 218
C28R	C28 20R − 5α(H),14α(H),17α(H)ergostane	C28H50	217, 218
C29S	C29 20S − 5α(H),14α(H),17α(H)stigmastane	C29H52	217, 218
C29ββR	C29 20R − 5α(H),14β(H),17β(H)stigmastane	C29H52	217, 218
C29ββS	C29 20S − 5α(H),14β(H),17β(H)stigmastane	C29H52	217, 218
C29R	C29 20R − 5α(H),14α(H),17α(H)stigmastane	C29H52	217, 218
C30S	C30 steranes	C30H54	217, 218

Table 3.8 Terpane Identification from m/z 191 Chromatogram.

TERPANES			
Code	Compound	Empirical formula	Target ions
TR19	C19 tricyclic terpane	C19H34	191
TR20	C20 tricyclic terpane	C20H36	191
TR21	C21 tricyclic terpane	C21H38	191
TR22	C22 tricyclic terpane	C22H40	191
TR23	C23 tricyclic terpane	C23H42	191
TR24	C24 tricyclic terpane	C24H44	191
(a) TR25A	C25 tricyclic terpane	C25H46	191
(b) TR25B	C25 tricyclic terpane	C25H46	191
TET24+TR26 A+TR26B	C26 (S + R) tricyclic terpanes	C24H42 + C26H48	191
(a) TR28A	C28 tricyclic terpane	C28H52	191
(b) TR28B	C28 tricyclic terpane	C28H52	191
(a) TR29A	C29 tricyclic terpane	C29H54	191
(b) TR29B	C29 tricyclic terpane	C29H54	191
Ts	Ts: 18α(H),21β(H)-22,29,30-trisnorhopane	C27H46	191
TH27	17α(H),18α(H),21β(H)-25,28,30-trisnorhopane	C27H46	191, 177
Tm	Tm: 17α(H),21β(H)-22,29,30-trisnorhopane	C27H46	191
TR30A	C30 tricyclic terpane 1	C30H52	191
TR30B	C30 tricyclic terpane 2	C30H52	191
H28	17α(H),18α(H),21β(H)28,30-bisnorhopane	C28H48	191
NOR25H	17α(H),21β(H)-25norhopane	C29H50	191, 177
H29	17α(H),21β(H)-30norhopane	C29H50	191
C29Ts	18α(H),21β(H)-30norneohopane (C29Ts)	C29H50	191
DH30	17α(H)-diahopane	C30H52	191
M29	17α(H),21β(H)-30norhopane (normoretane)	C29H50	191
OL	18α(H) and 18β(H)oleanane	C30H52	191, 412
H30	17α(H),21β(H)-hopane	C30H52	191
NOR30H	17α(H)-30-nor-29homohopane	C30H52	191
M30	17β(H),21α(H)-hopane (moretane)	C30H52	191
H31S	22S-17α(H),21β(H)30-homohopane	C31H54	191
H31R	22R-17α(H),21β(H)30-homohopane	C31H54	191
GAM	Gammacerane	C30H52	191, 412

Internal standard	17β(H),21β(H)-hopane	Internal standard	191
H32S	22S-17α(H),21β(H)-30,31-bishomohopane	C32H56	191
H32R	22R-17α(H),21β(H)-30,31-bishomohopane	C32H56	191
H33S	22S-17α(H),21β(H)-30,31,32trishomohopane	C33H58	191
H33SR	22R-17α(H),21β(H)-30,31,32trishomohopane	C33H58	191
H34S	22S-17α(H),21β(H)-30,31,32,33tetrakishomohopane	C34H60	191
H34R	22R-17α(H),21β(H)-30,31,32,33tetrakishomohopane	C34H60	191
H35S	22S-17α(H),21β(H)-30,31,32,33,34pentakishomohopane	C35H62	191
H35R	22R-17α(H),21β(H)-30,31,32,33,34pentakishomohopane	C35H62	191

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Source Rock Characterization

Well cuttings obtained from Tolanj-01 were subjected to screening analysis on the basis of total organic carbon (TOC) analysis, pyrolysis was conducted by Rock-Eval-6 and organic petrography using reflectance microscope. The organic richness of samples from three formations was determined based on total organic carbon content. kerogen type, hydrocarbon potential, expected hydrocarbon type and thermal maturity determined by Rock-Eval pyrolysis. Further vitrinite reflectance values supported the thermal maturity. Fifty-six (56) well cuttings are used for the purpose of screening of source rock from Tolanj-01 (three Paleocene age formations).

4.2 Assessment for Organic Richness (TOC)

The values of organic richness obtained by TOC analysis shows quantity of organic carbon preserved in sedimentary strata. The source rock must at least fair quantity of contain carbon for the petroleum generation (Table 4.1). This analysis provides the estimate of organic carbon content of source rock and first step in the evolution of source rock quality as per classification set forth by Peters and Casa, 1994 based on this parameter.

Table 4.1 Standard for Assessing Organic Richness of Source Rocks (Peters and Casa, 1994).

% TOC for Shale	% TOC for Carbonates	Descriptive Terms
0-0.5	0-0.2	Poor
0.5-1	0.2-0.5	Fair
1-2	0.5-1.0	Good
2-5	1-2	Very Good
>5	>2	Excellent

TOC values at present day do not reflect the original or total organic matter because with passage of time and with the increase in thermal maturity kerogen is converted into hydrocarbons and value of TOC decreases.

Table 4.2 TOC values for Paleocene, Patala, Lockhart and Hangu Formations.

Sr.	Depth (ft)	Formation	Lithology	TOC wt.%	Sr.	Depth (ft)	Formation	Lithology	TOC wt.%
1	4705	Patala	Shale	0.28	39	8400	Hangu	Shale	0.2
2	4850			0.29	40	8420			0.75
3	4905			0.38	41	8440			0.95
4	5005			0.35	42	8460			1.2
5	5110			0.23	43	8468			0.82
6	5205			0.18	44	8472			1.56
7	5305			0.41	45	8477			0.62
8	5405			0.27	46	8490			0.76
9	5535			0.22	47	8500			0.65
10	5605			0.16	48	8515			1.65
11	5705			0.11	49	8526			1.58
12	5805			0.19	50	8540			0.76
13	5905			0.2	51	8560			0.28
14	6150			0.24	52	8584			4.49
15	6300			0.76	53	8600			0.34
16	6405			0.81	54	8620			1.86
17	6505			0.76	55	8700			0.61
18	6705			0.18	56	8750			0.08
19	6815			0.15					
20	7010			0.31					
21	7305			0.14					
22	7405			0.13					
23	7605			0.18					
24	7745			0.17					
25	7850			0.13					
26	7950			0.18					
27	8015	Lockhart		0.29					
28	8035			0.47					
29	8150			0.27					
30	8205			0.51					
31	8230			0.47					
32	8250		Limestone	0.37					
33	8265			0.47					
34	8280			0.43					
35	8350			0.05					
36	8326			0.47					
37	8370			0.12					
38	8390			0.68					
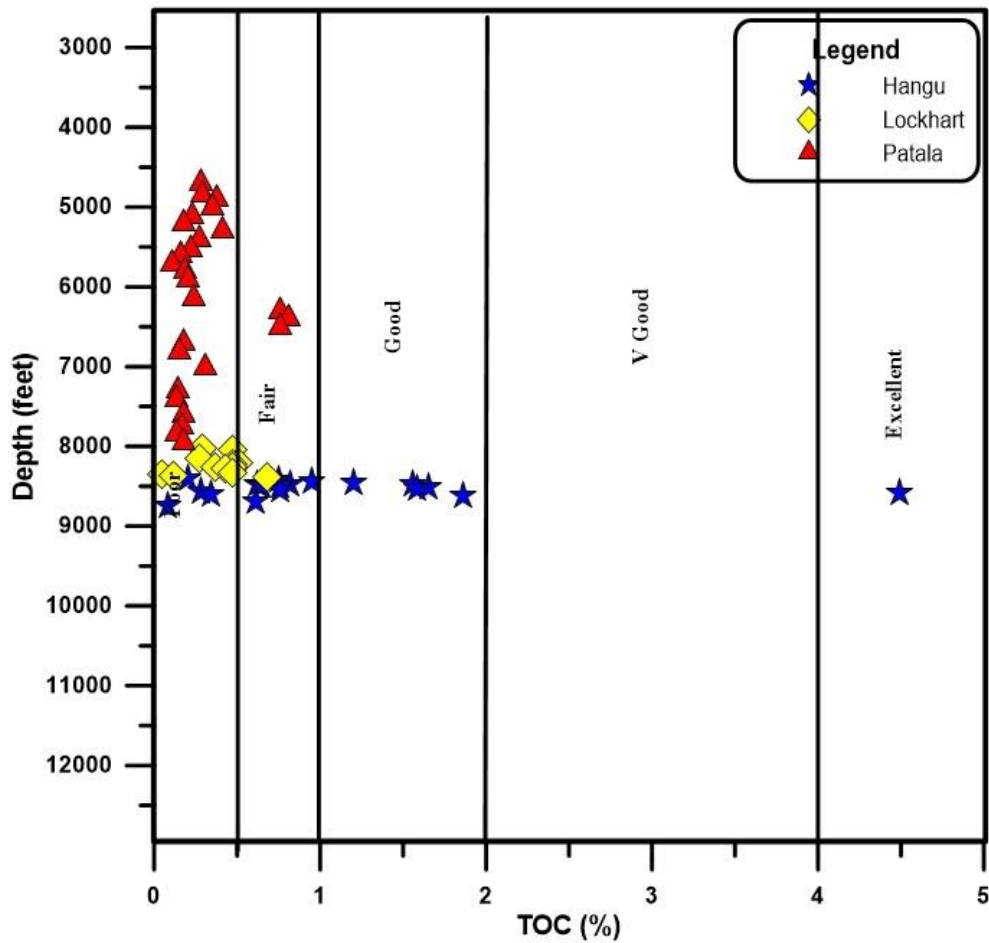
Figure 4.1 TOC vs DEPTH plot for Hangu, Lockhart and Patala Formations.

The current values of Hangu Formation fall in the category of poor to good range. Whereas for the Lockhart Limestone these values fall in the range from poor to fair zone. While for Patala Formation, TOC values fall in the poor to fair category (Fig. 4.1).

4.3 Rock-Eval Pyrolysis

This technique is the second screening step after TOC and efficient for geochemical analysis in the characterization of organic matter in sedimentary rocks. It helps us to determine the different characteristics of organic matter like type of kerogen, thermal maturity, etc. (Bajor et al., 1969).

H/C and O/C ratios have been derived from HI and OI values that are obtained by the Rock-Eval pyrolysis parameters S_2 and S_1 respectively (Espitalie et al., 1986). Pepper (1991) and Pepper and Corvi (1995) considered that the initial HI value as the

most essential parameter for determination of the potential of any sedimentary rock for the expulsion or generation of hydrocarbons.

The HI, S_2 and TOC are considered of high importance. There are changes in HI values are due to the expulsion and generation of hydrocarbons with increasing thermal maturity of the source. T_{max} values obtained by the pyrolysis are used for the determination of the thermal maturity of organic matter and therefore the extent of transformation of organic matter into hydrocarbons. Several other parameters like PI, GP etc. are calculated from the pyrolysis results (Cooles et al., 1986).

Table 4.3: Parameters and terms derived from Rock Eval pyrolysis (modified from Peters, 1986, Tissot and Welte,1984 and Jarvie et al., 2007).

Parameter	Parameter description
TOC (wt.%)	Total Organic Carbon (Analyzed and measured)
S1 (mg HC/g rock)	Free volatile hydrocarbons thermally flushed from a rock sample at 300°C (free oil content)
S2 (mg HC/g rock)	Products that crack during standard Rock Eval pyrolysis temperatures (remaining potential)
S3 (mg CO2/g rock)	Organic carbon dioxide released from rock samples
Tmax (°C)	Temperature at peak evolution of S2 hydrocarbons
HI (mg HC/g TOC)	Hydrogen Index = S2 x 100/TOC
OI (mg CO2/g TOC)	Oxygen Index = S3 x 100/TOC
GP (mg HC/g rock)	Genetic Potential = S1+S2
S1/TOC	Normalized Oil Content = S1 x 100/TOC
S2/S3	Describes type of hydrocarbons generated
PI	Production Index or Transformation Ratio = S1/(S1+S2)

Table 4.4 Rock Eval-6 for Paleocene, Patala, Lockart and Hangu Formations.

Depth (ft)	Formation	Lithology	TOC wt.%	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	Tmax (°C)	GP (mgHC/g rock)	HI (mgHC/g TOC)	OI (mgCO2/g TOC)	PI (S1/(S1+S2))
4705			0.28	0.08	0.22	0.05	450	0.3	79	1	0.27
4850			0.29	0.16	0.24	0.13	449	0.4	83	4	0.4
4905			0.38	0.14	0.35	0.12	451	0.49	92	5	0.29
5005			0.35	0.13	0.25	0.21	452	0.38	71	7	0.34
5110			0.23	0.07	0.15	0.12	449	0.22	65	3	0.32
5205			0.18	0.05	0.21	0.19	447	0.26	117	3	0.19
5305			0.41	0.13	0.35	0.29	450	0.48	85	12	0.27
5405			0.27	0.06	0.15	0.06	451	0.21	56	2	0.29
5535			0.22	0.07	0.15	0.12	446	0.22	68	3	0.32
5605			0.16	0.1	0.27	0.21	445	0.37	169	3	0.27
5705			0.11	0.11	0.25	0.06	366	0.36	227	1	0.31
5805			0.19	0.11	0.31	0.07	413	0.42	163	1	0.26
5905	Patala	Shale	0.2	0.13	0.29	0.07	358	0.42	145	1	0.31
6150			0.24	0.13	0.29	0.07	451	0.42	121	2	0.31
6300			0.76	0.1	0.13	0.3	455	0.23	17	23	0.43
6405			0.81	0.31	0.49	0.06	458	0.8	60	5	0.39
6505			0.76	0.31	0.42	0.18	457	0.73	55	14	0.42
6705			0.18	0.05	0.16	0.19	459	0.21	89	3	0.24
6815			0.15	0.05	0.15	0.21	455	0.2	100	3	0.25
7010			0.31	0.08	0.17	0.11	456	0.25	55	3	0.32
7305			0.14	0.08	0.19	0.19	455	0.27	136	3	0.3
7405			0.13	0.07	0.18	0.18	360	0.25	138	2	0.28
7605			0.18	0.05	0.15	0.21	336	0.2	83	4	0.25
7745			0.17	0.09	0.21	0.11	458	0.3	124	2	0.3
7850			0.13	0.13	0.27	0.12	413	0.4	208	2	0.33
7950			0.18	0.2	0.24	0.33	456	0.44	133	6	0.45
8015			0.29	0.19	0.24	0.33	460	0.43	83	10	0.44
8035			0.47	0.24	1.1	0.13	458	1.34	234	6	0.18
8150			0.27	0.19	0.25	0.74	419	0.44	93	20	0.43
8205			0.51	0.16	0.7	0.44	455	0.86	137	22	0.19
8230			0.47	0.07	0	0.21	461	0.07	0	10	1
8250	Lockhart	Limestone	0.37	0.05	0	0.16	416	0.05	0	6	1
8265			0.47	0.1	0.44	0.26	458	0.54	94	12	0.19
8280			0.43	0.05	0	0.29	416	0.05	0	12	1
8350			0.05	0.07	0.05	0.04	460	0.12	100	0	0.58
8326			0.47	0.08	0.01	0.32	339	0.09	2	15	0.89
8370			0.12	0.08	0.04	0.19	337	0.12	33	2	0.67
8390			0.68	0.12	0.51	0.27	450	0.63	75	18	0.19
8400			0.2	0.08	0.12	0.12	459	0.2	60	2	0.4
8420			0.75	0.13	0.39	0.63	456	0.52	52	47	0.25
8440			0.95	0	0	0	458	0	0	0	0
8460			1.2	0.07	0.44	0.03	455	0.51	37	4	0.14
8468			0.82	0.19	0.57	0.11	469	0.76	70	9	0.25
8472			1.56	0.27	1.09	0.15	473	1.36	70	23	0.2
8477			0.62	0.17	0.39	0.14	473	0.56	63	9	0.3
8490			0.76	0.16	0.17	0.15	458	0.33	22	11	0.48
8500			0.65	0.23	0.42	0.13	468	0.65	65	8	0.35
8515	Hangu	Shale	1.65	0.06	0.32	0.24	468	0.38	19	40	0.16
8526			1.58	0.37	0.68	0.46	463	1.05	43	73	0.35
8540			0.76	0.29	0.08	0.11	467	0.37	11	8	0.78
8560			0.28	0.25	0.51	0.79	453	0.76	182	22	0.33
8584			4.49	0.9	4.06	0.08	465	4.96	90	36	0.18
8600			0.34	0.11	0.16	0.83	471	0.27	47	28	0.41
8620			1.86	0.02	0.43	0.05	470	0.45	23	9	0.04
8700			0.61	0.1	0.03	0.69	467	0.13	5	42	0.77
8750			0.08	0.12	0.08	1.43	410	0.2	100	11	0.6

4.3.1 Source Potential

The parameters derived from the results of Rock Eval pyrolysis are applied for the assessment of different source rock characteristics described as following:

i. **HI vs TOC**

HI is obtained from the formula (S_2 /TOC x 100). Those values are then plotted against the TOC values for analyzing the type of hydrocarbon expected from the source rock based on organic matter type like marine, terrestrial or mixed source which have different values/range of hydrogen index.
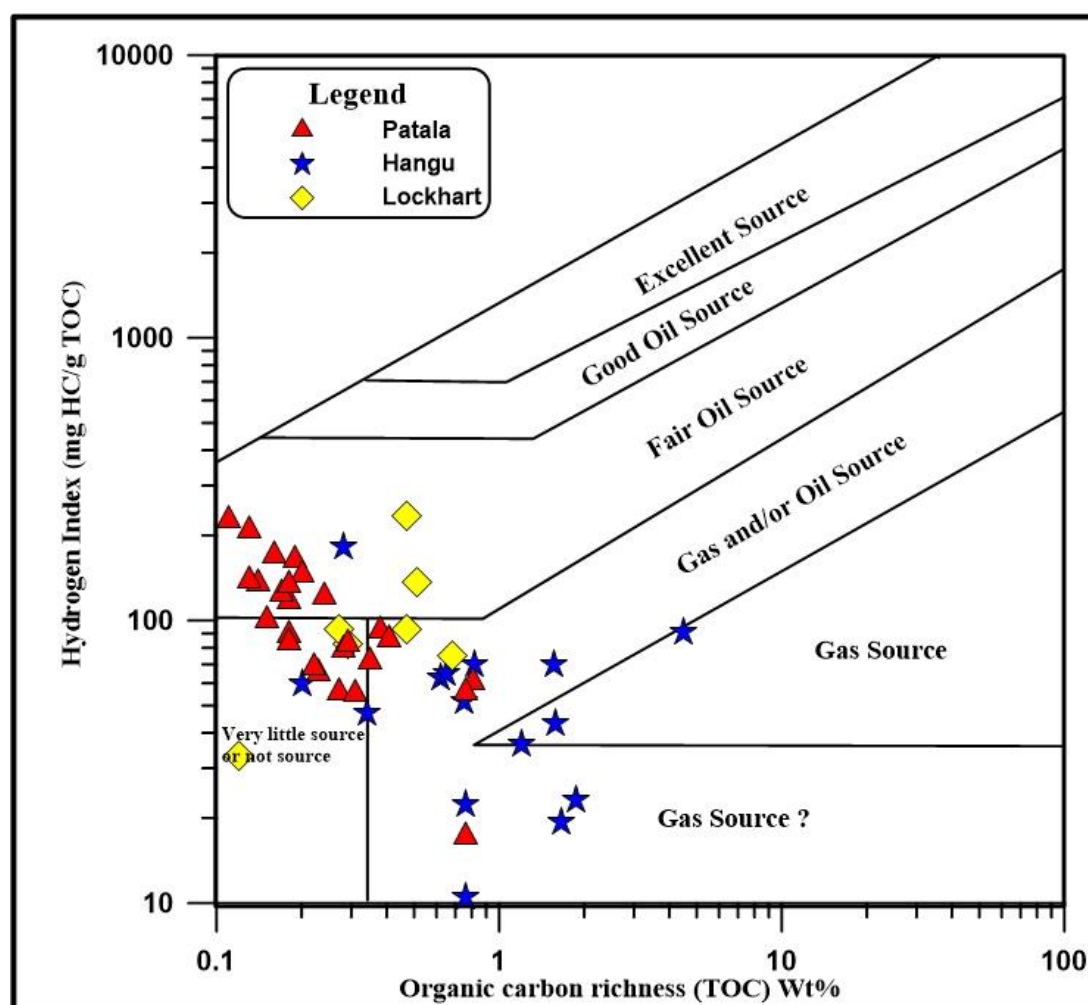

Figure 4.2 HI vs TOC plot for Hangu, Lockhart and Patala Formations.

Lockhart limestone and Patala Formation have potential to produce the both oil and gas source rock. Whereas Hangu Formation has potential for the gas generation (Fig. 4.2).

This parameter is calculated from the sum of values of S_1 and S_2 (Tissot and Welte, 1984).
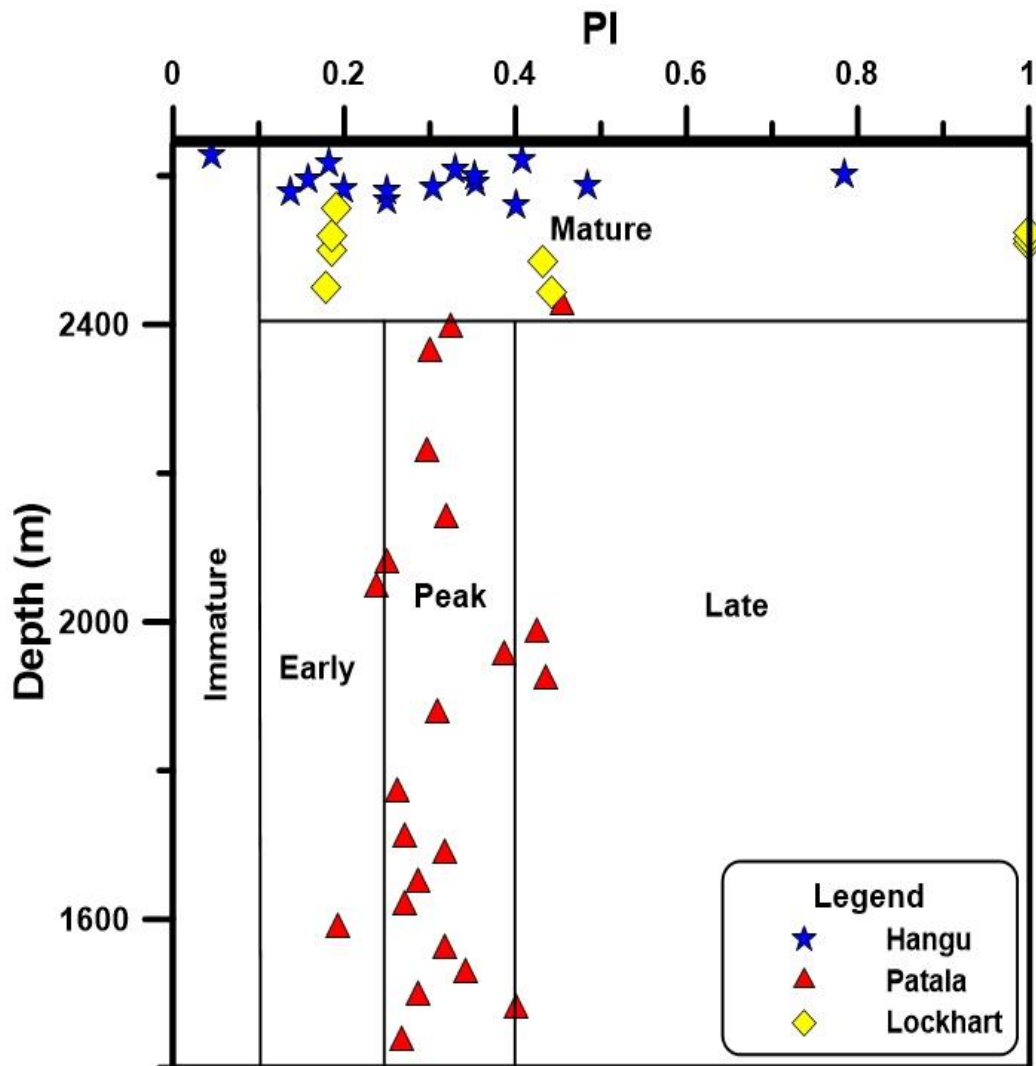

Figure 4.3. PI vs Depth plot for Hangu, Lockhart and Patala Formations.

Production Index Vs Depth plot shows the generation status of the source rock. According to this plot, the Patala Formation is in the peak stages of Hydrocarbon Generation. Most of samples from Patala Formation show peak stage of hydrocarbon generation. Whereas Lockhart Limestone and Hangu Formation are in the mature generation stage (Fig. 4.3).

4.3.2 Type of Kerogen

Different types of kerogen have potential to produce different types of hydrocarbons. Type-I kerogen which has marine organic matter input produces oil, Type-II kerogen produces both oil and gas (oil in major proportion), and Type-III kerogen only produces gas (Hunt 1996).

The different parameters obtained by rock-eval pyrolysis are used for the determination of type of kerogen of the samples by the help of several plots like HI vs OI, HI vs T_{max} and S_2 vs TOC.

   i.   HI vs OI

Type of kerogen can be predicted from the plot of hydrogen index vs oxygen index as per modified Van Krevelen diagram. These plots were first developed in the 1950 by the Van Krevelen which use the atomic ratios between Hydrogen, Carbon and Oxygen (used for the coal studies). These atomic ratios were later replaced by the HI and OI values by Tissot et al. (1979).
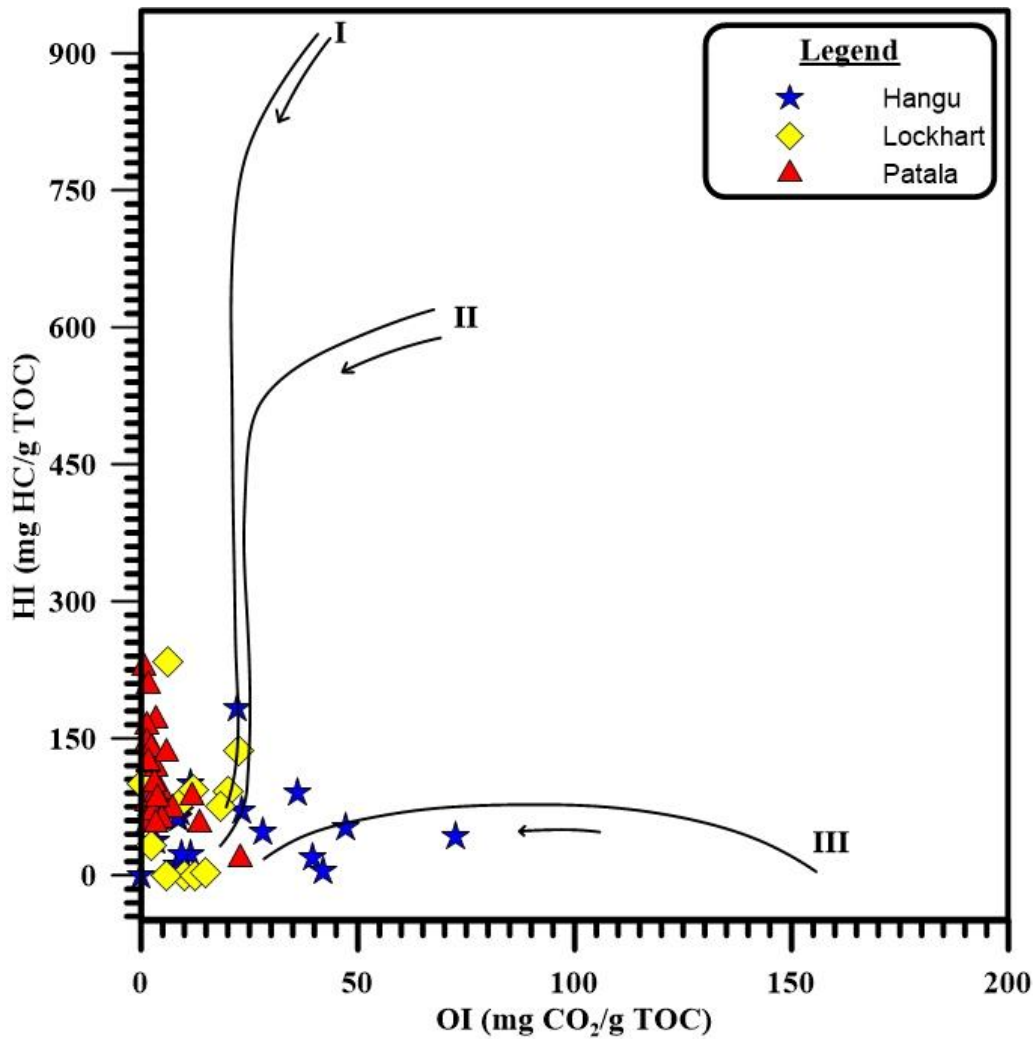
Figure 4.4. HI vs OI plot for Hangu, Lockhart and Patala Formations.

HI vs OI plot samples from Paleocene Formations is presented in (Fig.4.4). The plot shows the type of kerogen of all three Paleocene Age Formations. Hangu Formation having the value of HI less than 200 mostly falls in the category of Type-III. Lockhart Limestone and Patala Formation having the values of HI in the range of less than 100 to 250 falls in the category Type-III kerogen (Fig. 4.4).

ii. HI vs Tmax

Another plot which shows a correlation between Hydrogen Index and T_{max} is very useful in evolution of present kerogen type and stage of thermal maturity. T_{max} is thermal maturity parameter obtained from the Rock Eval pyrolysis.
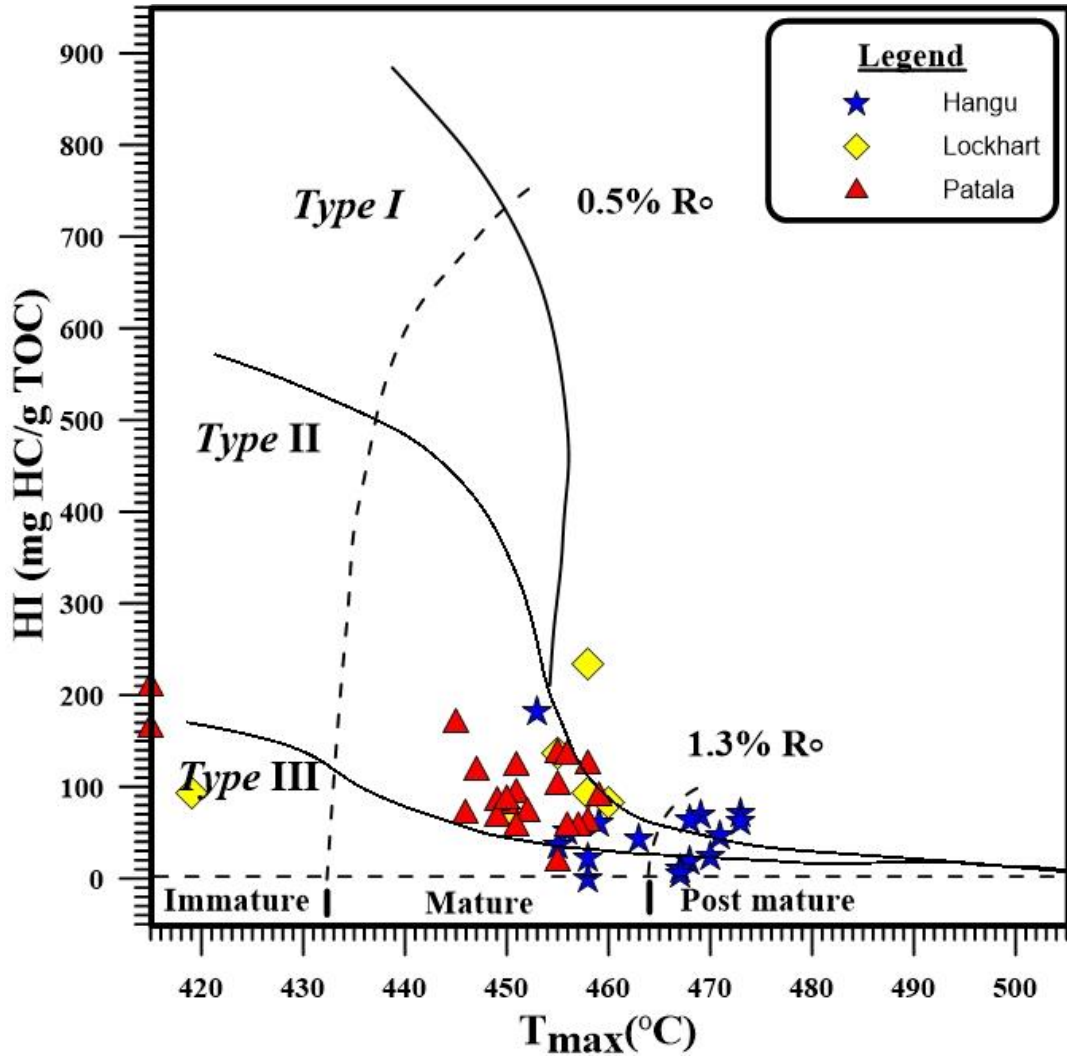

Figure 4.5. HI vs T_{max} plot for Hangu, Lockhart and Patala Formations.

HI vs T_{max} plot represents the type of kerogen for the Paleocene Formations. Hangu, Lockart and Patala Formation having the value of HI less than 200 mostly falls in the category of Type-III kerogen (Fig. 4.5).

iii. S₂ vs TOC

The remaining potential of hydrocarbons is represented by S_2 (mg HC/g rock) peak of program resulting from thermal cracking of kerogen during programed heating from 300-650 °C of rock eval analysis. S_2 is plotted against the TOC values for the determination the type of kerogen of the sample.
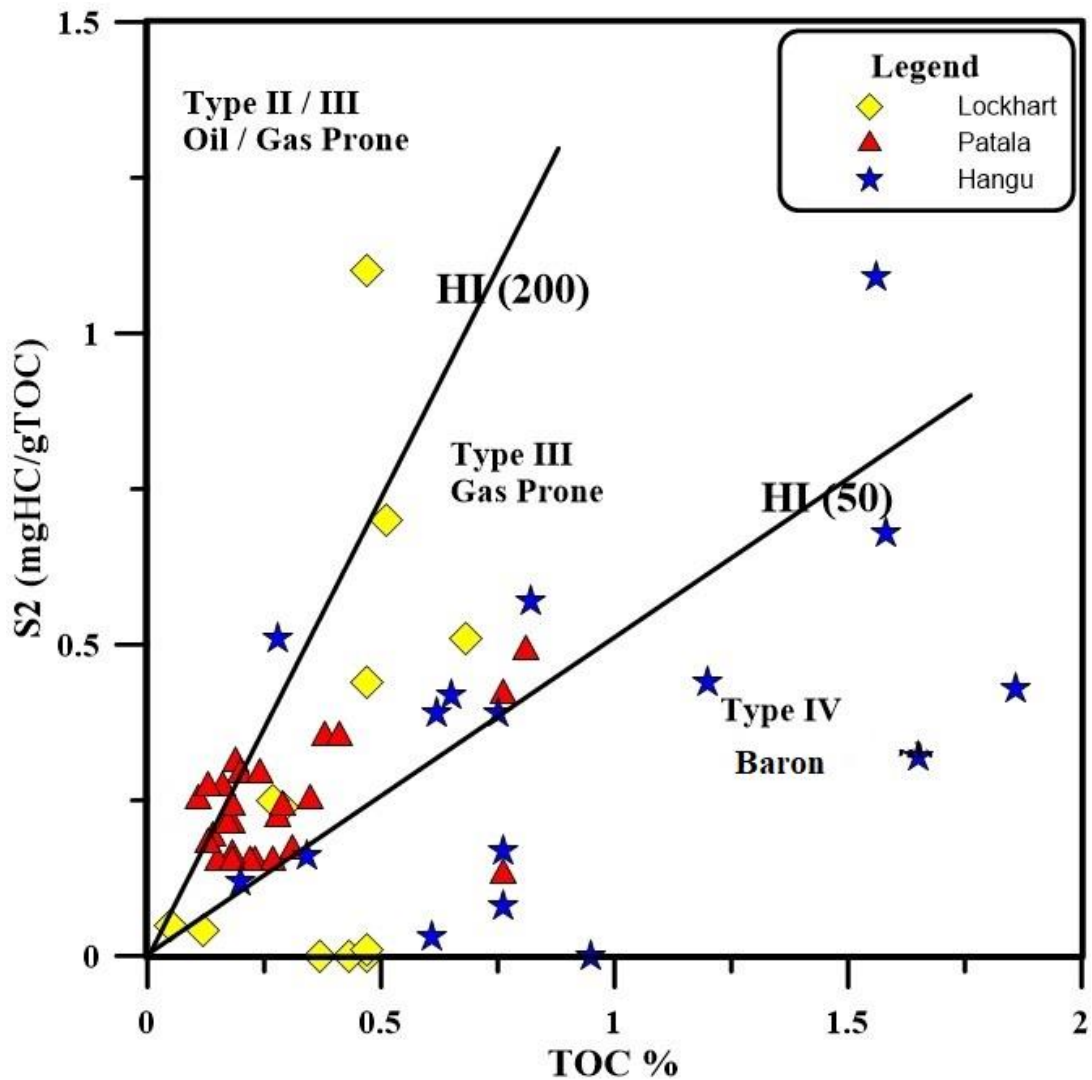

Figure 4.6. S2 vs TOC plot for Hangu, Lockhart and Patala Formations.

This plot is in sync with the HI vs OI plot which shows that Hangu Formation mostly falls in the Type III category which has potential to produce gas while those in Type-IV have not potential and considered baron. Lockhart Limestone mostly has Type III kerogen having potential for gas generation, some of the values lie in the zone of Type II/III kerogen which shows the potential of producing oil/gas and some of it can also be seen in the Type IV with no hydrocarbon potential. While Patala Formation falls

primarily in the category of Type-III with gas potential and some values lie in Type-II/III kerogen which has a potential to generate oil and gas (Fig. 4.6).

4.3.3 Thermal Maturity

Thermal Maturity of the samples were analyzed by different parameters obtained directly by the rock eval results. For evaluation of thermal maturity of source rock, parameters from rock eval pyrolysis are following.

i.   **T$_{max}$ vs Depth**

T$_{max}$ is the temperature at which the maximum amount of S$_2$ is produced and this temperature is used for understanding the thermal maturity of the rock, by plotting it against the depth of the sample shows the trend of thermal maturity with depth.

Figure 4.7. T$_{max}$ vs Depth for Hangu, Lockhart and Patala Formations.
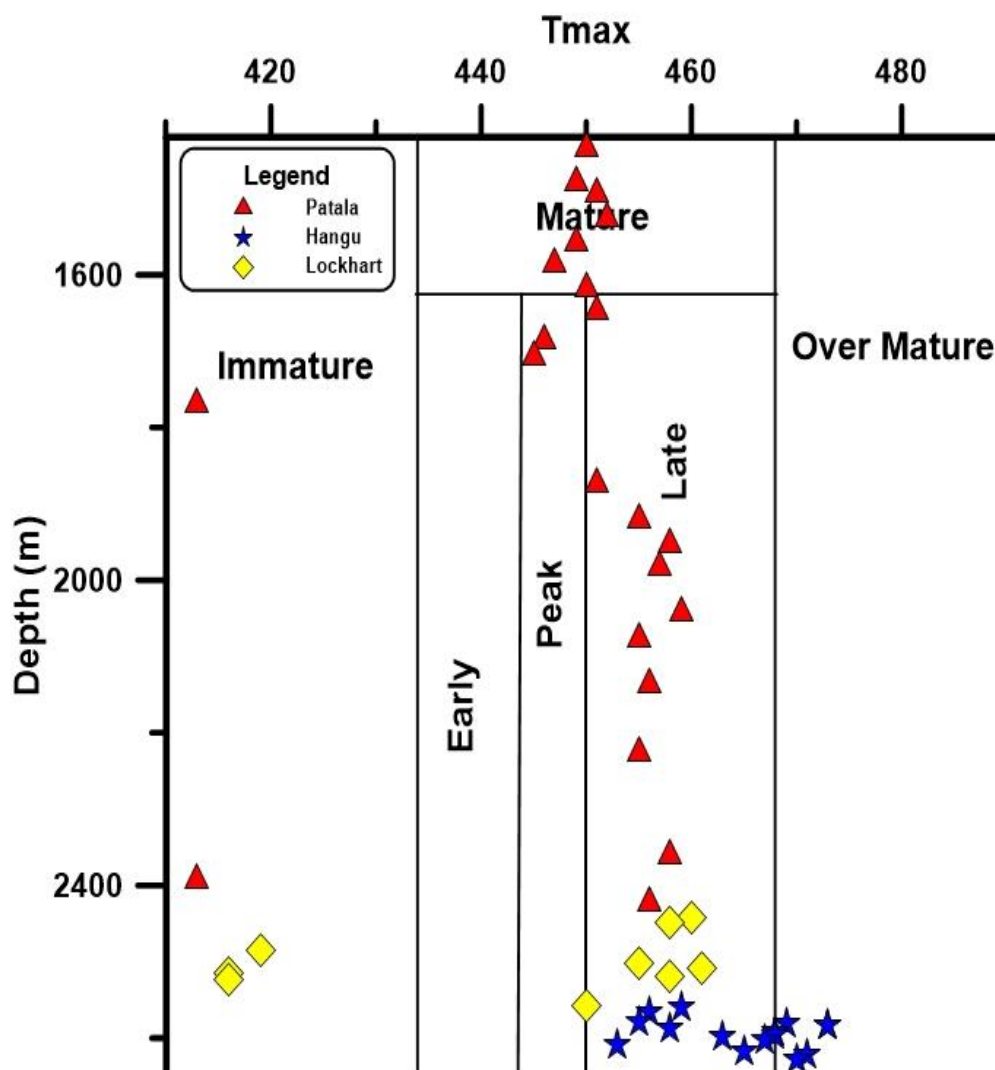
T_{max} values of all the samples from three Formations shows that it falls in oil window. Hangu Formation has highest thermal maturity than the other two. So Hangu Formation is in late oil window. Lockhart Limestone has the second highest values of thermal maturity and it is also in the late stage of oil window. Patala Formation has lower thermal maturity than the other two but it also falls in peak to late oil window (Fig. 4.7).

ii. PI vs T_{max}

S_1 are the free hydrocarbons so the value S_1 increases with increase in thermal maturity while that of S_2 shows decrease. So, with increase in thermal maturity of the rock value of PI increases with increase in S_1. PI is considered as thermal maturity indicator and shows variation in its value with changes in depth and subsequent thermal maturity stage (Pitman et al., 1987). Maturity and PI relationship is given in the Table 4.5 below:

Table 4.5 Relationship between Maturation and Production Index (Pitman et al., 1987).

Maturation	Production Index
Immature	< 0.10
Oil Generation	0.10-0.30
Gas Generation(Oil Cracking)	> 0.30

Both thermal maturity parameters T_{max} and PI are correlated to obtain the clear picture of thermal maturity stage of the sample and source rock drainage condition as well.
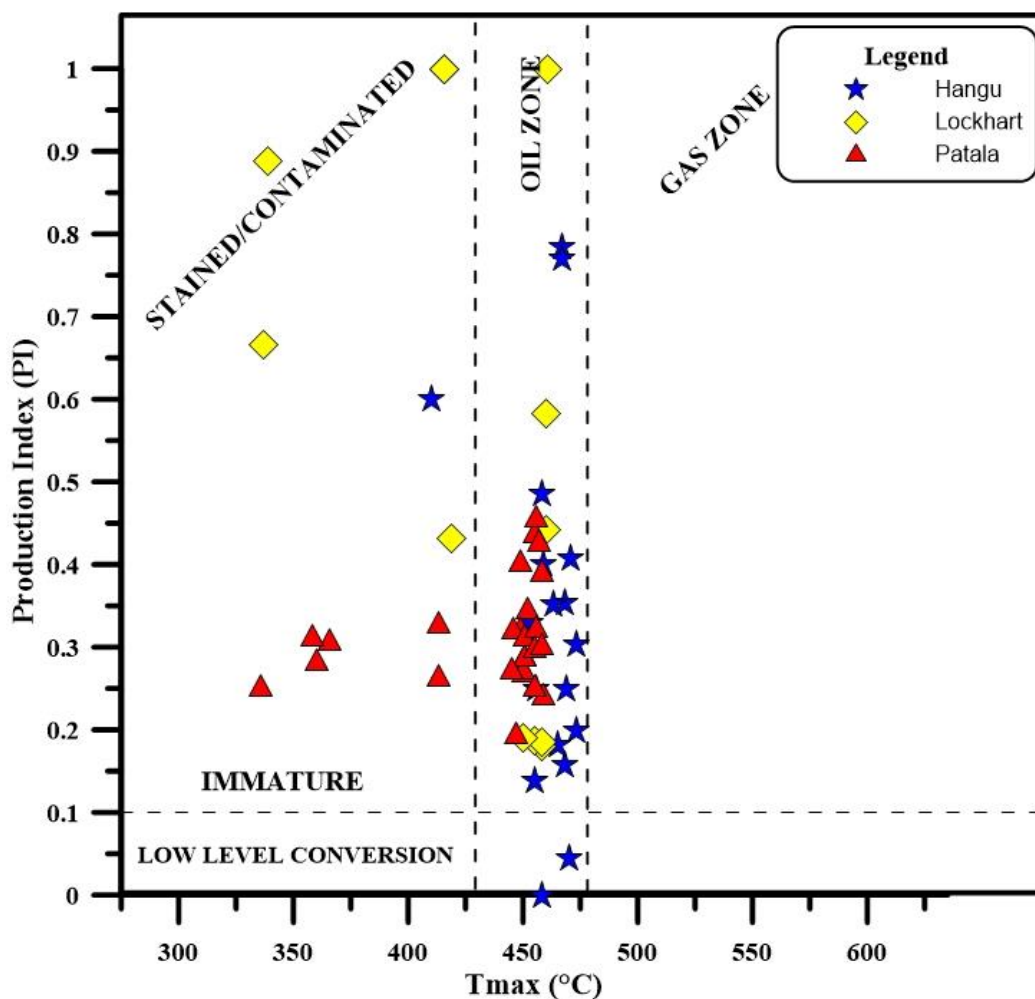
Figure 4.8. PI vs T$_{max}$ Plot for all three Formations.

PI vs T$_{max}$ values of all the three Paleocene Formations shows that they fall in oil window whereas some values falls in immature region and show oil staining/contamination (Fig. 4.8).

4.3.4 Genetic Potential (GP)

Genetic Potential (Demaison and Huizinga, 1991) is defined as the quantity of hydrocarbons that can be generated in a column of source rock under one square meter of surface area. According to Tissot et al., (1980) Genetic potential is a simple method for ranking source rock productivity. GP values determined from thermally mature or post mature sections can be low because of petroleum expulsion.

GP calculations in source rock based on S$_1$ and S$_2$ values. Based on the GP values, rocks are considered as poor, fair or good. GP values of less than 2 are poor, whereas values of 2-6 and greater than 6 are considered as fair and good respectively (Tissot and Welte, 1978).
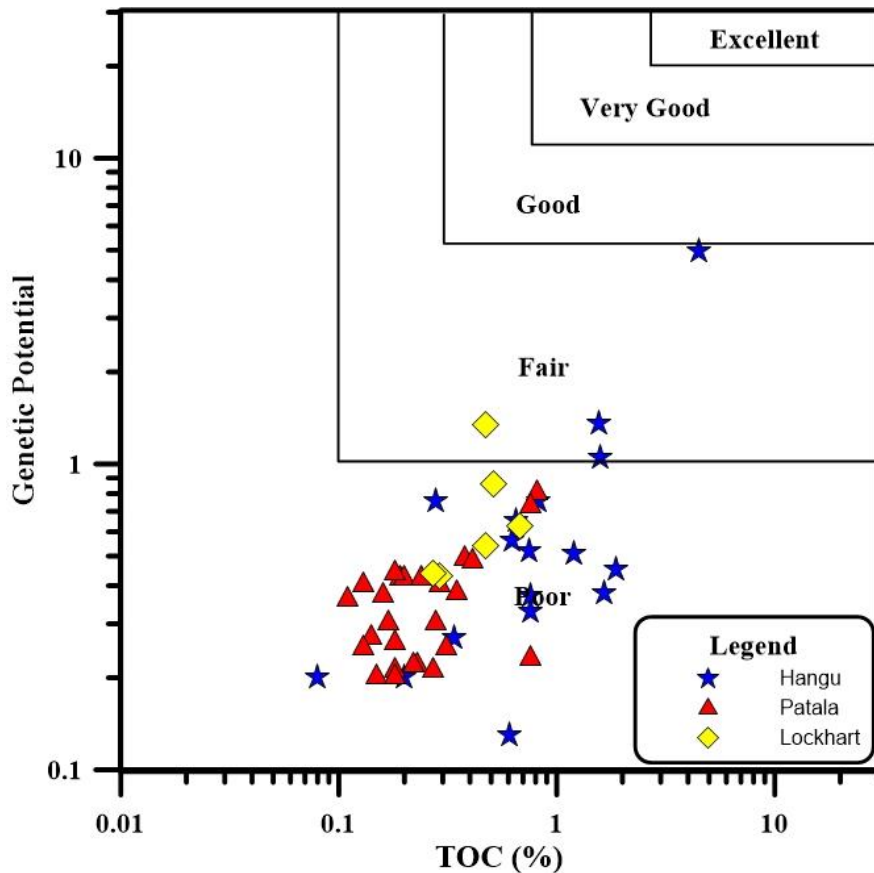
Figure 4.9. GP vs TOC plot for Hangu, Lockhart and Patala Formations.

The genetic potential of Hangu, Lockhart and Patala Formation well cuttings of Tolanj-01 is generally poor with exception of some samples of Hangu and Lockhart are fair genetic potential (Fig. 4.9).

4.4   Organic petrography

Vitrinite is that type of kerogen which has its origin from the terrestrial organic matter. This technique uses the amount of incident light which got reflected back from the polished surface of the sample. The quantity of light that got reflected is measured in the form of percentage and expressed as $\%R_o$. R_o represent the amount of reflectance obtained from samples that are immersed in oil. Immersion in oil improves the reflectance (Golin and Smyth, 1986).

This method is used to measure the thermal maturity of the given sample. Geothermal history of the sedimentary basin also affects the geochemical changes occurring in the vitrinite macerals which have positive correlation with the reflectance value (Smyth, 1988). Vitrinite reflectance shows the transformation stage of the organic

matter and gave the idea about the type of hydrocarbon formed by that sample as presented below in the (Fig. 4.10).

During the stage of catagenesis at the onset of the oil generation which is also known as oil window is represented by the 0.6 to 1.3% R_o. As the temperature increases the increase in thermal cracking forms the condensates (wet gas) which has the Ro value of 1.3 to 2%. R_o value of 2 to 3% shows the dry gas phase while the values greater than 3% shows that source rock is spent and has already produced all the hydrocarbons and does not possess enough hydrogen to produce further hydrocarbons (Smyth and Mastalerz, 1991).
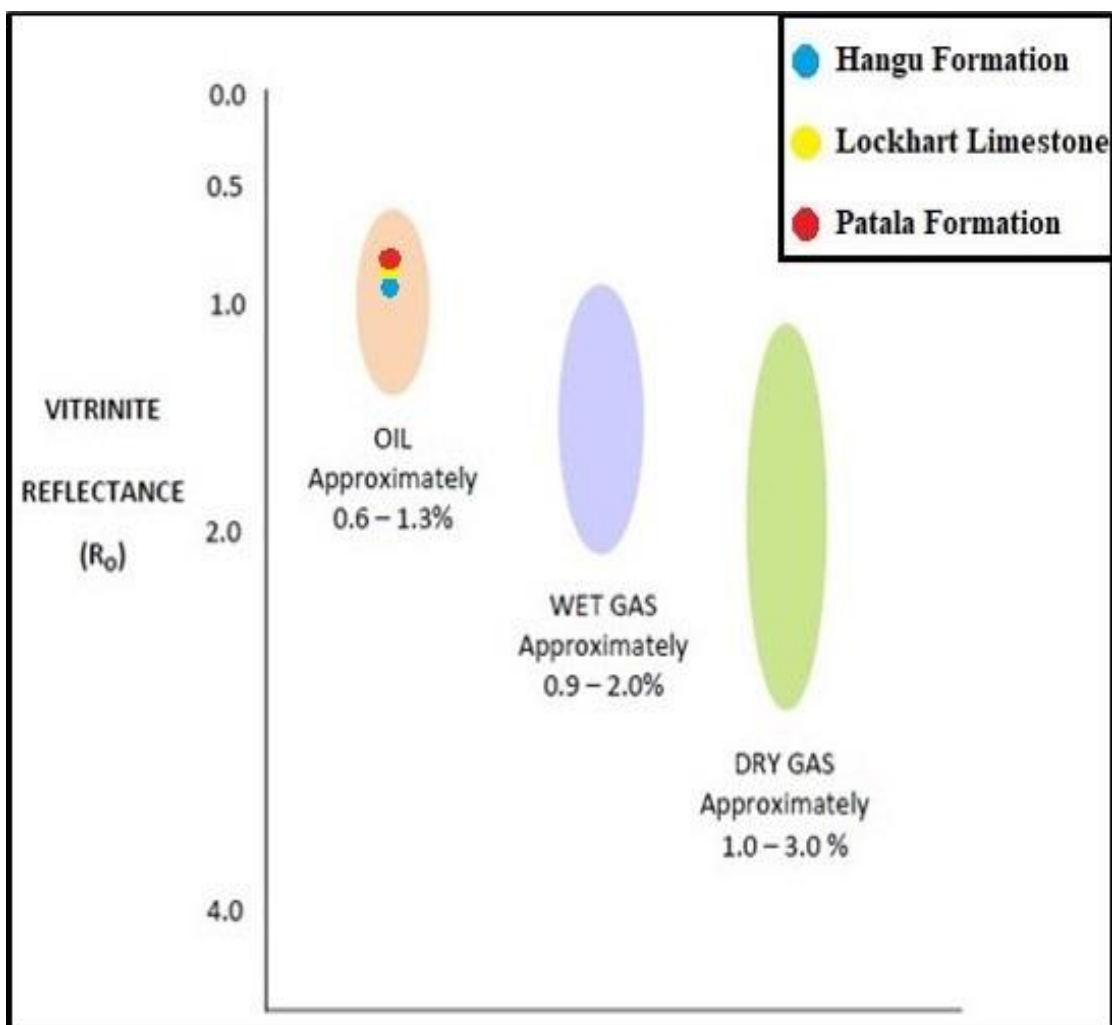

Figure 4.10. Vitrinite Reflectance values showing transformation into Hydrocarbon Types with increasing Thermal Maturity (Dow, 1977).

The prepared pellets were studied under white and blue light using Z1M Zeiss microscope. The vitrinite reflectance standards of 0.589 % 0.907 % and 1.711 % were used for calibration of microscope. The average of random vitrinite reflectance measurements of studied samples ranged from 0.82-0.95 % and the results are given in (Table 4.6).

Table 4.6 Vitrinite Reflectance Values of Well Cuttings from Tolanj-01.

Formation	R_o (%)
Hangu Formation	0.95
Lockhart Formation	0.89
Patala Formation	0.82

Hangu Formation has vitrinite reflectance value of 0.95 (Table 4.10) which falls in the category of Mature oil window. Lockhart Limestone has comparatively less value of vitrinite reflectance than Hangu Formation. Results of vitrinite reflectance for Lockhart also represents that it is in oil window. Patala Formation value also shows that it is in oil window thermal maturity but the values of vitrinite reflectance is least due to shallower depth of the Formation compared to rest of two Formations. The results of vitrinite reflectance for all three Formations are consistent with the results of T_{max} values which also shows that all three Formations has potential to generate oil.
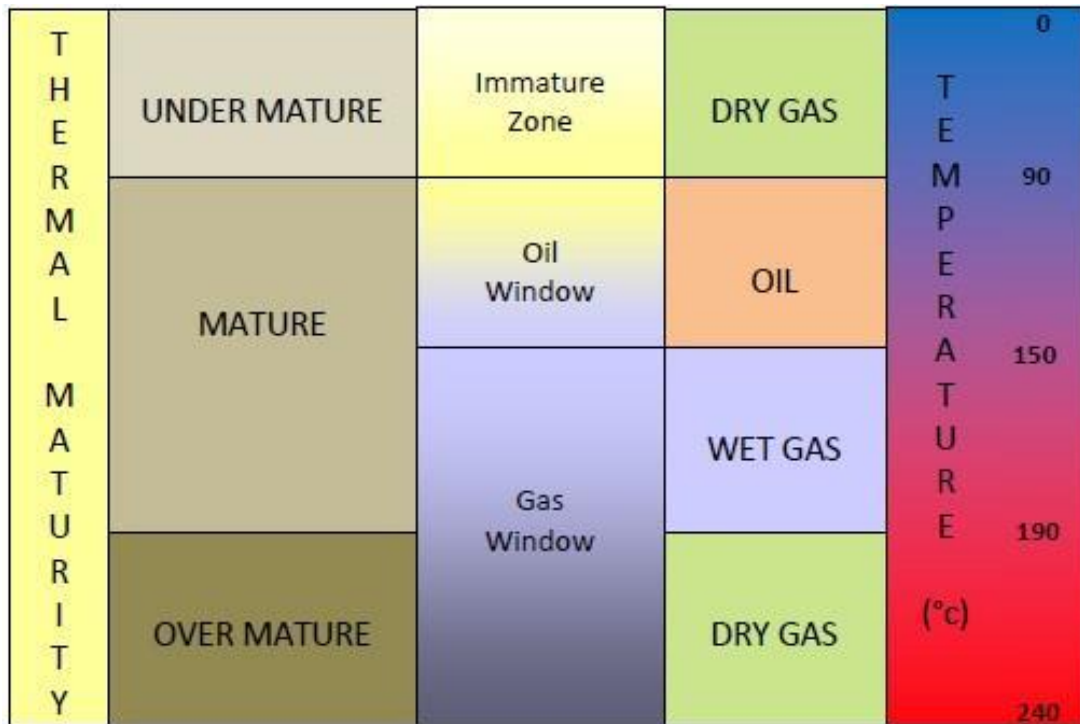
Figure 4.11. Thermal Maturity based on subsurface Temp and Hydrocarbon Types (BGS 2014).

The vitrinite reflectance values of organic matter shows oil window zone of organic matter of Hangu Formation, Lockhart Limestone and Patala Formation's well cuttings from Tolanj-01 well. This phase of thermal maturity corresponds to subsurface temperature in the range of 90-150 ˚C and oil window.

4.5   Biomarker Analysis

Biomarkers are that compounds which can be found in different materials like oil, rock units, soil extracts and recent sediments etc. and can be related to organic molecules present in the living organisms of that time periods. When these organisms die, some of molecular constituents get preserved in their original form without any major changes. All of these biomarkers terpanes, steranes, iso-alkanes and n-alkanes are dominant during oil window phase of of catagenesis. Methane shows dominance in the stage of metagenesis. Concentrations of these biomarkers are very minute in condensate/wet gas, but their presence are very useful for geoscientists for understanding the depositional environment, description and creating a correlation (Tissot & Welte 1984, Peters & Moldowan 1993).

Biomarkers also known as biological markers are actually the molecular fossils that have complex structure and are derived from organic matter that is produced by

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living organisms and get preserved with time. This stable structure of these compounds made them very useful for indicating organic matter's source, degree to which biodegradation occurs, lithology of the source rock, environment of deposition that were present at the time of diagenesis and the effect of change in thermal maturity during catagenesis. These compounds also have great application for evaluating the age of the rock units and oils. The most important of their application is in correlation of oil with source or oil with oil (Peters et al., 2005).

Biomarkers study are the study of saturated hydrocarbon fraction and aromatic hydrocarbons of the rock extracts. Three samples from Tolanj-01 well were analyzed by GC-MS, each from Hangu, Lockhart and Patala Formations. Different classes of hydrocarbon and chromatograms used for interpretation is given in (Table 4.7).

Table 4.7 Hydrocarbon classes and Biomarkers used for sample analysis.

Biomarker	Fragmentogram/ Mass/charge ion chromatograms (m/z)
n-alkanes	57
Pristane and Phytane	183
Aromatic Hydrocarbons	178 184, 192,
Tricyclic Terpanes	191
Hopanes	191
Homohopanes	191
Regular Steranes	217, 218

4.5.1   n-Alkanes

Saturated hydrocarbon fractions of rock extracts were studied using Gas chromatography to study composition of alkanes. Different parameters like thermal maturity, source input, biodegradation and oil to source correlation could be made from the relative abundance of alkanes and iso-alkanes (Waples, 1985; Peters et al., 2005).
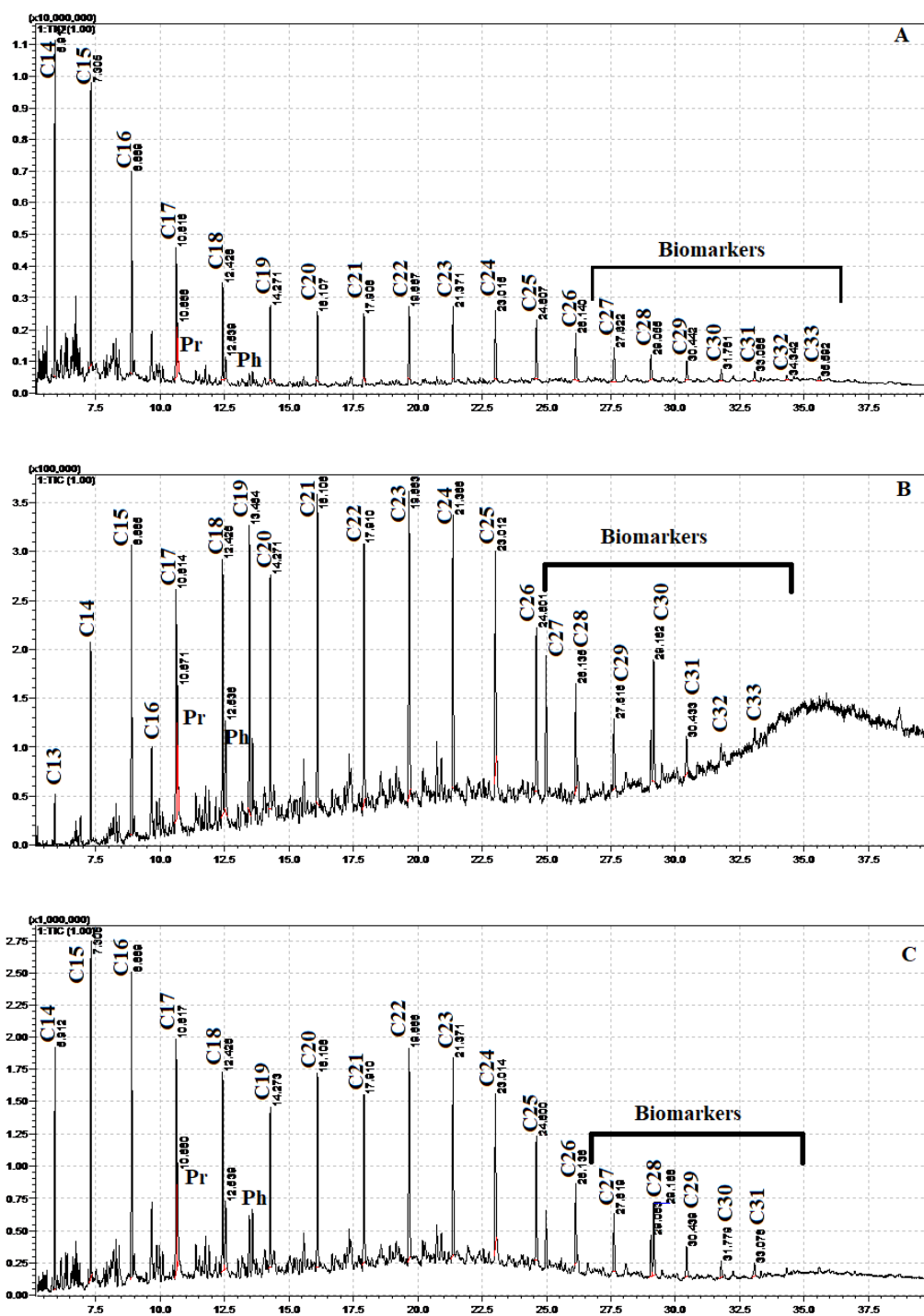

Figure 4.12 Chromatograms of saturate fractions of (A) Patala Formation (B) Lockhart Limestone (C) Hangu Formation.

i. Biodegradation

The Chromatograms of all three Paleocene Formations are given in (Fig 4.14). There is no visible sign of biodegradation in any of the three Paleocene Formation's rock extracts due to unavailability of unresolved complex mixture (UCM) in total ion chromatograms (Fig 4.14).

There is no visible shift in baseline of all Paleocene Formation's extracts so this can be said that there is very less or no biodegradation in all of the sample's organic matter (Fig 4.14).

Biodegradation generally effects the lighter content of the n-alkanes. Removal of the lighter contents will show the effect of biodegradation.

ii. Source Input

The n-alkanes distribution of source rock extracts of Hangu Formation and Lockhart Limestone shows even to odd predominance in alkanes of carbon number less than 22. Marine sediments have been considered as a source of even to odd predominance in the range of nC_{16} to nC_{24} (Nishimura and Baker, 1986). Even number predominance in n-alkanes distribution shows presence of special type of autochthonous bacteria present in lacustrine sediment (Wang et al., 2010). Organic matter origin was considered marine bacteria for such type of distribution. Such type of condition develops during low thermal maturity of the source and this phenomenon disappears with increasing thermal maturity.

Table 4.8 The parameters derived from n-alkanes of Source Rock Extracts.

Parameter	Patala	Lockhart	Hangu
TAR	0.10	0.26	0.12
CPI1	1.04	0.91	0.95
OEP1	1	0.92	0.95

Terrigenous aquatic ratio (TAR) :$(nC_{27}+nC_{29}+nC_{31})/ (nC_{15}+nC_{17}+nC_{19})$;, Carbon preference Index (CPI$_1$)**:**$2(C_{23}+C_{25}+C_{27}+C_{29})/C_{22}+2(C_{24}+C_{26}+C_{28})+C_{30}$, Odd to Even Predominance (OEP$_1$) :$(C_{21}+6C_{23}+C_{25}) /(4C_{22}+4C_{24.}$

The lower amount of longer chain alkanes and higher number of short chain alkanes in extracts of Hangu and Lockhart Limestone and Patala Formation point towards marine input. Short chain alkanes are produced by the benthic algae, zooplankton and phytoplankton which are major contributor to the origin of marine organic material (Tissot and Welte, 1978; Jones and Philp, 1990, Peters et al. 2005).

Terrestrial organic matter generally produces higher chain alkanes with odd number preference in the range of nC_{25} to nC_{33} which are quite low here in each of the rock extracts. Marine organisms generally gave rise to shorter olefins and shorter paraffins.

iii. Thermal Maturity

OEP can also be used to predict thermal maturity parameter, so with increase in thermal maturity this effect will disappear (Peters et al., 2005). So presence of this kind of distribution in Hangu Formation and Lockhart Limestone are in thermally mature zone as values is approximately 1. While in the case of Patala Formation there is more of unimodal distribution, no odd-even predominance were observed. CPI can also be used as thermal maturity indicator. With decrease in thermal maturity of the sample value of CPI increases. Thermal maturity effect the value of CPI as higher number of long chain alkanes will undergo thermal cracking and produce lower carbon number alkanes. For immature samples CPI value is around 10 but with increase in thermal maturity CPI decreases to lesser values. CPI values for Patala Formation (1.04), Lockhart Limestone (0.91) and Hangu Formation (0.95) represents the higher thermal maturity for all the samples of rock extracts (Fig. 4.12).

iv. Lithology of source rock

The n-alkanes that show dominance of even carbon numbers between nC_{22} to nC_{32} and have value of CPI 1 or less than 1 suggests calcareous source rocks and marine organic matter. While in case of shale CPI will be greater than 1. In case of Patala extracts CPI is 1.04 which suggests shale lithology (Table. 4.8).

4.5.2 Isoprenoids

From saturated fractions of the rock extracts and crude oil pristane and phytanes are the major two isoprenoids which are identified as being quite visible in each of the samples of the rock extracts. Isoprenoids present in sediments generally have C_{20} phytol chain as their precursor. This is actually an alcohol of Chlorophyll-A which has been bonded covalently with porphyrinic chromophores. In organic matter this isoprenoid alcohol can undergo transformation in several ways dependent upon the availability of oxygen (Tissot and Welte, 1978). When there is abundance of oxygen phytol undergoes conversion in to the pristane in case of oxidizing environment while in reducing environments the phytol will convert in to phytane. Hence, pristane/phytane ratio is an indicator for the assessment of redox potential of depositional environment (Didyk et al., 1978).

Isoprenoids or iso-alkanes are the biomarkers which are studied for evaluating the organic facies and maturity of source rock (Peters and Moldowan, 1993). Environment of deposition can be predicted by calculating the ratio of pristane to phytane (Waples, 1985). Different ratios of isoprenoids along with n-alkanes are used for the prediction of thermal maturity of the source, biodegradation extent and for correlating oil with source (Peters et al., 2005).

i. Environment of Deposition

Pr/Ph value of Paleocene strata is 1.8 for Patala, 1.23 for Lockhart, 1.33 for Hangu (Table 4.9). The values of all the three Paleocene Formations are greater than 1 and less than 3 which indicates sub-oxic environment of deposition. This ratio is a good indicator of paleo-environments but it should be used with great caution because thermal maturation change can have effect on the ratio (Tissot and Welte, 1984) and also difference in probable precursors and paleo-environments (Volkmann and Maxwell, 1980).

Table 4.9 The parameters derived Isoprenoids of Source Rock Extracts.

Parameter	Patala	Lockhart	Hangu
Pr/Ph	1.8	1.23	1.33
Pr/n-C_{17}	0.44	0.64	0.50
Ph/n-C_{18}	0.30	0.54	0.42

Pr: Pristane; Ph: Phytane; n-C_{17}: C_{17} normal alkane and n-C_{18}: C_{18} normal alkane.

Biodegradation

When biodegradation occurs then the microbes will selectively consume the n-alkanes leaving the isoprenoids behind so the ratio of isoprenoid/n-alkanes will decrease significantly with the increase in biodegradation (Waples, 1985). There is no or very little effect of biodegradation in source rock samples (Fig 4.13).
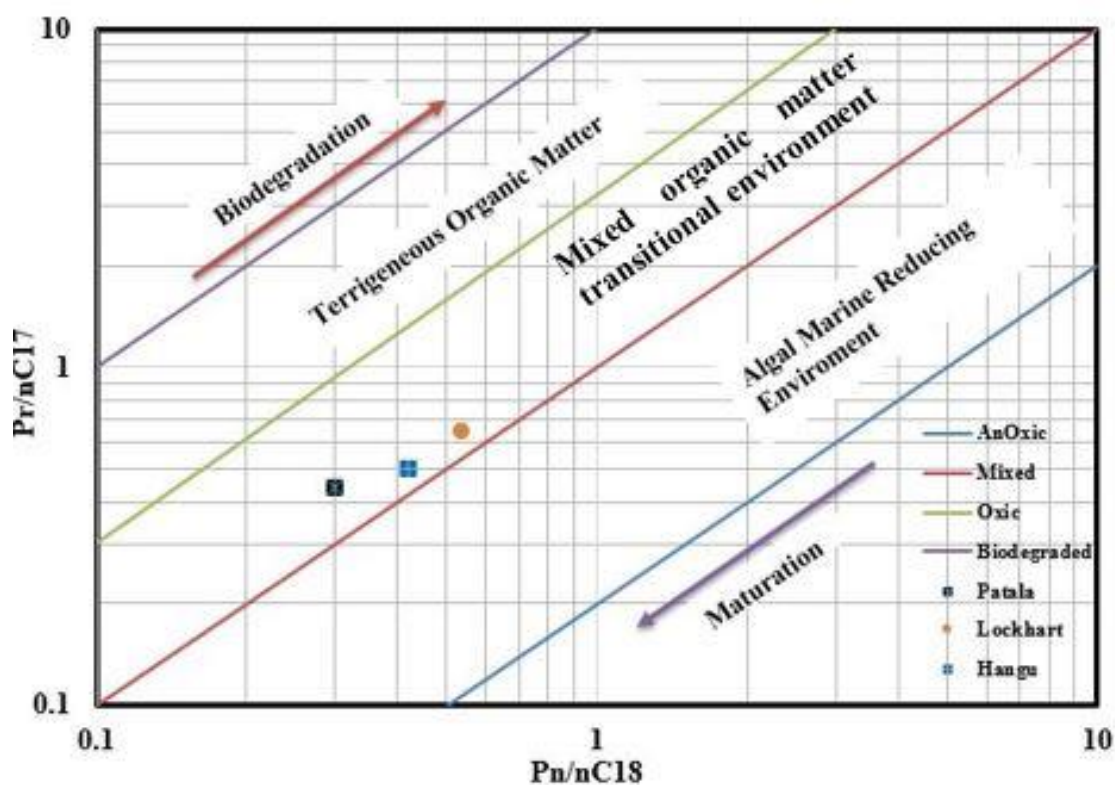

Figure 4.13 Plot of Pr/n-C_{17} versus Ph/n-C_{18} ratios Hangu Formation, Lockhart Limestone and Patala Formation Source Rock Extracts.

iii. **Source Input**

The Plot of Pr/n-C_{17} versus Ph/n-C_{18} ratios Hangu, Lockhart and Patala source rock extracts. The source rock extracts of Hangu, Lockhart and Patala falls in the category of mixed organic matter source deposited in transitional depositional settings (Fig 4.13).

iv. Thermal Maturity

The Plot of Pr/n-C$_{17}$ versus Ph/n-C$_{18}$ also give an idea about the transformation of organic matter caused by the change in thermal maturity. As far as thermal maturity is concerned, thermal cracking will give rise to n-alkanes so amount of n-alkanes will increase and isoprenoids will have no effect with increase in thermal maturity and the ratio of isoprenoids to n-alkanes will decrease (Waples, 1985) (Fig 4.13)

4.5.3 Aromatic Hydrocarbons

Aromatic Hydrocarbons are those hydrocarbons that have at least one benzene ring in their structure. These compounds have very large number of applications in source rock studies. One of the main application is understanding the thermal maturity of the rock extracts and oil. But other uses include understanding the lithology of source for crude oil, environment of deposition and source input by correlation of various parameters. These aromatic hydrocarbons can be effective in correlation of oil with source rocks (Bastow et al., 1998).

Several index and ratios can be used to calculate the thermal maturity stage of the rock and oil with the help of biomarkers and aromatic hydrocarbons. methylphenanthrene Index is the parameter used for thermal maturity prediction based on Phenanthrene and four isomer of methylpehenanthrene (Radke and Welte, 1983).

MPI-1 is calculated based on the assumption that if substituent methyl group is attached at α-position in the structure i.e. 9-MP and 1-MP, then these isomers have low thermodynamic stability and will decrease in abundance with increasing maturity compare to the isomers with methyl group at β-position, 2-MP and 3-MP. The latter pair of isomers are more stable so they are show increased relative abundance with increase in thermal maturity.

Presence of higher quantity of more stable isotopes i.e. 2-MP and 3-MP in case of all the three Patala, Lockhart and Hangu extracts shows relatively higher thermal maturity.
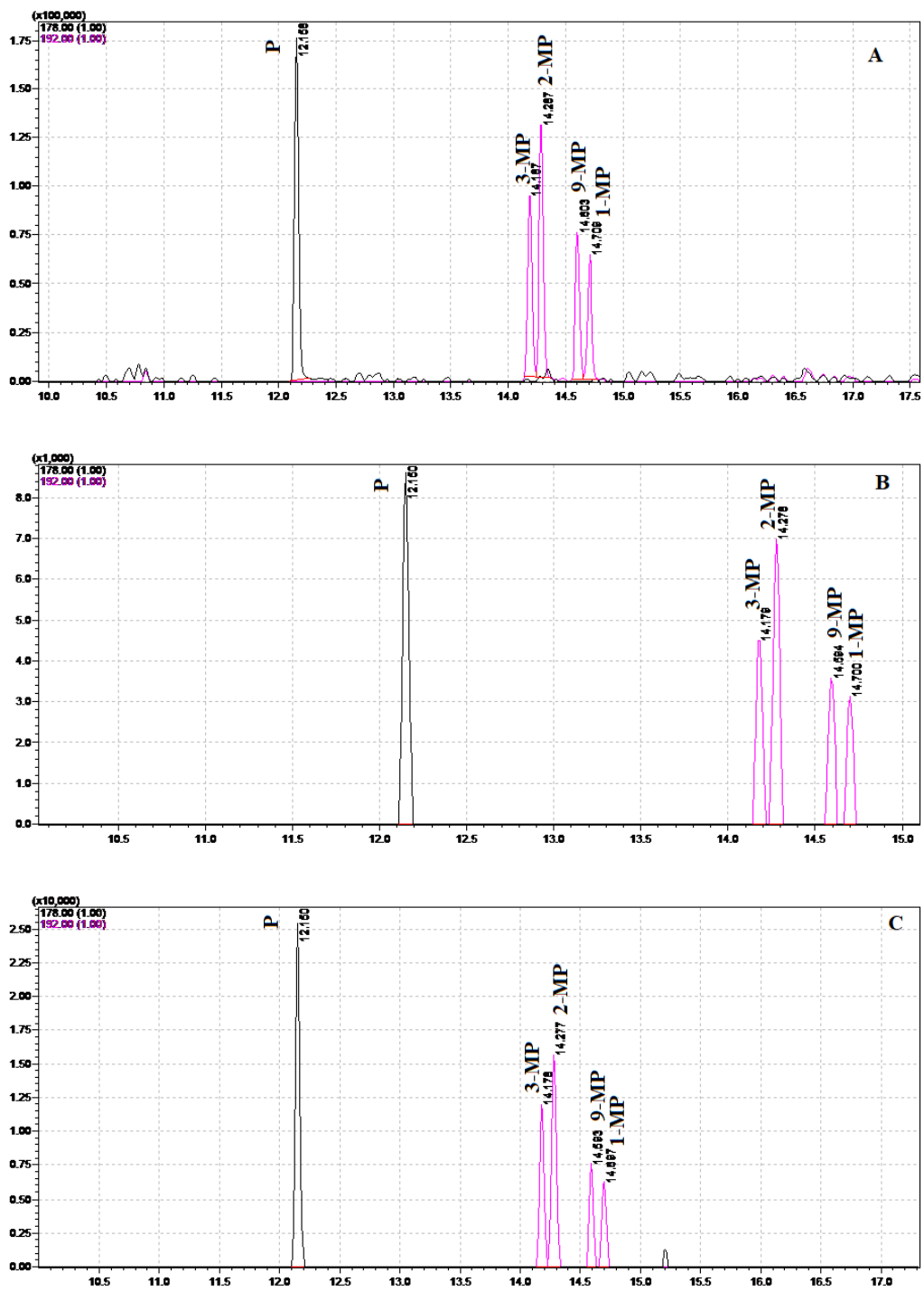
Figure 4.14. Combined Mass Chromatograms of m/z 178+192 showing phenanthrene (P), methylphenanthrene (MP) in Aromatic fractions of (A) Patala Formation (B) Lockhart Limestone (C) Hangu Formation.

Other parameters like MPI-3 and MPR-1 is also calculated and given in the Table 4.10.

Table 4.10 Geochemical Parameters derived from aromatic hydrocarbons.

Parameters	Patala	Lockhart	Hangu
MPI-1	1.083	1.195	1.143
MPI-3	0.941	1.10	1.263
Rc%	1.049	1.117	1.085
MPR-1	2.02	2.35	2.66

Methylphenanthrene Index (MPI-1): 1.5*(3MP+2MP)/(P+1MP+9MP), Methylphenanthrene index (MPI-3): (3+2MP)/(1MP+9MP), Rc%: 0.6*MPI-1+0.4, MPR-1: 2-MP/1-MP.

Table 4.11. Classification of Thermal Maturity based on MPI-3 and MPR-1 (Stojanovic et.al., 2007).

Maturity Phase	MPI-3	MPR-1
Low	<0.8	<0.95
Medium	0.8-1.0	0.95-1.2
Medium to High	1.0-1.3	1.2-1.5
High	>1.3	>1.5

MPI-3 values for Hangu and Lockhart extracts shows the medium to high maturity of studied samples. While Patala extract shows medium thermal maturity. In case of MPR-1 Patala, Lockhart Limestone and Hangu extract shows high thermal maturity (Table. 4.10).

4.5.4 Terpanes and Hopanes

Different ratios of tricyclic terpanes, tetracyclic terpanes. Hopanes, moretanes, gammacerane, Oleanane and homohopanes can be used to interpret the environment of deposition, source input, lithology of source for oil, thermal maturity, age of organic matter and oil-oil and oil-source correlation Table 4.12.

Table 4.12. Biomarker parameters derived from Terpanes through SIM-GCMS analysis.

Parameters	Patala	Lockhart	Hangu
$C_{19}/C_{19}+C_{23}$Triterpanes	C_{23}Present C_{19} is very low	C_{23}Present C_{19} is very low	C_{23}Present C_{19} is very low
C_{29}/H_{30} Triterpanes	0.8	0.68	0.86
Gammacerane/H_{30}	0.09	0.05	0.09
M_{30}/H_{30}	0.25	nil	0.04
Ts/Ts+Tm	0.50	0.49	0.50
$H_{32}S/H_{32}S+H_{32}R$	0.58	0.50	0.60
$C_{19}TCT/C_{19}TCT+ C_{23}TCT$	0.14	0.14	0.08
$C_{24}TeCT/C_{24}TeCT+C_{23}TCT$	0.4	0.33	0.3
$C_{22}TCT/C_{21}TCT$	0.5	0.3	0.2
$C_{24}TCT/C_{23}TCT$	0.5	0.6	0.5
S/ S + R HH_{32}	0.58	0.5	0.6

i.   Environment of Deposition

The rocks that are deposited in oxic depositional environment having Type-III kerogen have relatively lower C_{35} compared to C_{34} hopanes. Homohopanes indices for such rocks will be lower as well. Lower values of C_{35} homohopanes will directly correlate with the value of hydrogen index for that particular extract or oil (Rangel et al., 2000).

Relative abundance of C_{35} homohopane compared to C_{34} homohopane will be higher in case of anoxic environment of deposition (Peters et al., 2005). But here as far as rock extracts of Hangu, Lockhart and Patala are concerned C_{35} Homohopanes are missing that indicates environment of deposition was oxic (Fig. 4.15).

Gammacerane is a biomarker which is produced by the protozoan living in fresh water and this is formed by tetrahymanol which is precursor and converts during diagenesis. This biomarker was identified in rock extracts samples of Paleocene through the Selective Ion Monitoring method using the fragmentogram of m/z 191 in GC-MS. Gammacerane actually represent the water stratification during the process of sedimentation. This stratification can occur in both non-marine and marine conditions. Presence of this biomarker represents the hypersaline conditions which occurs usually in lagoonal environments of carbonate evaporites (Moldowan et al., 1985; Sinninghe Damste et al., 1995).

Values of Gammacerane in studied rock extracts is very low. Gammacerane index shows the values in the range of 5 to 10 percent. These low values for Gammacerance indicate very low hypersaline during deposition (Table. 4.12).
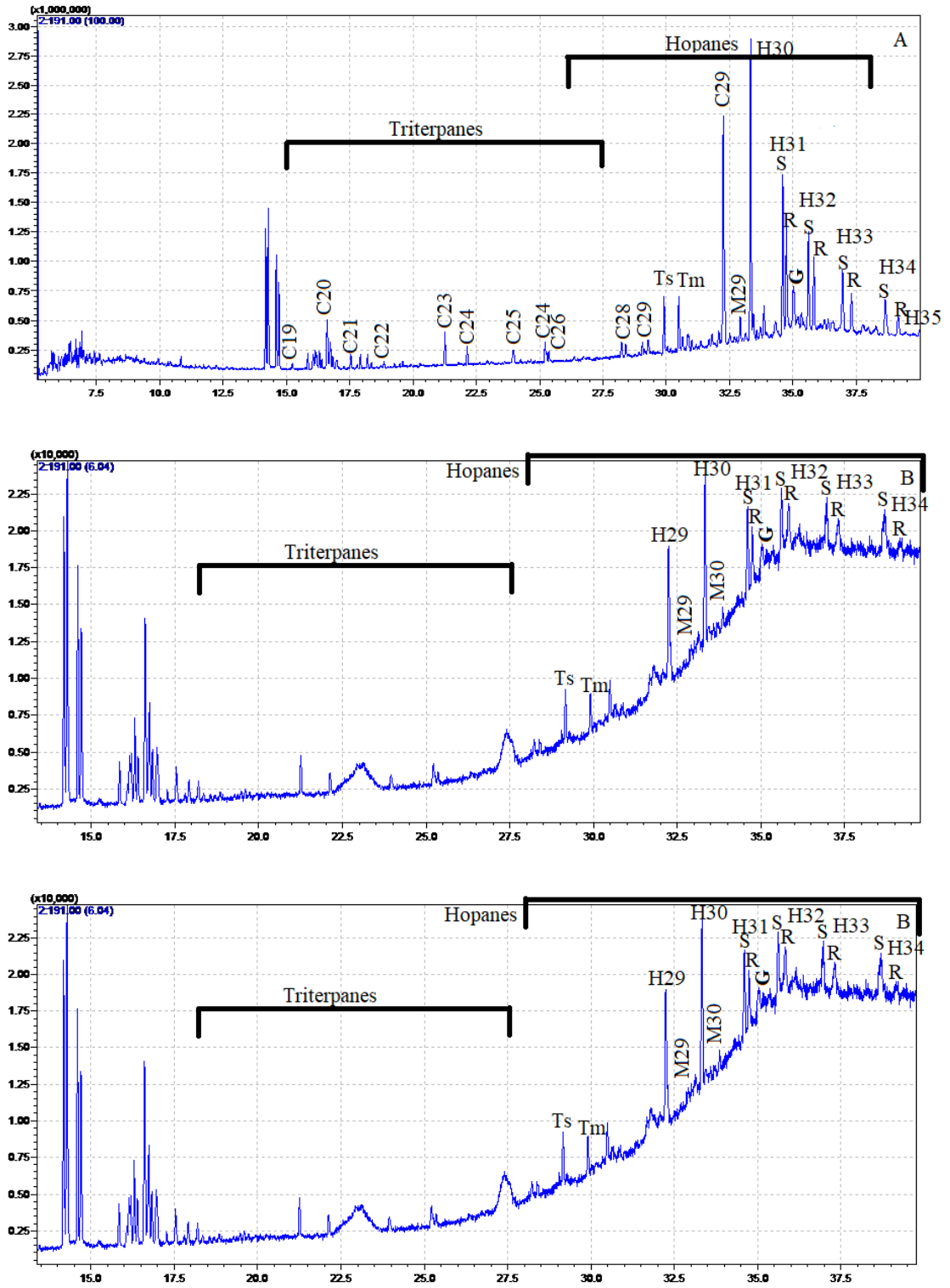
Figure 4.15 Mass Chromatograms of m/z 191 showing Terpanes and Hopenes fractions of extracts, (A) Patala Formation, (B) Lockhart Limestone, (C) Hangu Formation.

ii. Source Input

Several ratios have been used to interpret the source input and type of organic matter. C_{19} TCT / C_{19} TCT + C_{23} TCT ratio, indicates that the extracts are from the marine source input.
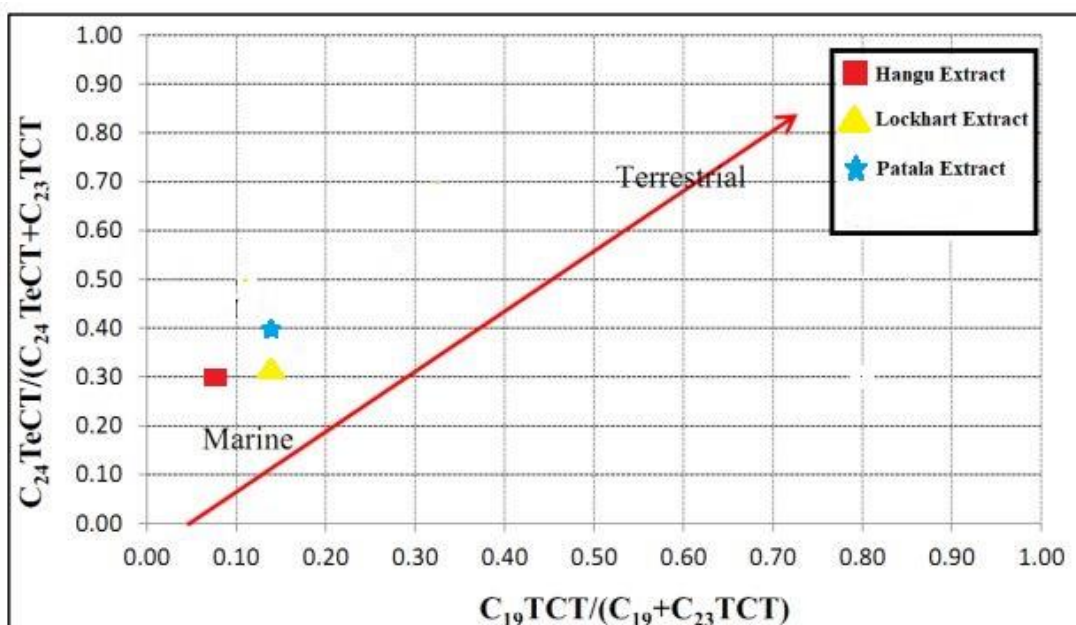

Figure 4.16 Cross plot of $C_{19}TCT/(C_{19}TCT + C_{23}TCT)$ vs $C_{24}TeCT/ (C_{24}TeCT + C_{23}TCT)$.(Zumberge, 1987).

The plot of $C_{19}TCT/C_{19}TCT + C_{23}TCT$ against the $C_{24}TeCT/C_{24}TeCT + C_{23}TCT$ is used for evaluation of the source input; marine or terrestrial source of organic matter (Fig. 4.16) The higher values of the former ratio will indicate the source as terrestrial. In case of all three Paleocene rock extracts the source is predominantly marine (Zumberge, 1987).

C_{29}/H_{30} ratios have been used by some researchers to identify the lithology of source rock of produced oil. If this ratio >1 then this indicates carbonate and evaporites source rocks (Clark and Philp, 1984). Paleocene extracts from Tolanj-01 has value of Patala (0.8), Lockhart (0.68), Hangu (0.86) which could be indication of shale lithology. Tetracycloterpanes are available in most of the rock extracts and oils, and range from $C_{24}TeCT/C_{27}TeCT$ (Aquino Neo et al., 1983). These are considered as indicators of the evaporite or the carbonate environment of deposition (Connan and Dessort, 1987). The extracts or oil which have their source input as clastic, the values of $C_{22}TCT/C_{21}TCT$ will be lower compared to $C_{24}TCT/C_{23}TCT$ values (Peters et al., 2005). This is the case

for Hangu and Lockhart extracts. But Patala Formation has almost same values for both ratios which indicates carbonate lithology (Table. 4.12).
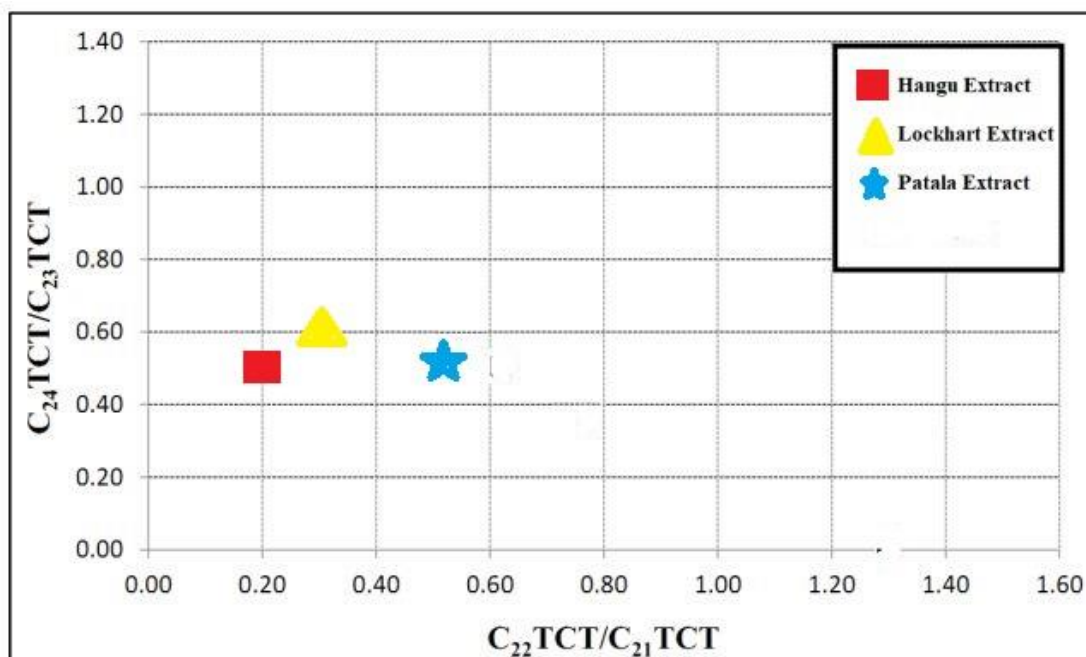

Table 4.17 Plot for $C_{24}TCT/C_{23}TCT$ vs $C_{22}TCT/C_{21}TCT$.

iii. Thermal Maturity

Moretane M_{30} to C_{30} Hopane ratio is a parameter which is used for thermal maturity indicator. C_{30} Moretane is less stable and during the stage of catagenesis it gets converted in to more stable C_{30} Hopane. The ratio will decrease with increase in thermal maturity and it will be 0.8 for immature and 0.15 to 0.05 for mature rock extracts and oils (Seifert and Moldovan, 1980). The values for this ratio for studied Patala 0.25 and Hangu 0.04 falls in thermally mature window (Table. 4.12).

$S/S + R\ HH_{32}$ ratio is used for evaluating the stage of thermal maturity and with increase in thermal maturity, values of this ratio will increase (Kara-Gulbay et al., 2008). The biological isomer of homohopane with R configuration is thermodynamically less stable and is converted into more stable isomer, S with increasing maturity. So, the rock extracts of Hangu, Lockhart and Patala Formation ratio values ranges between 0.58-0.6, falls in oil window and thermally mature (Table. 4.12).

Ts (C_{27} 18α-22,29,30-trisnorneohopane) is generally more stable than the Tm (17α-22,29,30-trisnorhopane). So with increase in maturity during the catagenesis stage Tm gets converted in to more stable Ts. Ts/ Ts + Tm ratio is used for calculating the stage of thermal maturity and with increase in thermal maturity of the rock extracts or the oils, values of this ratio will increase (Kolaczkowska, 1990). So, the rock extracts of Hangu, Lockhart and Patala Formation are thermally mature (Table. 4.12).

4.5.5 Steranes

Steranes are the biomarkers derived from sterols which precursors are present in variety of organisms, from marine algae, dinoflagellates to higher plants. Sterane distributions for the source rock extracts were studied through SIM/GCMS using the m/z 217 and 218 ions. The ion chromatograms m/z 217, of analyzed samples show distribution of C_{27}, C_{28} and C_{29} regular steranes and chromatograms m/z 218 show relative abundance of ββ isomers of C_{27}, C_{28} and C_{29} regular steranes (Fig. 4.18)
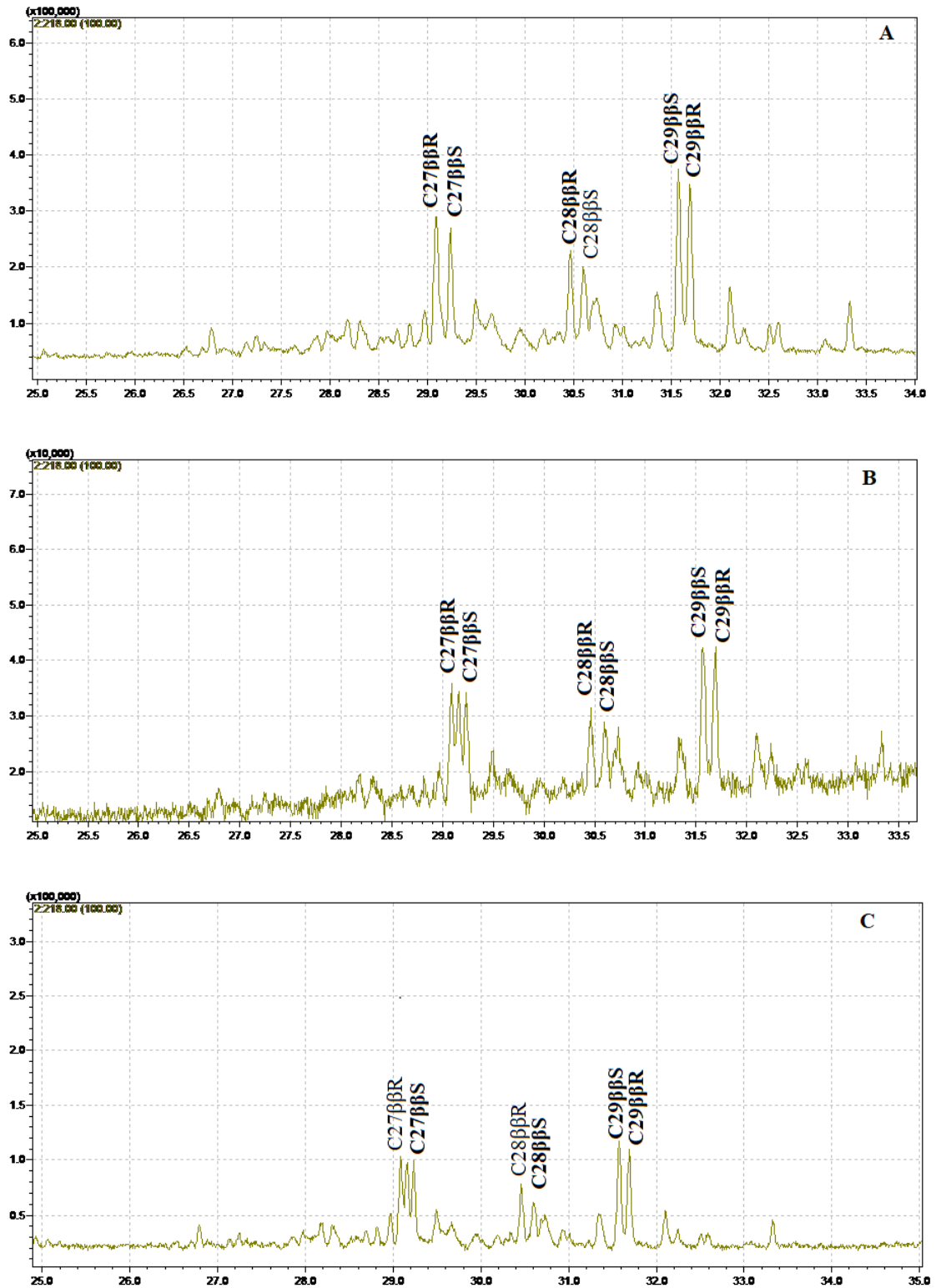
Figure 4.18 m/z 218 Chromatograms show distribution of C_{27}, C_{28}, C_{29} Steranes for (A) Patala Formation, (B) Lockhart Limestone, (C) Hangu Formation.

Different parameters are used for interpretation of source input, environment of deposition, thermal maturity, biodegradation, age of oil and source to oil correlation. The parameters used for these purposes are given in table 4.13.

Table 4.13 Biomarker derived from Regular Steranes.

Parameters	Patala	Lockhart	Hangu
C_{27} (%)	35	25	29
C_{28} (%)	31	26	22
C_{29} (%)	34	51	50
$C_{29}\beta\beta/(C_{29}\beta\beta+C_{29}\alpha\alpha)$	0.51	0.51	0.50
$C_{29}S/C_{29}S+C_{29}R$	0.50	0.49	0.50
C_{28}/C_{29}	0.91	0.50	0.44
C_{29}/C_{27}	0.9	2.04	1.72

Percentages of C_{27}, C_{28} and C_{29}, Steranes: $C_{29}\beta\beta/(C_{29}\beta\beta+C_{29}\alpha\alpha)$; $C_{29}S/C_{29}S+C_{29}R$, C_{28}/C_{29}, C_{29}/C_{27}.

i.   Source Input

The relative abundance of C_{27}, C_{28} and C_{29} regular steranes is widely used for the identification of organic matter inputs (Huang and Meinshein, 1979) and source rock organic facies (Palmer, 1984) and also for oil to oil and oil to source correlation (Mackenzie et al., 1983; Peters et al., 1989) (Fig. 4.19)
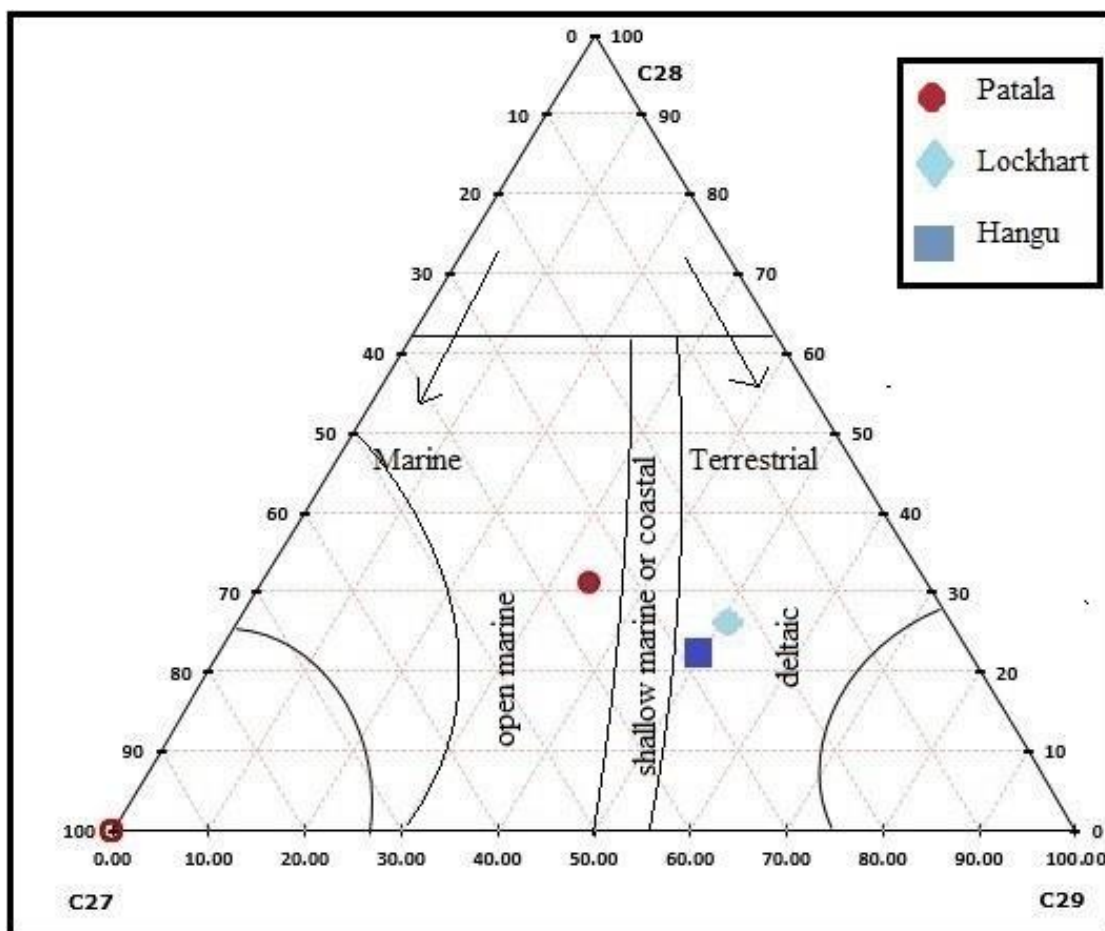
Figure 4.19 Ternary diagram showing distribution of Regular Steranes C_{27}, C_{28}, C_{29} Steranes for (A) Patala Formation, (B) Lockhart Limestone, (C) Hangu Formation.

C_{27} steranes comes from the marine source, along with C_{28} which are precursors usually abundant in phytoplanktons and zooplanktons. C_{29} steranes are derived from terrestrial sources. There is continuous increase in C_{28} sterane with increased biodiversity and therefore C_{28}/C_{29} sterane ratio is used as age indicator.

C_{29}/C_{27} ratio greater than 1 is interpreted as higher plant marker (Czochanska et al., 1988)). C_{29}/C_{27} ratio for Patala, Lockhart and Hangu is 0.9,2.04 and 1.72 respectively so it can be interpreted as higher plant input for Lockhart and Hangu while Patala shows higher marine input (Table. 4.13).

ii. Environment of Deposition

This ternary plot of C_{27}, C_{28} and C_{29} steranes can also be used to identify the environment of deposition. As C_{27} indicates marine source input so higher quantity of this steranes in organic matter of rock extracts or oil indicate marine environment of deposition. While higher C_{29} steranes indicates the presence of paralic or deltaic environment of deposition where oxygen was available to some extent.

In case of Hangu and Lockhart extracts shows deltaic and paralic environment of deposition while Patala extract shows open marine environment of deposition where terrestrial input to some extent were available too (Fig. 4.19).

iii. Thermal Maturity

The ratio of Steranes [$C_{29}\beta\beta/(C_{29}\beta\beta+C_{29}\alpha\alpha)$] increases from early to middle of oil window. The biological isomerC_{29} $\alpha\alpha R$ transformed into $C_{29}\alpha\alpha s$, $C_{29}\beta\beta S$ and $C_{29}\beta\beta R$. The equilibrium for this parameter is achieved at later stage of thermal alteration. The value of ratio $C_{29}\beta$ $\beta/C_{29}\beta$ $\beta+C_{29}\alpha\alpha$ is 0.51 for Patala, 0.51 for Lockhart, 0.50 for Hangu. The Equilibrium for this transformation is achieved at 0.67-0.70 (Seifert and Moldowan, 1984) corresponding to late oil window. These values reflect the status of Hangu, Lockhart and Patala Formations which have not attained maturity of late oil window (Fig. 4.18).

CONCLUSIONS

1. Well cuttings of Lockhart and Patala formations shows poor to fair and Hangu formations shows poor to Good present TOC content. On the basis of Rock Eval pyrolysis, source potential is mature stage of producing oil and gas.

2. Thermal maturity of the extracts shows high thermal maturity and mature oil zone. GP is generally poor but some of Lockhart and Hangu shows Fair potential. Vitrinite reflectance values are in the range of 0.82 to 0.95 %.

3. Pr/Ph values for Hangu (1.33) and Lockhart Limestone (1.23) and Patala Formation (1.8) are >1<3 which indicates the presence of sub-oxic environment of deposition.

4. $C_{19}TCT/C_{19}TCT+C_{23}TCT$ ratio, $C_{24}TeCT/C_{24}TeCT+C_{23}TCT$ ratio lower values of the former ratio will indicate the source as Marine and C_{29}/H_{30} ratio are utilized in evaluation of type of source input. Paleocene extracts from Tolanj-01 has value of Patala (0.8), Lockhart (0.68), Hangu (0.86) which could be indication of shale lithology. The ternary diagram of regular steranes (Fig. 4.19) indicates higher plant input of Hangu and Lockhart fall in terrestrial source region. While Patala has comparatively higher marine input.

5. CPI values for Patala (1.043), Lockhart (0.9) and Hangu (0.9), and 2-MP and 3-MP in case of Hangu and Lockhart extract shows relatively higher thermal maturity.

6. M_{30} to C_{30} Hopane values for this ratio for studied Patala (0.25) and Hangu (0.04) falls in thermally mature window. Value of (Ts/Ts+Tm) ratio of the rock extracts of Hangu, Lockhart and Patala Formation is relatively more thermally mature. Steranes $[C_{29}\beta\beta/(C_{29}\beta\beta+C_{29}\alpha\alpha)]$ values show the present status of Hangu, Lockhart and Patala Formations which are mature and falls in oil window.

RECOMMENDATIONS

This research can be improved by a number of ways.

1. Samples from other available wells can be obtained for further analysis.
2. Instead of well cuttings; well core samples (core data) can be used for more reliable results.

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