ธรณีเคมีปิโตรเลียมของหมวดหินห้วยหินลาด ภาคตะวันออกเฉียงเหนือของประเทศไทย

นายประวัติ แช่มช้อย

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR) เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต สาขาวิชาโลกศาสตร์ ภาควิชาธรณีวิทยา คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ปีการศึกษา 2557 ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย Petroleum Geochemistry of Huai Hin Lat Formation, Northeastern Thailand



A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science Program in Earth Sciences Department of Geology Faculty of Science Chulalongkorn University Academic Year 2014 Copyright of Chulalongkorn University

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ประวัติ แช่มช้อย : ธรณีเคมีปิโตรเลียมของหมวดหินห้วยหินลาด ภาคตะวันออกเฉียงเหนือของประเทศ ไทย (Petroleum Geochemistry of Huai Hin Lat Formation, Northeastern Thailand) อ.ที่ ปรึกษาวิทยานิพนธ์หลัก: ดร. เครือวัลย์ จันทร์แก้ว, หน้า.

การสำรวจปิโตรเลียมในที่ราบสูงโคราชบริเวณภาคตะวันออกเฉียงเหนือของประเทศไทยเริ่มขึ้นในปี พ.ศ. 2505 จนถึงปัจจุบัน (พ.ศ. 2558) มีการเจาะสำรวจไปแล้ว 55 หลุม สามารถทำการผลิตปิโตรเลียมในเชิง พาณิชย์ได้ 2 แหล่งคือ แหล่งน้ำพอง และแหล่งสินภูฮ่อม โดยสามารถผลิตแก๊สธรรมชาติจากชั้นหินปูนอายุเพอร์ เมียน หินดินดานในหมวดหินห้วยหินลาด และหินดินดานอายุเพอร์เมียนในกลุ่มหินสระบุรีมีศักยภาพเป็นหินต้น กำเนิด ในการศึกษานี้ได้เลือกตัวอย่างเศษขึ้นหินของหมวดหินห้วยหินลาดมาทำการวิเคราะห์คุณสมบัติทางธรณีเคมี ปิโตรเลียม เพื่อประเมินศักยภาพในการเป็นหินต้นกำเนิด ชนิดของสารอินทรีย์ ระดับความพร้อมในการให้ ปิโตรเลียม รวมทั้งสภาพแวดล้อมของการตกสะสมตัวในอดีต

ได้ทำการวิเคราะห์ตัวอย่างเศษขึ้นหินของหมวดหินห้วยหินลาดจาก 10 หลุมสำรวจในที่ราบสูงโคราช จำนวนทั้งหมด 22 ตัวอย่าง ด้วยวิธีทางธรณีเคมปิโตรเลียม โดยทำการวิเคราะห์หาปริมาณคาร์บอนอินทรีย์ทั้งหมด (TOC) การวิเคราะห์ด้วยเครื่อง Rock-Eval pyrolysis การหาชนิดของเคอโรเจนภายใต้กล้องจุลทรรศน์ การ วิเคราะห์หาค่า Vitrinite reflectance รวมทั้งการวิเคราะห์สารสกัดไฮโดรคาร์บอนด้วยเครื่องแก๊สโครมาโตรกราฟี และเครื่องแก๊สโครมาโตรกราฟี-แมสสเปกโตรมิเตอร์

ค่า Vitrinite reflectance และ thermal alteration scale แสดงให้เห็นถึงระดับความพร้อมในการให้ ปิโตรเลียมอยู่ในช่วงสุดท้ายถึงช่วงผ่านการให้ปิโตรเลียมไปแล้ว ค่า HI และ OI บ่งชี้ว่าในช่วงเริ่มต้นตัวอย่างหิน หมวดหินห้วยหินลาดประกอบด้วยเคอโรเจนชนิดที่ II, II/III และ III แต่ผลจากระดับความร้อนที่สูงส่งผลให้เคอโรเจน มีการแปรสภาพเป็นชนิดที่ IV ปริมาณสารอินทรีย์ตั้งต้น (TOC₀) ของตัวอย่างหินอยู่ในระดับที่ต่ำมากจนถึงสูงมาก แสดงให้เห็นว่าตัวอย่างหินมีศักยภาพการเป็นหินต้นกำเนิดปิโตรเลียมในระดับที่ต่ำจนถึงดีเลิศ ตัวอย่างหินหมวดหิน ห้วยหินลาดจากพื้นที่ Phu Phan Anticlinorium มีปริมาณสารอินทรีย์ที่สูงกว่าพื้นที่ชุมแพ และขอนแก่น-อุบล โดยที่ทางตอนกลางค่อนไปทางเหนือของพื้นที่ Phu Phan Anticlinorium มีปริมาณสารอินทรีย์ที่มากกว่า ทางด้านตะวันออกและตะวันตกของพื้นที่ Phu Phan Anticlinorium

จาก nonbiomarker และ biomarker บ่งชี้ว่าสารอินทรีย์ในตัวอย่างหินจากหมวดหินห้วยหินลาดมาก จากสิ่งมีชีวิตทั้งบนบกและในทะเล โดยมีการตกสะสมในสภาพแวดล้อมที่มีปริมาณออกซิเจนต่ำถึงไม่มีเลย นอกจากนี้ลักษณะของโครมาโตรแกรมของ n-alkane มีลักษณะเป็นสองยอด (bimodal) ซึ่งบ่งชี้ว่าสารอินทรีย์ใน ตัวอย่างหินมีสัดส่วนของสิ่งมีชีวิตจากบนบกที่สูงกว่าสิ่งมีชีวิตจากในทะเล แผนภูมิสามเหลี่ยมของ C₂₇-C₂₈-C₂₉ regular sterane บ่งชี้สภาพแวดล้อมในการตกสะสมตัวของตะกอนว่าน่าจะเป็นบริเวณปากแม่น้ำหรือทะเล ซึ่งการ พบ gammacerane ในทุกตัวอย่างก็สนับสนุนสภาพแวดล้อมดังกล่าว

ภาควิชา ธรณีวิทยา สาขาวิชา โลกศาสตร์ ปีการศึกษา 2557

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PRAWAT CHAMCHOY: Petroleum Geochemistry of Huai Hin Lat Formation, Northeastern Thailand. ADVISOR: KRUAWUN JANKAEW, Ph.D., pp.

Petroleum exploration in the Khorat Plateau, northeast of Thailand, began in 1962. Up until now (2015), 55 exploration wells were drilled in this area. In the Khorat Plateau, only Nam Phong and Sin Phu Horm fields have successfully produced gas from the Permian carbonate reservoirs. Potential source rocks are believed to be the organic-rich Triassic shale of Huai Hin Lat Formation and Permian shale of Saraburi Group. This study investigates well cutting samples of Huai Hin Lat Formation in order to assess the thermal maturity, source-potential, organic matter type and palaeodepositional conditions.

Twenty two cutting samples of Huai Hin Lat Formation from ten exploration wells in the Khorat Plateau were investigated by petroleum geochemical method, including total organic carbon determination, Rock-Eval pyrolysis, vitrinite reflectance, kerogen microscopy, gas chromatography, and gas chromatography/mass spectrometry of extractable hydrocarbon.

Vitrinite reflectance and thermal alteration scale (TAS) indicate that the samples of Huai Hin Lat Formation are within late mature to post mature stage. Based on HI and OI values, Huai Hin Lat Formation was likely to initially contain kerogen type II, II/III and III, but converted to kerogen type IV during thermal maturity process. The original total organic carbon (TOC_o) content of cutting sample are considered to be of very low to very high in organic richness (poor to excellent source rocks potential). Huai Hin Lat formation samples from Phu Phan Anticlinorium have more organic content than Chum Phae and Khon Kaen-Ubon Areas. Moreover, the north-central part of Phu Phan Anticlinorium has higher in organic richness than the eastern and western parts of Phu Phan Anticlinorium.

Nonbiomarker and biomarker parameters suggest the Huai Hin Lat Formation samples contain organic sources between terrestrial and marine organic matters deposited in less reducing to reducing environmental conditions. Bimodal distribution of n-alkane chromatogram indicates greater terrestrial higher plant organic matter input than marine organic matter. Ternary diagram of C_{27} - C_{28} - C_{29} regular sterane suggests the Huai Hin Lat Formation was possibly deposited in estuarine and/or marine environment, supported by a presence of gammacerane in all samples.

Department: Geology Field of Study: Earth Sciences Academic Year: 2014

 Student's Signature

 Advisor's Signature

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Chapter I

Introduction

Thailand's primary energy consumption is mostly from fossil fuels and the demand has increased every year. Thailand has limited domestic petroleum production and reserves, and imports make up a significant portion of the country's oil consumption. For decreasing imports of petroleum, Department of Mineral Fuels (DMF) has a strategic plan to establish and maintain the security of mineral fuel supply. In the 2013 annual report, DMF has made efforts to continuously promote the development of petroleum fields in the country especially the northeastern region (the Khorat Plateau).

The Khorat Plateau is located in the northeast of Thailand. It is defined by the large area of Mesozoic (mainly Cretaceous) continental sedimentary rocks of the Khorat Group, with an area of about 200,000 square kilometers (Chantong, 2007). Petroleum exploration in this plateau began in 1962. Up until now (2015), 55 wells were drilled in this area, but only 13 wells produced natural gas and condensate from two commercials fields, Nam Phong and Sin Phu Horm (Chantong et al., 2008). Moreover, gas accumulation is found in Dong Mun and Si That fields. Dong Mun field will be developed in the future.

The petroleum provinces in the Khorat Plateu have high potential for exploration and development. Petroleum in this plateau has been found in the Permian carbonate rocks of Pha Nok Khao Formation, Saraburi Group. A potential source rock in this area is the organic-rich Triassic shale of Huai Hin Lat Formation (Triassic Pre-Khorat Group) and Permian shale of Saraburi Group (Chantong, 2007). However, previous studies have focused on structure and trap but had overlooked source rock study. So, petroleum geochemistry data of these source rocks is not sufficient to prove where the petroleum found in the Khorat Plateau had originated from. It is expected that more study of the petroleum geochemistry of these rocks will describe the most probable source rocks for petroleum in the Khorat Plateau.

1.1 Study area

Selected cutting samples of the Huai Hin Lat Formation were collected from 10 exploration wells in the Khorat Plateau; Chonnabot-1, Dao Ruang-1, Dong Mun-1, Dong Mun-2, Kaset Sombun-1, Kham Palai-1, Non Sung-1, Phu Lop-1, Phu Phra-1 and Phu Wiang-1. The study area covers the Khorat Plateau, which is located in the northeast of Thailand between latitudes 15°50'N to 17°20'N and longitudes 101°50'E to 104°40'E as shown in Figure 1.1.



Figure 1.1 Location of exploration wells where cutting samples were used in this study.

1.2 Objectives

To evaluate source rocks properties and petroleum potential of Triassic shale of Huai Hin Lat Formation in the Khorat Plateau, using the biomarker data to establish petroleum geochemical characteristics of these rocks.

1.3 Data sources

The exploration data and cutting samples in this research are received from the Department of Mineral Fuels. Under the Petroleum Act of Thailand, the exploration data can be revealed when the concessionaire has already relinquished the concession. Data is composed of washed cutting samples, geochemical reports, and well completion reports.

1.4 Theories

In petroleum geology, source rock refers to organic-rich sedimentary rocks, where hydrocarbons have been generated or are capable of being generated. Organic matter in rocks can be divided in two fractions, kerogen and bitumen. Kerogen is the portion of organic matter preserved in sedimentary rocks that is insoluble in organic solvents because it has a high molecular weight. Bitumen is the portion of organic matter, which is soluble in organic solvents (Peters and Cassa, 1994).

Three parameters are used to screen the source rock potential for petroleum exploration: (1) quantity of organic matter (quantity), (2) types of organic matter (quality) and (3) maturation of organic matter (thermal maturity) (Tissot and Welte, 1984).

1.4.1 Quantity of organic matter

The quantity of organic matter is used to estimate the total organic carbon content (TOC, wt%). TOC is a primary screening parameter for petroleum potential, which is a measurement of the organic richness of a rock and reported in weight percent (wt.%), including both kerogen and bitumen. TOC is measured by the direct combustion of a crushed rock sample that is treated by acid in a crucible to remove carbonate, and analyzed as carbon dioxide. Generally, 0.5 wt.% of TOC is the minimum value for defining a petroleum source rock. Therefore, the petroleum source rocks, shale and limestone, in weight% are 0.5 wt.% and 0.2 wt.% respectively (Jarvie, 1991). TOC's criteria will be shown in Chapter III.

1.4.2 Quality of organic matter

Quality of the organic matter is measured by classification of the types of kerogen contained in the organic matter. Kerogens are capable of generating hydrocarbons which are derived from both marine and terrestrial sources. Study on the kerogens can be done two ways, first is to study under the binocular microscope and see the proportion of kerogen types. The second way is to analyze the kerogen by Rock-Eval Pyrolysis in which rock sample are pyrolysis at temperature 300°C - 600°C in an atmosphere of He. After that vaporized compounds will be detected by Flame Ionization detector (FID) and reported as three peaks as shown in Figure 1.2 (Tissot and Welte, 1984). The first peak (S1) represents the already generated hydrocarbon in the rock, while the second peak (S2) represents the amount of hydrocarbons generated by thermal cracking of kerogen in rocks. The third peak (S3) represents the trapped carbon dioxide (CO_2) that is released during pyrolysis temperature programing up to 390° C. The maximum temperature that generates peak S2 is called Tmax. It can be summarized that Rock-Eval pyrolysis is used to evaluate the potential of source rocks by providing information of: (1) quantity of organic matter, (2) quality of organic matter, and (3) maturation of organic matter.



Figure 1.2 Schematic diagram of Rock-Eval pyrolysis showing cycle of analysis and temperature program (Tissot and Welte, 1984).

Kerogen types are recognized by using a Van Krevelen diagram, which is plotted between the atomic H/C and O/C as shown in figure 1.3a (Peters, 1986). This diagram is showing different types of kerogens as Type I, Type II, Type III, and Type IV. Espitalié et al. (1977) modified Van Krevelen diagrams by using the Rock-Eval method which plots the Hydrogen Index (HI) and Oxygen Index (OI). This diagram is called a Pseudo-Van Krevelen diagram as shown in figure 1.3b. Results of HI and OI are produced faster and at less cost than the results of atomic H/C and O/C. Hydrogen index (HI) is a measure of the hydrogen richness of the source rocks and is calculated from a ratio of S2 to TOC, [HI = (S2/TOC) × 100]. Oxygen index (OI) is a measurement of the oxygen richness of the source rock and calculated from a ratio of S3 to TOC, [OI = (S3/TOC) × 100].



Figure 1.3 Classification of kerogen types by (a) Van Krevelen diagram (b) modified Van Krevelen diagram (Pseudo-van Krevelen diagram) (Peters, 1986).

The following information on different types of kerogen is from Peters and Cassa (1994).

Type I kerogen is oil prone, indicates a potential for generating liquid hydrocarbons, which comprise of aliphatic chain and an abundant amount of hydrogen (high HI). This kerogen type originates from alginite macerals that are derived from lacustrine algae.

Type II kerogen is oil prone which contains aromatic and napthene rings and moderate HI. This kerogen type originates from several different sources, with the potential for oil and natural gas. Maceral of type II kerogen includes exinite derived from pollens and spores, cutinite derived from terrestrial plant cuticles, resinite derived from terrestrial plant resins and animal decomposition resins and liptinite derived from terrestrial plant lipids and marine algae.

Type III kerogen is gas prone, mainly aromatic and O-functional groups compounds with low HI. They have a potential for natural gas. Maceral of type III kerogen includes vitrinite derived from lignin and cellulose of land plants.

Type IV kerogen is dead carbon, no potential to generate hydrocarbon, which shows a very low HI. Maceral of kerogen is dominated by inertinite derived from other kerogen types that have been reworked or oxidized.

1.4.3 Maturation of organic matter

Maturation of organic matter or thermal maturity is the degree of heating of a source rock in the process of converting sedimentary organic matter into petroleum. Due to increasing the depth of deposition of rocks, temperature and pressure will be increased, the organic matter in rock will convert to oil, condensate, wet gas and lastly dry gas. There are three levels of thermal maturation; immature, mature and post mature (Tissot and Welte, 1984). Immature source rocks have been affected by diagenesis, in which organic matters are changed by physical, chemical and biological processes during and after deposition of sediments with burial temperatures between 60° - 80° C, and microbial gas is a product. Mature source rocks are in the oil window and have been affected by thermal process or catagenesis of about 60° - 175° C, that is the temperature range for generating oil. Post mature source rocks is the gas window, wet and dry gas zones, it has been heated at high temperatures of about 175° -225°C that generated only small amounts of hydrocarbon gases as shown in Figure 1.4. Source rock maturity can be estimated using many methods such as vitrinite reflectance (Ro), fluorescence, thermal alternative index (TAI), thermal alternative scale (TAS) and Tmax from Rock-Eval pyrolysis.



Figure 1.4 Typical temperature ranges that oil and gas are generated (https://spec2000.net/11-vshtoc.htm).

Vitrinite Reflectance (Ro) is a measurement of the ability of light reflecting off vitrinite particles in the rock, which can be used as an indicator of the maturity of source rocks. Vitrinite reflectance data is presented in units of %Ro, which is measured in oil immersion. The classification of maturity levels is shown in Chapter III.

Tmax from Rock-Eval Pyrolysis is used to indicate thermal maturation of source rock. Tmax value is the maximum temperature of hydrocarbon production (S2), which is generated during pyrolysis. Thus, Tmax is dependent on the types of kerogen in source rocks. In addition, production index (PI) is calculated from the S1/(S2+S3) and can show the level of maturity, for Tmax and PI criteria see Chapter III.

1.4.4 Biomarkers

Biomarkers or biological markers are complex organic compounds that are composed of carbon, hydrogen and other elements. Biomarkers are found in crude oils, bitumen and petroleum source rocks, where they show little or no change in structure from their parent organic molecules that are found in all living organisms (Peters et al., 2005b). They are useful for learning more information about their origins. Petroleum geochemists use biomarker fingerprinting to characterize oils in term of organic matter origin types in source rocks, indicative depositional environmental conditions, assess thermal maturity of oil during burial, and determine the migration pathways of oil from source rocks to the reservoirs correlating of oil-tooil and oil-to-source rock.

In addition, Gas Chromatography-Mass Spectroscopy (GC-MS) method is used to analyze biomarker compounds characteristic in major biomarker groups. Some examples of biomarkers found in petroleum as follows;

1) The pristane/phytane ratio (Pr/Ph) is used to determine the oxicity of the depositional environment. Pr/Ph ratio less than 1.0 indicates anoxic conditions, and more than 3.0 indicates oxic conditions. The ratio values between 1.0 and 3.0 were interpreted as sub-oxic conditions (Didyk et al., 1978).

2) The isoprenoids/n-alkanes ratio ($Pr/n-C_{17}$ and $Ph/n-C_{18}$) provides valuable information on biodegradation, maturation and diagenetic conditions. The early effect of microbial degradation can be monitored by the ratios of biodegradable to the less degradable compounds. Isoprenoid hydrocarbons are generally more resistant to biodegradation than normal alkanes (Hunt, 1996).

3) The tricyclic terpanes (m/z 191) can be used to correlate crude oils and source rock extracts, to interpret organic matter input and to evaluate the extent of thermal maturity and biodegradation (Peters and Moldowan, 1993). Predominant C_{19} tricyclic terpanes reflects terrigenous organic matter, while higher C_{23} tricyclic terpanes indicate marine organic matter (Moldowan et al., 1985).

4) Gammacerane (m/z 191) has been found in sediments from the Late Proterozoic (Summons et al., 1988), which is used as an indicator for water stratification during source deposition with both marine and lacustrine environments (Sinninghe-Damsté et al., 1995).

5) The Trisnorneohopanes (Ts) and Trisnorhopane (Tm) ratio is used as a maturity indicator. Ts is more stable than Tm, at higher in maturity (Seifert and Moldowan, 1981).

6) The $17\beta(H)$, $21\alpha(H)$ -moretanes and $17\alpha(H)$, $21\beta(H)$ -hopanes ratio are used as maturity indicators. Moretanes are thermally less stable than hopanes, and the abundance of moretanes decreases relatively to the corresponding hopanes with thermal maturity (Seifert and Moldowan, 1986).

7) The homohopanes distribution (m/z 191) is derived from bacteriopolyhopanol of prokaryotic cell membrane. Homohopane index can be used as an indicator of the associated organic matter type, and it can also be used to evaluate the oxic/anoxic conditions of organic matter during and immediately after deposition of the source sediments (Yalçın et al., 2006).

8) The Homohopane isomerization ratio, 225/(22S+22R), can be used to assess the maturity of geological samples. This ratio reflects the more thermally stable 22S isomer compared to the biologically derived 22R stereochemistry (Peters et al., 2005b).

9) The distribution of steranes (m/z 217) is a characteristic fragment in the sterane series. Steranes are derived from sterols, where they are widely distributed in microorganisms and plants. The relative amounts of C_{27} - C_{28} - C_{29} steranes can be used to indicate characteristic source inputs and sedimentary facies. The predominance of C_{27} steranes show a marine influenced system and source input of plankton (algae), while C_{29} sterane predominance shows a terrestrial higher plant input and a swamp shallow water environment. C_{28} sterane is a unique biomarker signature of organic matter deposited in lacustrine facies (Peters and Moldowan, 1993).

10) The regular steranes/17 α (H)-hopanes ratio reflects input of eukaryotic (mainly algae and higher plants) versus prokaryotic (bacteria) organisms to the source rock (Peters and Moldowan, 1993).



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Chapter II

Literature Reviews

2.1 General geology

The Khorat Plateau is located in northeastern Thailand between latitudes 14[°] and 19[°] North and longitude 100[°] and 106[°] East, covering an area about 200,000 square kilometers. The average elevation is about 130-250 meters above sea level, the highest elevation about 900 meters above sea level (Department of Mineral Resources, 2007). The northern and eastern borders are bordered by the Lao People's Democratic Republic (Lao PDR) and the Mekong River. The southern part is connected to Cambodia and the western part is bounded by central and northern Thailand.

The topography of the Khorat Plateau is elevated table land, in which the main central part is covered by plains and a chain of hills sloping southeastwards to the Mekong River and extending northward and eastwards across the Mekong River into the Lao PRD. The Khorat Plateau contains two fold belts; the Northwest-Southeast trending Phu Phan range in the central part and the North-South trending Loei-Phetchabun fold belt in the western area. The Phu Phan Mountains divided the central part into two basins; the northern Udon-Sakon Nakhon basin and the southern Khorat-Ubon basin. Both basins tilt towards the southeast, and drained to the Mun and Chi rivers. The plateau is separated from Central Thailand by the Loei-Phetchabun fold belt and the Dong Phaya Yen Mountain Range in the west, the San Kamphaeng Range in the southwest and the Phanom Dongrak Mountains in the south (Sattayarak, 2005).

The general geology of the Khorat Plateau consists mainly of sediment of the Khorat Group, the Mesozoic sequence, except the western rim, which consists of Triassic Pre-Khorat Group and Permo-Carboniferous rocks. In addition, the Quaternary basalt rarely covers the southern part of the plateau (Chantong, 2007).

The origin and development of the Khorat Plateau is complex. The majority of events in the late Paleozoic and Mesozoic can be attributed to the sequential docking of continental microplates with the Indochina block that forms the underlying continental crust in this region. The basin in this area is structurally complex and underwent compressive deformation in the Late Permian to Middle Triassic followed by Late Triassic extension with a marked sinistral strike-slip fault component. Furthermore, subsequent major tectonic events affecting the area include mid-Cretaceous inversion and Late Cretaceous-Tertiary uplift and erosion.

The Khorat Plateau underwent four major events that had an effect on the litho-straitgraphic unit (Chantong, 2007). Firstly, the South China and Indochina blocks collided in the Late Carboniferous period, which caused the Saraburi Group to be deposited over the Carboniferous rocks after collision. Seconly, Indosinian Orogeny I and Indosinian Orogeny II occurred in Permian to Triassic (Polachan et al., 2010). Indosinian Orogeny I is the Shan-Thai and Indochina blocks collided together during Triassic and occurred the Nan-Uttaradit suture. After the collision, crustal extension caused the development of a number of the northwest-southeast/west-east trend system of half graben in the Khorat Plateau and deposited Huai Hin Lat Formation. Then, Indosinian Orogeny II is the inversion of the half graben with local fault reactivation in Late Triassic. Following Indosinian Orogeny II, the Khorat group which composed of continental sediments deposited and inverted in middle Cretaceous and Tertiary. Thirdly, the Myanmar and Shan Thai blocks collided in the Cretaceous period.

2.2 Stratigraphy of the Khorat Plateau

Based on the exploration well data and the seismic stratigraphy of the Khorat Plateau, the detail of the stratigraphic sequence from the oldest to the youngest can be summarized as shown in Figure 2.1, the details of stratigraphy are described below.



Figure 2.1 Stratigraphy of the Khorat Plateau (Chantong, 2007).

2.2.1 Pre-Permian Basement

This section consists of the oldest Late Carboniferous rocks from Na Mo Group, Pak Chom Group, and Wang Saphung Group (ATOP Technology Co Ltd, 2006).

1) Na Mo Group of Middle Silurian is the oldest metamorphic basement and is comprised of low grade metamorphic rocks of upper greenschist facies; chorite schist, quartzite, metatuff, and phulite. This unit is exposed in the Loei province area, in the northeastern margin of the Khorat Plateau. 2) Pak Chom Group of Late Silurian to Early Carboniferous uncomformably overlies the Na Mo Group, which mainly consists of shallow marine sediments of limestone, grey wacke, shale, conglomerate and tuff.

3) Wang Saphung Group of Middle to Late Carboniferous unconformably ovelies the Pak Chom Group, which mainly consists of silicalstic of conglomerate, shale, siltstone, and sandstone interbedded with limestones and volcanics. Moreover, the grey to black shales are also recorded in the sequence that is considered to be the gas prone source rocks. The outcrops of this unit are widely distributed in Loei province area especially in Wang Saphung district.

2.2.2 Saraburi Group

Saraburi Group is defined in the Late Carboniferous to Late Permian, and consists of shallow to deep marine sedimentary environment. This group is a carbonate sequence mainly consisting of limestone, dolomites, and clastic sediments of shale, sandstone and siltstone, which are indicative of sediment deposition in various environments ranging from delta plain, shale platform, and deep basin. The outcrops of Saraburi Group have been exposed along the western edge of the Khorat Plateau, extending from Loei, Phetchabun to Saraburi province. Saraburi Group can be divided into four formations; Si That Formation, Nam Duk Formation, Pha Nok Khao Formation and Hua Na Kham Formation (Chantong, 2007).

1) Si That Formation is the Lower Clastics of the Late Carboniferous to Early Permian and consists of shallow marine sediments; grey to dark grey shale interbedded with limestone, dolomite, and siltstone with some conglomerate in the lower part.

2) Nam Duk Formation deposited from Early to Middle Permian and consists of shale, dark grey sandstone and yellow to brown fine-grained limestone interbedded with chert in limestone. This sequence is indicated to deep-sea basin environment. 3) Pha Nok Khao Formation is ranging from the Early to Middle Permain. The rock units consist of predominantly massive white to dark grey limestone with minor beds of dark shale, chert, siltstone and fine-grained sandstone, and dolomite. These sequences indicate the depositional environment was intertidal and tidal flat, fore reef to back reef and lagoon. The Pha Nok Khao Formation outcrops are found in Saraburi and Nakon Rachasima Province.

4) Hua Na Kham Formation is the Upper Clastics of the Late Permian that overlies conformably on the Pha Nok Khoa Formation. This unit has been informally named the Upper Clastics, which consists of light grey to grey shale, siltstone, conglomeratic sandstone, and sandstone with minor beds of limestone. The sedimentary rocks were deposited in a shallow-platform marginal marine environment due to finding fusulinids in limestone. The outcrops of this formation are widely distributed in the northern edge of Khorat Plateau near Laos's border in Loei province.

2.2.3 Triassic Pre-Khorat Group

The Triassic Pre-Khorat Group is represented as the Huai Hin Lat Formation in the geological map. This unit consists of conglomerate limestone, conglomerate grey to dark grey sandstone; siltstone; black shale and marl containing plant fossils, which was deposited under fresh water lakes and streams environment in Middle to Late Triassic. The thickness of this formation is about 20 to 1,300 meters. The unit is divided into two large sequences and five members; the upper and the lower sequence as shown in Figure 2.2. The lower sequence consists of the Pho Hai and Sam Khaen Members. The upper sequences consist of the Dat Fa, Phu Hi and the I Mo Members (Chonglakmani and Sattayarak, 1978).



Figure 2.2 Members of Huai Hin Lat Formation (Treerotchananon, 2012).

1) Pho Hai Member mainly consists of volcanic rocks such as tuff, agglomerate, rhyolite and andesite with some intercalations of sandstone, mudstone, and conglomerate This unit angular conformably overlies the Permian shale and siltstone.

2) Sam Khaen Member is a widely distributed unit of the Huai Hin Lat Formation, which mainly consists of limestone conglomerate intercalated with limestone beds, conglomerate often polymictic and red in colour, and intercalated with red sandstone and shale. The lower contact is at the base of conglomerated bed and on the upper Permian strata. Moreover, the lower contact is on top of the volcanic rocks of Pho Hai member in some areas. The red color of the matrix in the basal conglomerated indicates that it was deposited under a warm terrestrial environment.

3) Dat Fa Member consists of grey to black, carbon-rich, calcareous, well bedded shale; argillaceous limestone thin beds. In addition, the member contains both terrestrial flora and fauna indicating a Late Triassic (Norian age). This unit conformably overlies the Sam Khaen Member with the lower contact at the top of the basal conglomerate of Sam Khaen Member where the upper contact is at the base of sandstone or conglomerate of the Phu Hi Member.

4) Phu Hi Member consists of grey sandstone, shale and argillaceous limestone with some intercalation of conglomerate bed in the lower half of the member. This member conformably overlies the Dat Fa Member with the lower contact at the top of grey shale and limestone of the Dat Fa Member while the upper contact is at the base of Nam Phong Formation, Khorat Group.

5) I Mo Member is the top and youngest member of Huai Hin lat Formation, it consists of grey sandstone, shale, limestone, grey diorite, tuff and agglomerate.

2.2.4 Khorat Group

The Khorat Group is defined as Jurassic to Cretaceous age. This group consists of continental sediments; very high thickness of red clays, siltstone, sandstone, and conglomerate. This sequence is found in both the Loei-Phetchabon fold belt and the Khorat Plateau and divided into eight formations; Nam Phong Formation, Phu Kradung Formation, Phra Wihan Formation, Sao Khua Formation, Phu Phan Formation, Khok Kruat Formation, Maha Saraham Formation and Phu Thok Formation (Department of Mineral Resources, 2007).

1) Nam Phong Formation is the lowest unit of the Khorat Group. This Formation is a reddish color and consists of interbedded red sandstone, siltstone, and conglomerate. The Nam Phong Formation overlies the Huai Hin Lat Formation conformably and the Permian limestone unconformably in some areas. The thickness of the formation ranges from 100-1,500 meters. The Nam Phong Formation can be considered as two parts; an upper part and lower part. The Upper Nam Phong Formation is comprised of predominantly dusky red to red brown to purple siltstone, minor sandstone, and claystone together with thin limestone. The Lower Nam Phong Formation consists of red-brown sandstone, siltstone, and claystone.

2) Phu Kradung Formation consists of brown siltstone, greenish grey sandstone, mudstone, shale, and calcareous conglomerate. The formation overlies the Nam Phong Formation. In some locations, if the Nam Phong Formation is not present, the Phu Kradung Formation overlies the Permian rocks. The thickness of this formation is approximately 800-1,200 meters. Bones and teeth of plesiosaurs and dinosaurs were also found in this formation.

3) Phra Wihan Formation consists of cross-bedded white quartz sandstone with thin-bedded and dark grey interbedded siltstone. The sandstone is off white to grayish green, fine to medium grain but locally is coarse to very coarse grained, with calcareous cementing. The thickness of the formation is about 100-250 meters.

4) Sao Khua Formation is comprised of thick-bedded siltstone, mudstone, and sandy conglomerate. It contains gastropod (Naticoid), bivalves (Trigonioides sp. and Plicatounio sp.), and herbivorous dinosaur fossils, these are an Early Cretaceous indicator. The thickness of the formation is approximately 200-760 meters.

5) Phu Phan Formation is comprised of thick and cross-bedded pebbly sandstone interbedded with siltstone. The sandstone is off white to light grey, greyish green, reddish brown, occasionally light brown, moderately hard, sub angular, partly micaceous with traces of siltstone and limestone lithoclasts. The unit was found to contain some fragments of dinosaur bones and contains some carbon compounds. The thickness of the formation is approximately 80-140 meters. The Phu Phan Formation underlies the Khok Kruat Formation and overlies the Phra Wihan Formation.

6) Khok Kruat Formation consists of red to brown to purple siltstone, off white to light grey to reddish brown sandstone, red to reddish brown claystone, caliche siltstone, and conglomerate. The formation was found to contain fragments of herbivorous dinosaurs, turtles, and fish. The thickness of the formation is about 430-700 meters.

7) Maha Sarakham Formation can be considered as two parts, which consists of siltstone and shale in the upper part and anhydrite and salt in the lower part. The salts indicate a non-marine restricted hypersaline lacustrine depositional environment. Sediments of the formation were deposited in two basins; the Khorat Basin and Sakon Nakhon Basin. The age of this sequence is Late Cretaceous based on paleomagnetic and isotopic dating. The thickness of the formation is about 610-1,000 meters.

8) Phu Thok Formation consists of small cross-bedded and reddish finegrained sandstones, which deposit by stream and wind. The thickness of the formation is approximately 200-730 meters. The Phu Thok Formation overlies the Mahasarakham Formation uncomformably.

2.2.5 Cenozoic Rocks

The uppermost rock unit overlies the Khorat Group and Quaternary sediments. These rocks are known as the Tha Chang Formation, which are consisted of semi consolidated to consolidated, mudstone, and conglomerate. The formation was deposited on the Himalayan Unconformity, more than 20 meters in thickness (Chantong, 2007).

2.3 Petroleum provinces of the Khorat Plateau

The petroleum provinces of the Khorat Plateau can be divided into 7 regions based on geomorphology, geology, and geologic structures, excluding the western part covering Loei, Phetchabun, and Chumphae areas, as shown in Figure 2.3 (Sattayarak, 2005).

1) The Loei-Petchabun Fold Belt is located to the western part of the Northeast, extends from Nakhon Ratchasima in the south to Loei in the north, and forms the western boundary of the Plateau that separated from the central region of Thailand. The north-south trending mountain belt is composed mainly of folded pre-Permian rocks with some igneous rocks and outlining hills of the non-marine Mesozoic Khorat sediments.

2) The Chum Phae Area is confined between the Fold Belt and the Plateau, covering Non Bua Lamphu, Chum Phae, Phu Kiew and Kaset Sombun. Topography of this area is a combination of flat top mountains of Mesozoic Redbeds and their eroded low lands.

3) The Phu Phan Anticlinorium consists of complex anticlines and synclines trending Northwest-Southeast, covering from Khao Nam Phong in the west through Khao Suan Khwang, Khao Phu Phan, and Pha Taem to the east. This province in underlain by Permo-Carboniferous rocks, Triassic Pre-Khorat Group, and the minor folding of Jurassic-Cretaceous redbeds in the upper part.

4) The Nong Khai-Tat Phanom area is located north of Phu Phan Range from Nong khai in the west extending to Udon Thani and Nakhon Phanom in the east. This area is covered by a plain represented by the younger rock unit such as Phu Thok and Maha Sarakham Formation that overlie the redbeds of the Khorat Group including the lower part of Triassic. The Permo-Carboniferous rocks may be present at the lowest section in some areas.

5) The Phon Pisai-Nakhon Phanom area is located north of Nong Khai-Tat Phanom region, which its northern edge is bounded by the Mekong River. From well reports, the underlying units are thick sandstone of Phu Tok Formation that was deposited by the eolian process. The lower units encountered are rock salt of the Maha Sarakham Formation and the redbeds of the Khorat Group on the basement rocks.

6) The Khon Kaen-Ubon area covers mainly Khon Kaen and Ubon Ratchathani Province lying in an East-West direction. The stratigraphy like the Nong Khai-Tat Phanom area, but the thickness of the Khorat Group and the overlying sediments are much greater.

7) The Chok Chai-Det Udom area is covered by gravel beds and basalt that overlie the redbeds of the Khorat group and the basement rock. The pre-Khorat rocks are found in some places based on the well data.

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Figure 2.3 Petroleum provinces of the Khorat Plateau (Sattayarak, 2005) and location of exploration wells where cutting samples are used in this study.

2.4 Petroleum system of the Khorat Plateau

The properties and the characteristic of sedimentary strata of the Khorat Plateau can be summarized in petroleum system as follow.

2.4.1 Source rocks

Based on petroleum geochemistry data of rock samples in borehole and outcrop, the source rock in the Khorat Plateau was divided into 3 groups, the fluvial sediment of the Khorat Group, Huai Hin Lat Formation and Clastic sedimentary rocks of the Upper Saraburi Group, summary as show in Table 2.1 (Sattayarak, 2005) and (Thongboonruang, 2008).

1) Permian Group

The shallow marine shale and limestone of the Permian Group overlies the older rocks unconformably and can be divided in to three parts. Firstly, the lower part, Lower Clastics or upper part of the Wang Saphung Formation, consists of shales interbedded with limestone and occasional lignite beds. Secondly, the middle part, the Middle Carbonates, comprises limestone and dolomite. The upper part, Upper Clastics or the Hua Na Kham Formation, is shales interbedded with sandstones and occasional limestone. The Permian outcrop samples contain TOC content values about 0.29-1.59 wt.% (very low to moderate organic richness), are maturity level is post mature where the product is dry gas. Moreover, petroleum geochemical data summarized by Thongboonruang (2008), who collected data from 4 exploration wells: Phu Lop-1, Phu Wiang-1, Dao Ruang-1 and Kham Palai-1, the results showed sedimentary rocks of the Upper Saraburi group have very low to very high organic richness (poor to excellent potential source rocks) with kerogen type III/IV and the maturity stage is late mature to post mature.

2) Huai Hin Lat Formation

The Huai Hin Lat Formation overlies the Permian or older rocks unconformably and underlies the Khorat Group with a local unconformity. This sequence is represented as the Huai Hin Lat Formation and comprises shale, sandstone, limestone, conglomerate and volcanic rocks, which were deposited in a lacustrine environment. The Huai Hin Lat can be separated into two facies depending on the sedimentary environment of the lake; the dark gray sediments and the brownish red sediments. The rock samples contain TOC content values about 0.2-5.76 wt.%, vitrinite reflectance value of 0.9-4.57%Ro (low to very high organic richness), which are considered to be potential gas-prone source rocks.

3) Khorat Group

The Khorat Group, the Mesozoic non-marine sequence, consists mainly of brownish red sediments which were deposited in streams and lakes under arid climate. Generally, this sequence contains very low quantity organic matter (low TOC) with kerogen type II and the maturity stage is mature. Moreover, it may contain rich woody organic matter beds or thin coal beds at some places, which can be a potential source rock.

2.4.2 Reservoir rocks

The most significant reservoir rocks in the Khorat Plateau are the Permian carbonate, which comprises dolomites and limestone from coral reef with high porosity and permeability indicating good reservoir characteristics. Moreover, the shallow marine Upper Clastic or the Hua Na Kham Formation, the Upper Triassic fluvio-lacustrine Huai Hin Lat Formation, and sandstones of the Nam Phong, Phu Kradung and Phra Wihan Formations are also considered to be high potential reservoir rocks (ATOP Technology Co Ltd, 2006).

1) Permian Reservoirs

The characteristics of the Permian carbonate reservoir rocks were deposited on platform and consisted mainly of fossiliferous packstone and grainstone, with minor wackstone and mudstone. The porosity of these rocks is generally low with values ranging 0-18% with the matrix porosity about 4%. The permeability of these carbonates depends on the micro fractures. Form drilling in the Khorat Plateau, we understand that the Permian carbonate of Pha Nok Khao Formation is the only unit that has been proven to be commercial reservoir quality (Chantong, 2007).

Table 2.1 Summary of organic richness, kerogen type and thermal maturity level of source rocks in the Khorat Plateau (Sattayarak, 2005) and

	Organic	Kerogen	Thermal
Group/Formation	richness	type	maturity
Khorat Group			
Phu Phan Formation	High	-	Mature
Low organic material, coal laminated			
Sao Khua Formation	Very low	-	-
Claystone/sandstone			
Phra Wihan Formation	Very low	111	Late Mature
Shale/Sandstone			
Phu Kradung Formation	Very low	-	Late Mature
Sandstone, claystone, siltstone/limestone			
Nam Phong Formation	Very low	-	Mature
Claystone, siltstone, sandstone, poor			
source potential			
Triassic Pre-Khorat Group			
Huai Hin Lat Formation	Low to very	1/111	Late Mature to
Lacustrine gray shales, mudstones &	high		Post mature
limestone			
Saraburi Group			
Upper clastics	Very low to	III/V	Late Mature to
Gray shales	very high		Post mature

(Thongboonruang, 2008).

2) Triassic Reservoirs

The reservoir rocks of Triassic comprise fluvial sandstones and basal conglomerates that are tight and compact. The porosity value of these rocks range only 3-8%, not good reservoir rocks.

3) Post-Triassic Reservoirs

The sandstones of the Khorat Group have good reservoir properties, which are found in various formations. The sandstones of the Nam Phong, Phu Kradung, Pra Wihan, Sao Khuan, Phu Phan, and Khok Kruat Formations are fine-grained to medium-grained. The average porosities of sandstones are 4.9, 6.4, 5.9, 11.5, 10.8, and 11.0 percent, respectively that indicates fair quality reservoir potential (DMF, 2006).

2.4.3 Seal rocks

The seal rocks in the Khorat Plateau consist of shale and thick claystone, which are found in the Permian Group, Triassic Group, Nam Phong Formation and Phu Kradung Formation. In addition, the Nam Phong and Phu Kradung Formations consist of volcanic clastic and conglomerate that are compacted with argillaceous matrix and relatively low permeability. The seal rocks overlie the carbonate reservoirs. The fine-grained rocks of Permian age also process good seal characteristics (Sattayarak, 2005).

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2.4.4 Traps

The geology of structures and stratigraphic petroleum traps in the Khorat Plateau are summarized as four groups; 1) the angular unconformity between the Permian Saraburi Group and the Triassic Huai Hin Lat Formation, 2) the Permian reefal limestones in the foreslope, 3) the structure of half-graben under the Khorat group which consists of Permian and Triassic sediments, and 4) the anticline of Triassic and Khorat rocks which formed in the Early Tertiary (ATOP Technology Co Ltd, 2006).

2.5 Previous studies

The petroleum system in Khorat Plateau had been studied by Porwal and Jain (2008) in block L39/48 and L22/50, and Koysamran and Comrie-Smith (2011) in block L26/50. They used 1D basin modeling integrated with well data to determine the burial and erosional history, lithology, and kerogen thermal history of the area. They proposed two possible source rocks, Huai Hin Lat Formation in Triassic Pre-Khorat Group and Upper and Lower Permian Nam Duk Formation in the Saraburi Group. (1) The Huai Hin Lat Formation was deposited during the Late Triassic, which consists of lacustrine kerogen type I/II dominated by algal-derived organic matter with some humic higher land plant material with the potential for oil. It begins to generate oil in the Mid-Cretaceous time and reached peak oil window in the Tertiary inversion, as shown in Figure 2.4. Following Cretaceous burial, Schenk (2011)suggested the hydrocarbon migrated upward along faults into Permian carbonate reservoirs and possibly into Triassic synrift clastic reservoirs within structural traps. Finally, the oil cracked to gas following continued burial and thermal exposure. (2) The Upper and Lower Permian Nam Duk Formation included shallow marine to deltaic facies containing organic rich shales, micritic carbonates and coals, which have the potential to provide natural gas, and generate gas in the Tertiary.

The petroleum geochemistry of cutting samples from 4 wells; Dao Ruang-1, Kham Palai-1, Phu Lop-1 and Phu Wiang-1 well. From well report, Huai Hin Lat Formation have very low to low organic richness and poor petroleum potential with Kerogen type III/IV and have thermal maturity in the level of late mature to post mature, the details of data are as follows.

– Abolins (1993) studied cutting samples from Dao Ruang-1 well. The Huai Hin Lat Formation thickness is about 1,330 feet and consists of conglomerate, sandstone, claystone and limestone. TOC content about 0.15 -0.74 wt.% that indicates very low to low organic richness, and poor petroleum potential because the S2 value is less than 0.5 mg HC/g rock. Moreover, the samples are in late mature stage (1.07-1.17 %Ro) with kerogen type III/IV.



Figure 2.4 1D Thermal modeling result (Porwal and Jain, 2008).

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- From Kham Palai well report (Unocal Petroleum, 1994), the thickness of Huai Hin Lat Formation is not less than 1,500 feet. This unit consists of sandstone, siltstone, claystone and limestone which yielded TOC value from 0.01-0.52 %wt. (very low to low organic richness) with post mature level (1.81-1.95%Ro).

- Villain et al. (1994) studied geochemistry of Phu Lop-1 cutting samples with Rock-Eval pyrolysis. The Huai Hin Lat Formation thickness is about 279 feet with predominate siltstone, some claystone, minor sandstone and traces of limestone. The Huai Hin Lat Formation has very low organic richness (TOC 0.03-0.12 wt.%) and poor petroleum potential (S2 0.35-1.00 mg HC/g rock). - Huai Hin Lat Formation of Phu Wiang-1 thickness is about 1,040 feet, which consisted mainly of claystone, sandstone, shale and siltstone. One cutting sample from this unit, dark grey claystone at depth 11,299 feet, had TOC content 0.215 wt.% (very low organic richness) and S2 0.13-0.33 mg HC/g rock (poor petroleum potential) (Kaye, 1998).

Outcrop samples of Triassic Pre-Khorat were studied by Phillips Petroleum Company (1982) and Unocal Petroleum (1994). The samples had low to very high organic richness (TOC 0.59-5.76 wt.%) and poor hydrocarbon potential (S2 0.02-0.88 mg HC/g rock) with kerogen type III/IV. Thermal maturity of outcrop samples is peak mature to post mature state (0.98-2.23%Ro). Moreover, Khositchaisri (2012) had studied the petroleum geochemistry of Huai Hin Lat Formation in Amohoe Nam Nao, Phetchabun Province and Amphoe Chumpae, Khon Kaen Province. By studying outcrop samples, the Huai Hin Lat Formation has low to very high organic richness (TOC 0.79-13.80 wt.%) and poor source rock potential (S2 0.06-1.97 mg HC/g rock) with the thermal maturity level ranging from late mature to post mature (1.05-2.04 %Ro) and the organic matter is kerogen type III. Biomarkers data indicates the original source rock was from mixed sources between terrigenous and marine organic matter, which deposited in a reducing environment, as show in Figure 2.5. The summarized of previous studies are shown in Table 2.2.

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Figure 2.5 (a) Pr/nC_{17} versus Ph/nC_{28} plot and (b) ternary diagram of $C_{27}-C_{28}-C_{29}$ regular steranes of Huai Hin Lat Formation outcrop samples by Khositchaisri (2012).

Table 2.2 Summary of organic richness, potential to generate petroleum, kerogen type and thermal maturity level of cutting and outcrop from Huai Hin Lat Formation in this study compare with previous studies.

		тос	52	Kerogen	Vitrinite
	Sample	(u+ 0()		type	reflectance
		(Wt.%)	(mg HC/g rock)		(%Ro)
Abolins (1993)	Dao Ruang-1	0.15-0.74	0.69	III/IV	1.07-1.17
	cutting				
Unocal	Kham Palai-1	0.01-0.52	-	-	1.81-1.95
Petroleum (1994)	cutting				
Villain et al.	Phu Lop-1 cutting	0.03-0.12	0.35-1.00	-	-
(1994)					
Kaye (1998)	Phu Wiang-1	0.215	0.13-0.33	-	-
	cutting				
Phillips	Outcrop	0.59-4.51	0.02-0.65	III/IV	0.98-2.23
Petroleum					
Company (1982)					
Unocal	Outcrop	1.66-5.76	0.13-0.88	-	1.67-2.07
Petroleum (1994)					
Khositchaisri	Outcrop	0.79-13.80	0.06-1.97	III	1.05-2.04
(2012)					

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CHAPTER III

METHODOLOGY

A total of 22 cuttings samples from 10 exploration wells were made available for this study by the Department of Mineral Fuels (DMF). The method used in this study can be summarized as a flow chart as shown in Figure 3.1.



Figure 3.1 Flow chart of method used in this study.

3.1 Literature review

Literature review of the previous studies and published papers were undertaken to understand the general geology, stratigraphy, source rock geochemistry and petroleum system of the Khorat Plateau. In this study, previous studies reports, final well reports were well logging were also reviewed to help in choosing cutting samples.

3.2 Cutting samples

Twenty two cutting samples from 10 exploration wells in the Khorat Plateau; Chonnabot-1, Dao Ruang-1, Dong Mun-1, Dong Mun-2, Kaset Sombun-1, Kham Palai-1, Non Sung-1, Phu Lop-1, Phu Phra-1 and Phu Wiang-1 containing Huai Hin Lat Formation were selected for this study. The samples intervals were selected from shale and claystone intervals based on gamma ray and resistivity logs of the wells which were drilled using water-based mud. The locations of these exploration wells are shown in Figure 1.1 and their coordinates are listed in Table 3.1.

Each sample in this study was combined from many bags of cuttings samples because each cutting bag was collected every 10 feet of drilling depth and the quantity of cuttings in one bag is not enough for studying petroleum geochemistry. So, one combined sample represents a depth range between 30-200 feet and has a weight of about 40-70 grams.

All cutting samples were studied for lithology under a binocular microscope. After that, they were crushed using an agate ball mill. The ball mill is washed with distilled water and then rinsing with acetone followed by dichloromethane before grinding the next sample, to prevent organic matter contamination from previous sample (Jankaew, 2002).

		Loc	ation	Huai Hin Lat	Sample Depth (ft.)		
Sample name	Imple Well name Latitude Longitude (E) (N)		Formation Depth Range (ft.)	Range	Average		
CNB1	Chonnabot-1 ⁽¹⁾	15 ⁰ 52' /19"N	102 ⁰ 26' 35"E	9 31/1-11 810	9,470-9,610	9,540	
CNB2	Chonnabot 1	15 52 47 10	102 20 JJ L	7,514 11,010	10,540-10,690	10,615	
DR1		16 ⁰ 27' 10"N	102 ⁰ 10' 41"E	3 280 4 610	3,580-3,720	3,650	
DR2	Dao Ruang-1	10 27 19 1	102 10 41 E	3,200-4,010	4,360-4,460	4,410	
DM11					7,740-7,860	7,800	
DM12	Dong Mun-1 ⁽³⁾	16 [°] 47' 36"N	103 [°] 11' 52"E	7,685-8,870	8,130-8,230	8,180	
DM13					8,650-8,750	8,700	
DM21	Dong Mun-2 ⁽⁴⁾	16 [°] 45' 42"N	103 [°] 18' 27"E	7,750-9,054	7,750-7,860	7,805	
KSB1					860-1,000	930	
KSB2	Kaset Sombun-1 ⁽⁵⁾	10 [°] 12' 30"N	101 [°] 55' 43"E	678-3,105	1,610-1,750	1,680	
KSB3					2,910-3,060	2,985	
KPL1		10 ⁰ 421 15"N	104 ⁰ 201 20.7F	7.405.0.007	7,420-7,520	7,470	
KPL2	KIIdIII Palai-1	10 45 15 N	104 39 30 E	1,425-0,921	7,920-8,020	7,970	
NS1	Non Sung 1 ⁽⁷⁾	16 ⁰ 02' 27"N	101 ⁰ 25' 25"5	2 007 6 664	5,550-5,700	5,625	
NS2	NON SUNG-1	10 UZ 57 N	104 33 33 E	5,997-0,554	6,200-6,350	6,275	
PL1	Dbu Lon 1 ⁽⁸⁾	17 ⁰ 11' 47"N	102 ⁰ 24' 02"F	4.076.4.264	4,106-4,180	4,144	
PL2	Phu Lop-1	17 11 47 N	105 54 05 E	4,076-4,364	4,298-4,364	4,331	
PP1				1	6,620-6,780	6,700	
PP2	Dhu Dhra 1 ⁽⁹⁾	17 ⁰ 14' 02"N	102 ⁰ EOL 41"E	6 229 9 760	6,790-6,910	6,850	
PP3	Phu Phra-1	17 14 23 N	105 50 41 E	0,200-0,760	7,950-8,150	8,050	
PP4					8,400-8,430	8,415	
PW1	Phu Wiang-1 ⁽¹⁰⁾	15 [°] 53' 00"N	102 [°] 26' 30"E	10,771-11,811	11,339-11,545	11,442	

Table 3. 1 Cutting sample wells, locations and depth.

⁽¹⁾(ESSO Exploration and Production Khorat Inc, 1982), ⁽²⁾(Dorman and Adams, 1994), ⁽³⁾(Gearhart Geodata Services Ltd, 1990), ⁽⁴⁾(Benesch et al., 1991)⁽⁵⁾(ESSO Exploration and Production Khorat Inc, 1983)⁽⁶⁾(Halliburton Drilling Systems, 1993), ⁽⁷⁾(ESSO Sakon, 1985), ⁽⁸⁾(TOTAL Khorat Limited, 1994), ⁽⁹⁾(ESSO Exploration Inc, 1984), ⁽¹⁰⁾(Amerada Hess Exploration (Thailand) Co Ltd, 1998)

3.3 Total organic carbon (TOC)

Total organic carbon (TOC) is the first screening parameter for determining the petroleum potential of source rocks. All cutting samples were analyzed for TOC with the Total Organic Carbon Analyzer HT 1300 at the Environmental Research Institute, Chulalongkorn University (ERIC) to determine their potential as source rock.

Approximately 200 mg of the powdered sample was put into a porcelain crucible and inorganic carbon in the form of carbonates is removed with concentrate 2 N hydrochloric acid (HCl) until the reaction of the de-carbonating stopped (no bubbling). Then, the sample was dried at 105°C to evaporate off HCl from the sample. Then, the samples were analyzed with the Total Organic Carbon Analyzer HT 1300 by burning in an oxygen atmosphere at 1,200°C. The detector measured the amount of carbon dioxide and calculated the amount of carbon in grams per kilogram or carbon percentage to sample weight. Table 3.2 shows the classification of source rock richness between shale and carbonate (Peters and Cassa, 1994).

Course Dotoutial	тос	EOM	
Source Potential	Shale Carbonate		(ppm)
Poor	<0.5	<0.2	<500
Fair	0.5 - 1	0.2-0.5	500-1,000
Good	1 – 2	0.5-1.0	1,000-2,000
Very good	2 – 4	1.0-2.0	2,000-4,000
Excellent	>4	>2.0	>4,000

Table 3.2 Classification of source rock richness based on Total Organic Carbon content and Extractable organic matter (Peters and Cassa, 1994).

3.4 Vitrinite reflectance (%Ro)

Eighteen cutting samples were analyzed by Core Laboratories (Core Lab), Malaysia for vitrinite reflectance. Vitrinite reflectance is a technique for determining the thermal alteration of source rocks. Origin of vitrinite particles came from terrigenous higher plants which are found dispersed throughout most sedimentary rock samples which are younger than Silurian in age, because land-plant communities were well developed by Devonian time (Peters et al., 2005a). When vitrinite reflectance increases regularly with increased thermal alteration, a reflectance measurement can be used to determine the degree of thermal maturation of that sediment. In order to perform reflectance readings, the cuttings or pulverized rock fragments are embedded in an epoxy resin plug. The hardened plug is polished and the reflectance of the individual vitrinite particles identified is measure under reflected light microscope. A histogram of reflectance values for the sample is reported (Core Lab).

The number of individual reflection measurements will be dependent on the abundance of vitrinite particles in the sample. Vitrinite reflectance may be correlated with the main zones and thresholds of petroleum generation as in Table 3.3 (Peters and Cassa, 1994).

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	Level of thermal maturity		Vitrinite	Production Index	Tmax ([°] C) for kerogen			
			Reflectance	(DI = S1/(S1 + S2))	type			
			(Ro, %)	(FI = 31/(31+32))	Type I	Type II	Type III	
	Immat	ture	0.2-0.6	<0.10	<445	<435	<440	
		Early	0.6-0.65	0.10-0.25				
	Mature	Peak	0.65-0.9	0.25-0.40	445-455	435-460	440-470	
		Late	0.9-1.35	>0.40				
	Post m	ature	>1.35	-	>455	>460	>470	

Table 3.3 Parameters for describing the level of thermal maturation of source rock by %Ro, PI (Peters and Cassa, 1994), and Tmax (Bacon et al., 2000).

3.5 Rock-Eval pyrolysis

The Rock-Eval pyrolysis method is the most basic petroleum geochemical analysis of source rocks. Laboratory pyrolysis of the organic matter in sedimentary rocks aims to parallel the changes in the subsurface and provides a useful technique for characterizing organic matter, which can evaluate the petroleum-generative potential and thermal maturity of rocks. Twenty two cutting samples of source rock were analyzed by PTT Research and Technology Institute (PTT RTI), PTT Public Company Limited, Wangnoi, Ayutthaya.

Rock-Eval pyrolysis is a technique that decomposes organic matter by heating in an inert atmosphere, usually helium or nitrogen, followed by the recovery and measurement of the volatile components. There are three peaks (S1, S2 and S3) which are recorded from pyrolysis as follows, as shown in Figure 1.2 (Peters, 1986).

Rock-Eval pyrolysis parameter can divide 2 measurements, direct measurements and derived measurements (Peters and Cassa, 1994). Direct measurements are S1, S2, S3 and Tmax. Derived measurements are hydrogen index, oxygen index, production index and potential index.

– S1 peak is the amount of free or adsorbed hydrocarbon C_1 - C_{23} in the rock generated under the temperature of 300°C which is present in the rock before pyrolysis, measured as mg hydrocarbon/g rock (mg HC/g rock). S1 minimum value for good source rock is 1.0 mg HC/g rock

- S2 peak is the amount of hydrocarbons generated from the thermal breakdown of kerogen or from C_{24+} bitumen by heating up to 600°C, measured as mg HC/g rock. S2 minimum value for good source rock is 5.0 mg HC/g rock.

- S3 peak is the trapped carbon dioxide, which is released during pyrolysis up to 390° C. This value is proportional to the oxygen present in the kerogen. The unit of measurement is mg CO₂/g rock. Carbonate rocks may increase S3 values.

- Tmax is the temperature at the maximum amount of S2 hydrocarbons generated which is supposed to increase with increasing maturity.

- Hydrogen Index (HI) corresponds to the quantity of hydrocarbon from S2 relative to the TOC (HI = $(S2 \times 100)/TOC$) in the sample, which is measured as mg HC/g TOC. HI is a measure of the hydrogen richness of the source rock.

- Oxygen Index (OI) corresponds to the quantity of carbon dioxide from S3 relative to the TOC (OI = $(S3 \times 100)/TOC$) in the sample, which is measured as mg CO₂/g TOC. OI is a measure of the oxygen richness of a source rock and can be used in conjunction with HI to estimate the quality and thermal maturity of source rocks.

- Production Index (PI) is defined as the ratio S1/(S1+S2), which is the ratio of already generated hydrocarbon to potential hydrocarbon. Low ratio indicates either immaturity or extreme post mature organic matter. And, high ratio indicates either the mature stage or contamination by migrated hydrocarbons or drilling additive. The PI values increases with depth and associated hydrocarbon generation.

- Potential yield (PY) is the summation of S1 and S2 (S1+S2) that is quantifies the hydrocarbon generation potential.

Rock-Eval pyrolysis data can be used to estimate the organic matter type in rock samples by plotting HI values against OI values in the Pseudo-Van Krevelen diagram, as shown in Table 3.4 and Figure 1.3(b). In addition, maturation of the source rock samples can be classified using Tmax and PI as shown in Table 3.3. However, the range of Tmax depends on kerogen types contain in the samples and Tmax values for small S2 peaks (<0.2 mg HC/g TOC) are unreliable (Peters, 1986). Table 3.5 shows S2 and PY values that are used to describe potential source rocks.

Kerogen type	Hydrogen index (mg HC/g TOC)	Main product at peak
		maturity
I	>600	Oil
II	300-600	Oil
/	200-300	Oil/gas
Ш	50-200	Gas
IV	<50	None
	· 2 4 4 4	

Table 3.4 Kerogen type and expelled products based on Hydrogen index (HI) (Peters and Cassa, 1994).

Table 3.5 Parameters for classified the petroleum potential of source rocks ⁽¹⁾(Peters, 1986), ⁽²⁾(Tissot and Welte, 1984).

	- /////			
S	2 ⁽¹⁾	PY ⁽²⁾		
mg HC/g rock	Source Potential	mg HC/g rock	Source	
			Potential	
<2.5	Poor	<2.0	Low potential	
2.5-5.0	Fair			
5.0-10.0	Good	2.0-6.0	Moderate	
			potential	
10.0-20.0	Very good			
>20.0	Excellent	>6.0	High potential	

3.6 Kerogen typing

Sixteen cutting samples were analyzed by Core Laboratories (Core Lab), Malaysia. Kerogen typing is visual kerogen analysis. Kerogen is separated from the rock matrix. High-powered microscope examination of kerogen are done in transmitted light and under ultraviolet light to determine the thermal maturation state and whether the type or organic matter is favorable for petroleum generation. The kerogen composition is reported as %alginite, plus fulorescent and nonfluorescent amorphous; % exinite/cutinite; %vitrinite and %inertinite. The ability of the various kerogen types to yield oil decreases in the following order: alginateexinite-vitrinite-inertinite. The color of the spore and pollen grains present is also used as an indicator of thermal maturation level. For visual kerogen analysis, standard palynological techniques are used to separate the kerogen from the rock matrix. The isolated organic matter (kerogen) is mounted on glass slide and examined under a high powered Leitz microscope.

3.7 Extractable organic matter (EOM)

Extractable organic matter (EOM) is a technique which extracts soluble organic matter from rock sample by using organic solvents and a soxhlet extraction apparatus. The powdered cutting samples were loaded into cellulose thimbles and covered with cotton wool, both cellulose thimbles and cotton wool were extracted with dichloromethane in soxhlet apparatus for at least two hours before using. The organic solvent used in the extraction is a mixture of dichloromethane (93%) and methanol (7%). Approximately 550 ml of solvent mixture was divided into two portions. First portion, 200 ml of solvent was poured into a 1,000 ml round bottom flask with a few anti-bumping granules. Then, the flask was connected to soxhlet extractors and the powder filled thimble was put into the extractor with tweezers. Second portion, 350 ml of solvent was filled into the soxhlet apparatus that ensure the solvent volume was enough for recirculation. The sample was extracted at temperature of about 40° C for at least 48 hours. When the extraction was finished, the thimble was removed with tweezers and left to dry before wrapped in aluminum foil. All glassware and tweezers were cleaned with distilled water and followed with acetone and dichloromethane respectively before extracting the next sample.

The extract solution in round bottom flask was evaporated off with Rotary Vacuum Evaporator at a temperature of 40°C until the amount of solution is about 5 ml. Then, the sample solution was transferred into a 2-ml pre-weighted vial, which has been rinsed several times with dichloromethane. The vial was set on a stand and left for solvent to evaporate off and the vial has more space to transfer the remaining solution. This process may be repeated until all the sample solution is transferred to a vial and the flask was rinsed several times with dichloromethane to ensure no sample was left. The sample vial was left overnight in the fume hood before being re-weighted. The amount of total extracted organic matter left in the vial is the extractable organic matter (EOM) value. EOM criteria is shown as Table 3.2 (Peters and Cassa, 1994).

3.8 Separation of the extract

The sample extract was separated using a column chromatography method, which is a method commonly used to separate molecules in complex mixtures. In column chromatography, the stationary phase is packed into a vertical glass column and the mobile phase is added on the top and passed through the column by either gravity or external pressure. In this study, stationary phase is silica gel (70-230 mesh) and mobiles phase are n-pentane for saturated hydrocarbon fraction and n-pentane/dichloromethane (7:3 v/v) for aromatic hydrocarbon fraction. The column used in separation was prepared from a Pasteur pipette that is about 22 cm long and 5.7 mm in diameter.

Before separation, the column needed to be rinsed with acetone and dichloromethane to prevent contamination. Silica gel was activated at 120° C for at least 8 hours and cooled in a desiccator. Pasteur pipette was plugged with a small amount of cotton wool to prevent the adsorbent from leaking out. Approximately 0.6 g of activated silica was added into the column. The n-pentane was added to the top of the silica gel for pre-eluting the column.

The extracted sample, about 10-20 mg, is dissolved in a minimum volume of n-pentane. This solution is loaded onto the top of column. Once the sample is in the column, 2.0 ml of n-pentane is added to the top and ready to begin the elution process by gravity for saturated hydrocarbon fraction. The eluted solvent is collected in a first pre-weighted vial. Then, the column is eluted again with 2.0 ml of n-pentane/dichloromethane for aromatic hydrocarbon fraction and eluted solvent is collected in a second pre-weighted vial. Both vials are left overnight in the fume hood before being re-weighted.

3.9 Gas Chromatography (GC-FID)

Gas chromatography (GC-FID) is a type of chromatography used to separate volatile components of a mixture. A small amount of the sample to be analyzed is drawn up into a syringe and the syringe needle is placed into a hot injector port of the gas chromatography. The injector is set to a temperature higher than the components boiling points, which caused components of the mixture evaporate into the gas phase. A carrier gas flows through the injector and pushes the gaseous components of the sample onto the GC column. It is within the column that separation of the components takes place. After components of the mixture move through the GC column, they reach a flame ionization detector (FID). The detector sends a signal to the recorder which results in a peak on the chromatogram. The area of the peak is proportional to the number of molecules generating the signal (Amonsit and Petchsom, 1992).

In this study, the whole samples extract were dissolved in dichloromethane and analyzed with Agilent 6890N GC of the Department of Mineral Fuel (DMF) Laboratory, Phra Padaeng, Samut Prakan. This GC is equipped with a 30 m long HP-5 (5% Phenyl Methyl Siloxane) with 320 μ m inner diameter and 0.25 μ m film thickness. Initial column temperature and hold time were 70°C and 4 minutes, respectively. The column temperature was increased by 5°C/minute up to 310°C and held at 310°C for 53 minutes. The total analysis time is 105 minutes. The injector was set at 325°C in the splitless, helium gas was used as the carrier gas with a head pressure of 9.52 psi.

3.10 Gas Chromatography- Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometry (GC-MS) is an instrumental technique, comprising the gas chromatography (GC) coupled to the mass spectrometer (MS) to identify complex mixtures within a sample. The sample solution is injected into the GC, flows through the column and separated into compounds. The separated substances emerge from the column opening, and then flow into the MS. MS identifies compounds by the mass of the analysis molecule (Amonsit and Petchsom, 1992).

In this study, the saturated hydrocarbon fraction was dissolved in n-pentane and analyzed with Agilent 7890B GC and Agilent 7000C GC/MS at Scientific and Technological Research Equipment Centre (STREC), Chulalongkorn University, with the ion source temperature of 250°C and ionizing energy of 70eV. The column used in this study is a 30 m long HP-5MS (5% Phenyl Methyl Siloxane) with 250 μ m inner diameter and 0.25 μ m film thickness. Starting temperature is 80°C and held for 2 minutes. The column temperature is heated from 80°C to 310°C at 4°C/minutes and held for 30 minutes at 310°C. The total analysis time is 90 minutes. Data were acquired in selected-ion-monitored for compound identification and integration: nalkane (m/z 85), terpanes and hopanes (m/z 191) and steranes (m/z 217).

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CHAPTER IV

RESULT AND INTERPRETATION

For this study, twenty two cutting samples were taken from ten exploration wells, including Chonnabot-1, Dao Ruang-1, Dong Mun-1, Dong Mun-2, Kaset Sombun-1, Kham Palai-1, Non Sung-1, Phu Lop-1, Phu Phra-1 and Phu Wiang-1. The samples depth of each exploration well in this study can be summarized in Figures 4.1 and 4.2. Samples were selected based on cutting availability within the Huai Hin Lat Formation in the study area and were analyzed for quantity of organic matter, quality of organic matter, thermal maturation and biomarkers. The results are interpreted and shown below.

Cutting samples were studied for lithology under a binocular microscope and shown detail in Table 4.1. Most samples consisted mainly of claystone 40-100% and minor of siltstone and sandstone. Samples are divided into two groups based on claystone color; reddish-brown group and grey to black group. Moreover, three samples from Phu Phra-1 well (PP2, PP3 and PP4) consisted of only black shale.

Sample	Sample Dept	h (ft.)	3 FR M M 1 3 M 5 16 5
name	Depth range	Average depth	GKORN UNIVERSITY Lithology
CNB1	9,470-9,610	9,540	Claystone: reddish-brown (100%)
CNB2	10,540-10,690	10,615	Claystone: dark grey (90%) Siltstone: reddish-brown (10%)
			Sandstone: light grey, grey and dark grey (50%)
DR1	3,580-3,720	3,650	Claystone: white to light grey (40%)
			Shale: dark grey (10%)
200	42(0 4 4(0	4 4 1 0	Sandstone: light grey to grey (60%)
UKZ	4,500-4,400	4,410	Claystone: light grey to grey (40%)
			Claystone: reddish-brown to dark reddish-brown (50%)
DM11	7,740-7,860	7,800	Siltstone: reddish-brown (40%)
			Sandstone: reddish-brown (10%)
	9 120 9 220	9 1 9 0	Claystone: reddish-brown (60%)
DIVITZ	0,100-0,200	0,100	Siltstone: brown (40%)

Table 4.1 Cutting	samples	studied: sam	ple name.	, sample o	depth	and lithology.

Sampla	Sample Dept	:h (ft.)			
name	Depth range	Average depth	Lithology		
			Claystone: reddish-brown (60%)		
DM13	8,650-8,750	8,700	Siltstone: reddish-brown (30%)		
			Sandstone: quartz and calcite (10%)		
			Claystone: reddish-brown (60%)		
DM21	7,750-7,860	7,805	Siltstone: reddish-brown (35%)		
			Sandstone: white and reddish-brown (5%)		
	860 1 000	020	Claystone: reddish-brown (90%)		
N2R1	860-1,000	930	Calcite: white and light reddish-brown (10%)		
KCDO		1 (0 0	Claystone: reddish-brown (50%)		
NODZ	1,010-1,750	1,000	Siltstone: reddish-brown (50%)		
	2 0 1 0 2 0 6 0	2 0.95	Siltstone: reddish-brown (50%)		
N2R2	2,910-3,060	2,965	Claystone: grey (50%)		
			Sandstone: transparent, light reddish-brown (40%)		
KPL1	7,420-7,520	7,470	Claystone: reddish-brown (30%)		
			Siltstone: reddish-brown (30%)		
			Sandstone: transparent, light reddish-brown (40%)		
KPL2	7,920-8,020	7,970	Claystone: reddish-brown (30%)		
		J.	Siltstone: reddish-brown (30%)		
			Sandstone: transparent, light grey (35%)		
NIS1	5 550-5 700	5 6 2 5	Siltstone: grey (25%)		
1121	5,550-5,700	9.1416.10	Claystone: grey (25%)		
	C	N NIN ALON	Claystone: reddish-brown (15%)		
NS2	6,200-6,350	6,275	Claystone: black (100%)		
			Sandstone: reddish-brown and grey (60%)		
PL1	4,106-4,180	4,144	Siltstone: reddish-brown (20%)		
			Claystone: reddish-brown (20%)		
PI 2	1 298-1 361	1 331	Sandstone: grey and brown (60%)		
	4,270 4,304	4,551	Claystone: reddish-brown (40%)		
DD1	6 620-6 780	6 700	Claystone: light grey (50%)		
	0,020 0,100	0,700	Siltstone: light grey (50%)		
PP2	6,790-6,910	6,850	Shale: black (100%)		
PP3	7,950-8,150	8,050	Shale: black (100%)		
PP4	8,400-8,430	8,415	Shale: black (100%)		
			Siltstone: dark grey (30%)		
D\\\/1	11 330 <u>-</u> 11 5/15	11 // 0	Limestone: grey (30%)		
1. AA T	11,339-11,545	11,442	Claystone: grey (30%)		
			Shale: grey (10%)		

Table 4.1 Cutting samples studied: sample name, sample depth and lithology (cont.).



Figure 4.1 Location of exploration wells in different petroleum provinces in the Khorat Plateau.



Figure 4.2 The cutting samples depths of each exploration wells from west to east in this study.

4.1 Quantity of organic matter

Quantities of organic matter in sedimentary rocks are used to consider a potential of rocks to be petroleum source rock. Organic matter in the source rock should reflect quantity of the petroleum capable of generating from the source rock. In this study, the parameters used to determine organic richness; total organic carbon (TOC) content, S2 and potential yields (PY) from Rock-Eval pyrolysis, and extractable organic matter (EOM).

4.1.1Total organic carbon content (TOC)

TOC is the first screening parameter for measuring the potential for petroleum generation of source rocks. Twenty two cuttings samples from ten exploration wells were analyzed for TOC content by TOC analyzer HT-1300 at Environmental Research Institute (ERIC), Chulalongkorn University.

<u>Result</u>

The TOC values of twenty two cutting sample from ERIC range from 0.018 wt.% to 2.950 wt.%, which classifies them as having poor to very good source potential. Only seven of the samples have TOC values more than 1.0 wt.%, indicating good to very good hydrocarbon generating potential. TOC values for each sample are summarized in Table 4.3 and Figure 4.3.

Most cutting samples have very low organic content (TOC less than 0.5 wt.%), suggesting poor potential to generate petroleum. Six cutting samples; DR1, DM11, DM12, DM21, NS2 and PW1, contain rocks with low to moderate organic contents (TOC 0.530-1.600 wt.%) indicative of fair to good potential for petroleum generation. PP2, PP3 and PP4 samples have high organic content (TOC 2.760, 2.950 and 2.630 wt.% respectively) indicating very good hydrocarbon generating potential.



Figure 4.3 Present-day TOC from this study sorted by exploration wells.

TOC data from laboratory is present-day TOC, which is decreased from original TOC (TOC₀) with thermal maturity due to the conversion of organic matter to hydrocarbon. The TOC measurement may include carbon contain in oil or bitumen, which may not be completely removed during the typical decarbonation step before the TOC analysis. The measured TOC values can be converted to the TOC₀ with a correction factor based on the type of kerogen and level of maturity as shown in Table 4.2

Because visual kerogen analysis (Table 4.5) revealed that samples contain mostly of inertinite (type IV) and amorphinite of non-fluorescent amorphous (Type III/IV) which could originally be organic matters of kerogen type I-III before experiencing thermal maturation, the minimum TOC_0 has been calculated from kerogen type III and maximum TOC_0 has been calculated from kerogen type I using criteria of vitrinite reflectance more than 1.0%. The range of TOC_0 values are shown in Table 4.3 and Figure 4.4, which classifies them as having poor to excellent source potential

Karagan tuna	Vitrinite reflectance				
Kelogen type –	<0.8	0.8-1.0	>1.0		
I	1.00	2.00	2.50		
Π	1.00	1.33	2.00		
III	1.00	1.05	1.15		

Table 4.2 Correction factor TOC values (Hunt, 1996).

From Figure 4.1, ten exploration wells in this study can be separated into three petroleum provinces; Chum Phae Area, Khon Kaen-Ubon Area and Phu Phan Anticlinorium. TOC_0 of each petroleum province is summarized in below and shown in Figures 4.5.

Chum Phae Area has two wells; Kaset Sombun-1 and Dao Ruang-1. Two samples from Kaset Sombun-1 (KSB1 and KSB2) mainly composed of reddish-brown claystone and siltstone and one sample (KSB3) consisted of grey claystone. They are considered very low in organic richness (poor source rock potential). Two samples from Dao Ruang-1 (DR1 and DR2) mainly consisted of light grey to grey to dark grey sandstone and white to light grey to grey claystone. Both samples are considered having very low to moderate organic richness (poor to good source rock potential).

Khon Kaen-Ubon Area has Chonnabot-1 and Phu Wiang-1 wells, which Phu-Wiang-1 well is a redrilled Chonabot-1 well in 1997 by Amerada Hess Exploration (Thailand) Co. Ltd. (ATOP Technology Co Ltd, 2006). Two cutting samples of Chonnabot-1 (CNB1 and CNB2) and one cutting samples of Phu Wiang-1 (PW1) were analyzed. CNB1 consisted of reddish-brown claystone, CNB2 consisted of dark grey claystone and reddish-brown claystone, and PW1 consisted of dark grey siltstone, grey limestone, grey claystone and grey shale. Both Chonnabot-1 samples are considered very low in organic richness (poor source rock potential), while PW1 is considered moderate to high organic richness (good to very good source rock potential).

Sample	Average depth	Present-day TOC		٦ kero)	TOC _o (kerogen type III)		TOC ₀ (kerogen type I)		юм
name	(ft.)	(wt.%)	potential	(wt.%)	potential	(wt.%)	potential	(ppm)	potential
CNB1	9,540	0.174	Poor	0.200	Poor	0.435	Poor	1,829	Good
CNB2	10,615	0.126	Poor	0.145	Poor	0.315	Poor	2,022	Very good
DR1	3,650	0.530	Fair	0.610	Fair	1.325	Good	2,329	Very good
DR2	4,410	0.225	Poor	0.259	Poor	0.563	Fair	1,761	Good
DM11	7,800	1.500	Good	1.725	Good	3.750	Very good	10,676	Excellent
DM12	8,180	1.290	Good	1.484	Good	3.225	Very good	11,331	Excellent
DM13	8,700	0.327	Poor	0.376	Poor	0.818	Fair	3,607	Very good
DM21	7,805	1.330	Good	1.530	Good	3.325	Very good	11,900	Excellent
KSB1	930	0.041	Poor	0.047	Poor	0.102	Poor	141	Poor
KSB2	1,680	0.065	Poor	0.075	Poor	0.162	Poor	862	Fair
KSB3	2,985	0.041	Poor	0.047	Poor	0.102	Poor	909	Fair
KPL1	7,470	0.018	Poor	0.021	Poor	0.045	Poor	875	Fair
KPL2	7,970	0.225	Poor	0.259	Poor	0.563	Fair	517	Fair
NS1	5,625	0.074	Poor	0.085	Poor	0.184	Poor	794	Fair
NS2	6,275	1.600	Good	1.840	Good	4.000	Very good	1,152	Good
PL1	4,144	0.271	Poor	0.312	Poor	0.678	Fair	2,316	Very good
PL2	4,331	0.213	Poor	0.245	Poor	0.533	Fair	2,475	Very good
PP1	6,700	0.387	Poor	0.445	Poor	0.968	Fair	909	Fair
PP2	6,850	2.760	Very good	3.174	Very good	6.900	Excellent	2,935	Very good
PP3	8,050	2.950	Very good	3.393	Very good	7.375	Excellent	3,150	Very good
PP4	8,415	2.630	Very good	3.025	Very good	6.575	Excellent	2,411	Very good
PW1	11,442	0.960	Fair	1.104	Good	2.400	Very good	2,000	Very good

Table 4.3 Present-day TOC, original TOC (TOC $_{\rm O}$) based on type III and I kerogen, and EOM contents for cutting samples studied.



Figure 4.4 Original TOC (TOC₀) from this study sorted by exploration wells.



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Figure 4.5 Original TOC (TOC $_{0}$) results of cutting samples from each exploration well from west to east in this study.

Phu Phan Anticlinorium has six exploration wells; Dong Mun-1, Dong Mun-2, Phu Lop-1, Phu Phra-1, Kam Palai-1 and Non Sung-1. Samples from Dong Mun-1 (DM11, DM12 and DM13), Dong Mun-2 (DM21), Phu Lop1 (PL1 and PL2), Kham Palai-1 (KPL1 and KPL2) consisted of reddish-brown claystone, reddish-brown siltstone and reddish brown sandstone. DM11, DM12 and DM21 are considered to have moderate to high organic richness (good to very good source rock potential), while DM13, PL1, PL2, KPL1 and KPL2 are classified as having very low organic to low organic contents (poor to fair source rock potential). There are four samples of Phu Phra-1. PP1 consisted of light grey claystone and light grey siltstone that is considered very low to low organic richness (poor to fair source rock potential). PP2, PP3 and PP4 which consisted of black shale are considered as having high to very high organic richness (very good to excellent source rock potential). In this petroleum province, the north central part has high organic richness when compared with the eastern and western parts of the petroleum province.

4.1.2 Extractable organic matter (EOM)

Extractable organic matter (EOM) analysis involves grinding the fine-grained rock and extracting with organic solvents. After extraction, the solvents are removed by evaporation, which residue remaining is referred to as bitumen (Hunt, 1996). It contains the hydrocarbons plus asphaltic nitrogen, sulfur and oxygen compounds. The hydrocarbon range in extract may start as low as C_{11} or C_{12} that depend on the method of solvent removal. Furthermore, EOM is separated by column chromatography into the saturated and aromatics. The saturated fraction is used in biomarker study in this study.

<u>Result</u>

The EOM values of twenty two cutting samples are summarized in Table 4.2 and Figure 4.6, which range from 141 ppm to 11,900 ppm, indicating poor to excellent source potential. KSB1 is the only sample that has an EOM value less than 500 ppm, indicating poor potential to generate hydrocarbon. Only three samples have EOM more than 4,000 ppm; DM11, DM12 and DM21, indicating excellent source potential.



Figure 4.6 EOM results from this study sorted by exploration wells.

4.1.3 S2 and potential yields (PY) from Rock-Eval pyrolysis

Rock-Eval pyrolysis is used to evaluate the hydrocarbon-generative potential and thermal maturity of rocks. Samples were analyzed using Rock-Eval 6 analyzer at PTT Research and Technology Institute (PTT RTI), PTT Public Company Limited, Wangnoi, Ayutthaya. S2 and PY are parameters used to measure the potential for petroleum generation of source rocks. S2 represents the hydrocarbon generation through thermal cracking. Minimum value for good source rock is 5.0 mg HC/g rock. PY is the summation of S1 and S2 value.

<u>Result</u>

S2 values of twenty two cutting samples are shown in Table 4.4 and Figure 4.7. Most of the samples have S2 values less than 2.5 mg HC/g rock, which indicates poor source potential. Only three samples have S2 value from 2.5 to 5.0 mg HC/g rock; DM11, DM12 and DM21. No sample has on S2 value more than 5.0 mg HC/g rock.

PY values of twenty two cutting samples are shown in Table 4.4 and Figure 4.8. Most of samples have a PY value less than 2 mg HC/g rock indicating poor hydrocarbon generating potential. Only three samples, DM11, DM12, and DM21, have PY values more than 6 mg HC/g rock. PP2, PP3 and PW1 cutting samples have PY value from 2 to 6 mg HC/g rock that is considered to have moderate source potential.

Comple	A	S2		PY	
Sample	Average		Source		Source
name	depth (ft.)	mg HC/g rock	potential	mg HC/g rock	potential
CNB1	9,540	0.25	Poor	0.33	Low
CNB2	10,615	0.17	Poor	0.30	Low
DR1	3,650	0.83	Poor	1.40	Low
DR2	4,410	0.64	Poor	1.17	Low
DM11	7,800	3.38	Fair	8.07	High
DM12	8,180	3.87	Fair	9.64	High
DM13	8,700	0.74	Poor	1.77	Low
DM21	7,805	3.70	Fair	8.54	High
KSB1	930	0.41	Poor	0.71	Low
KSB2	1,680	0.24	Poor	0.42	Low
KSB3	2,985	0.29	Poor	0.41	Low
KPL1	7,470	0.24	Poor	0.38	Low
KPL2	7,970	0.26	Poor	0.42	Low
NS1	5,625	0.35	Poor	0.55	Low
NS2	6,275	0.37	Poor	0.68	Low
PL1	4,144	0.72	Poor	1.04	Low
PL2	4,331	0.59	Poor	0.77	Low
PP1	6,700	0.57	Poor	0.90	Low
PP2	6,850	1.33	Poor	2.55	Moderate
PP3	8,050	1.12	Poor	2.10	Moderate
PP4	8,415	0.73	Poor	1.79	Low
PW1	11,442	1.28	Poor	2.05	Moderate

Table 4.4 S2 and potential yields (PY) from Rock-Eval Pyrolysis results for cutting samples in the study area.



Figure 4.7 S2 results from this study sorted by exploration wells.



Figure 4.8 Potential yields (PY) results from this study sorted by exploration wells.

4.2 Quality of organic matter

Many organisms provide to the organic matter present in petroleum source rocks. These organisms differ in their contents of lignin, lipids, resin, etc. Organic matter type has important influence on the nature of the hydrocarbon products. So, the quality of organic materials is used to evaluate the potential of source rock. In this study, parameters used for the evaluation of the type of organic matter are: kerogen typing, hydrogen and oxygen indices (HI & OI) from Rock-Eval pyrolysis, and cross plot of S2 versus TOC.

4.2.1 Kerogen typing

The study of visual kerogen analysis is used to identify the types of kerogen present in the source rocks. There are four types of kerogen in sedimentary rocks. Type I composes of oil-prone kerogen, which has hydrogen-rich organic matter generally in lacustrine and some marine sediment. Type II composes of oil-prone and gas-prone kerogen that has hydrogen-rich organic matter mainly in marine sediment. Type III composes of gas prone kerogen that is low in hydrogen content, generally found in terrestrial sediment. Type IV composes of dead or inert carbon that has little or no generating capacity (Atta-Peters and Garrey, 2014).

<u>Result</u>

Sixteen cutting samples were analyzed by Core Laboratories (Core Lab), Malaysia and the percentages of macerals identified are shown in Table 4.5. Most samples contain 70-90 percent of inertinite, kerogen type IV. Except, KSB1 and PL1 which contained less than 20 percent inertinite, both samples have 76% and 77% of non-fluorescent amorphous of amorphinite respectively. Non-fluorescent amorphous originates from phytoplankton or bacterially derived or terrestrial plants (kerogen type I-III/IV) and has a character in transmitted light microscope as opaque dark brown to black minute particles and amorphous organic matter (Sawada et al., 2012).
			* * *			3	3									
Sample	Average	Amorp (Type I	hinite -III/IV)			(Typ	nite e I/II)			OPK	Vitrinite	Semi fusinite	Inertinite	,	Rec. of	e H
name	depth (ft.)	NF.A . %	F.A %	∢ %	υ%	s %	к %	% SB	L %	%	Type III %	Type IV %	Type IV %	Preserv.	Organic Matter	TAS
CNB1	9,540	27	1	ï	x	1	х	x		2	1	,	02	U	D-M	5
CNB2	10,615	17	1	5	9	Ļ	9	3	ы	2	1	а	80	X	P-M	2
DR1	3,650	26	ī	ī	Ţ.	Ļ	x	x	ı	1	3	г	02	N	U	5-5/6
KSB1	930	76	1	5	7	7	9	9	\leftarrow	4	9	я	20	Z	P-M	5-5/6
KSB2	1,680	22	ŝ	ï	1	1	Ţ	£	7	2	1	,	20	X	M-4	5-5/6
KSB3	2,985	00	1	ĩ	3	1	9	2	ч	2	3	а	06	X	U	5/6-6
KPL1	7,470	2	1	î	ε	7	Ļ	ε	r.	3	£	Б	06	X	٧P	5/6-6
KPL2	7,970	18	1	ä	-	Ļ	9	2	-	4	3	4	75	X	P-M	5/6-6
NS2	6,275	16	ŕ	î	τ	Ţ	c	ε	Ŀ	1	3	Б	80	Z	DN	6-6/7
PL1	4,144	22	1	ä	2	Ţ	3	2	a.	2	1	a	20	N	N	9
PL2	4,331	15	1	Ţ	ĸ	Ţ	ε	E	\leftarrow	4	1	Б	80	X	٧P	5-5/6
PP1	6,700	2	1	ĩ),	-	X	X	а	2	3	а	90	V	VP-P	5/6-6
PP2	6,850	16	Ē	Ē	6	Ţ	6	6	E	1	3	Б	80	X	DN	5/6-6
PP3	8,050	5	1	ĩ	X	7	3	X	а	2	3	a	06	M-G	U	5/6-6
PP4	8,415	15	1	Ē	6	Ţ	6	6	r.	2	3	г	80	N	U	9
PW1	11,442	18	1	ĩ	x	1	x	x	ı.	2	5	,	75	W	ŋ	6-6/7
NF.A: Non A: Alginite; OPK: Oil Pr	Fluorescent / C: Cutinite; S one Kerogen;	Amorphou S: Sporinite ; TAS: The	Is; F.A: Flu e; R: Resin rmal Alte	uorescing lite; SB: S ration Sc	g Amc Suberi sale;	irphou: nite; L:	Lipiod	etrinite								

Table 4.5 Visual keroren and TAS data of cuttine samples in the study area.

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G: Good; M: Moderate; P: Poor

4.2.2 Hydrogen index (HI) and oxygen index (OI) from Rock-Eval pyrolysis

Rock-Eval pyrolysis data is used to describe the type of kerogen in rock samples by using a graph plotted between hydrogen index (HI) and oxygen index (OI), called Pseudo-Van Krevelen diagram.

<u>Result</u>

The Rock-Eval pyrolysis results from this study are shown in Table 4.6. HI values for each sample against the depth are shown in Figure 4.9. HI and OI plot of samples are shown in Figure 4.10. Most cutting samples have HI values between 50-200 mg HC/g TOC and 200-300 mg HC/g TOC, which indicates kerogen type III (gas-prone organic matter) and mixed kerogen type II/III. Five samples (DM11, DM12, DM21, PL1 and PL2) show HI values greater than 300 mg HC/g TOC, which indicates oil-prone Type II kerogen. However, in the case of samples PL1 and PL2 due to very low TOC contents of the samples, which may lead to relatively high HI values, the interpretation of kerogen type (i.e. type II) may not be justified. These two samples also have very high OI values (Figure 4.10) Very low TOC content of these samples accompanied with high S3 values are the reason for their apparent high OI values. High S3 values in these two samples may be caused by their high carbonate contents. However, this study does not analyze carbonate content of the samples, therefore this cannot be verified by this study. Moreover, two samples (NS2 and PP4) have HI values less than 50 mg HC/g TOC, which indicates kerogen type IV.

Sample name	Average depth (ft.)	S1	S2	S3	Tmax (°C)	TOC ⁽¹⁾	王	ō	Ы	ΡY
CNB1	9,540	0.08	0.25	0.54	411	0.11	227	491	0.24	0.33
CNB2	10,615	0.13	0.17	0.75	380	0.15	113	500	0.43	0.30
DR1	3,650	0.57	0.83	0.45	341	0.50	166	90	0.41	1.40
DR2	4,410	0.53	0.64	0.52	323	0.23	278	226	0.45	1.17
DM11	7,800	4.69	3.38	0.40	357	1.01	335	40	0.58	8.07
DM12	8,180	5.77	3.87	0.46	375	1.14	339	40	0.60	9.64
DM13	8,700	1.03	0.74	0.65	327	0.27	274	241	0.58	1.77
DM21	7,805	4.84	3.70	0.74	360	1.08	343	69	0.57	8.54
KSB1	930	0.30	0.41	0.16	354	0.13	315	123	0.42	0.71
KSB2	1,680	0.18	0.24	0.18	345	0.08	300	225	0.43	0.42
KSB3	2,985	0.12	0.29	0.35	364	0.15	193	233	0.29	0.41
KPL1	7,470	0.14	0.24	0.18	344	0.08	300	225	0.37	0.38
KPL2	7,970	0.16	0.26	0.21	335	0.10	260	210	0.38	0.42
NS1	5,625	0.20	0.35	0.35	431	0.17	206	206	0.36	0.55
NS2	6,275	0.31	0.37	0.75	361	1.50	25	50	0.46	0.68
PL1	4,144	0.32	0.72	2.20	340	0.23	313	957	0.31	1.04
PL2	4,331	0.18	0.59	1.52	340	0.16	369	950	0.23	0.77
PP1	6,700	0.33	0.57	1.00	449	0.26	219	385	0.37	0.90
PP2	6,850	1.22	1.33	1.26	425	2.08	64	61	0.48	2.55
PP3	8,050	0.98	1.12	1.56	426	1.66	67	94	0.47	2.10
PP4	8,415	1.06	0.73	0.70	425	1.69	43	41	0.59	1.79
PW1	11,442	0.77	1.28	1.27	373	0.81	158	157	0.38	2.05

Table 4.6 Rock-Eval Pvrolvsis results from cutting samples in the study area.

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Figure 4.9 HI results from this study sorted by exploration wells.



Figure 4.10 Diagrams for Hydrogen Index (HI) versus Oxygen Index (OI) for cutting sample in this study sorted by exploration wells.

4.2.3 TOC versus S2

S2 value from Rock-Eval pyrolysis can be used to evaluate the properties of organic material within a source rocks to plot a graph S2 versus present-TOC is an effective tool. This diagram uses a linear regression curve on the S2 versus TOC, which is the way of calculating HI. The diagram shows the petroleum potential and the type of kerogen (Yalçın et al., 2006).

<u>Result</u>

In Figure 4.11, most of the cutting samples consist predominantly of kerogen type II, type II/III and III. Four samples; NS2, PP2, PP3 and PP4, indicate kerogen type IV, with good to very good potential from TOC value but poor potential from S2 value.

TOC value consists of three components; the carbon in extractable organic matter (EOM carbon or S1 peak), convertible carbon (S2 peak) and residual carbon fraction (Jarvie, 1991). The EOM carbon is composed of carbon contain in the hydrocarbon already formed. Normally, EOM carbon fraction is a less than convertible carbon fraction of the TOC. By increasing maturity, EOM carbon fraction will increase until the point of expulsion, while convertible carbon fraction decreases. Therefore, the result in this study, especially the case of sample NS2, PP2, PP3 and PP4 which have high TOC value but low S2, may be influenced from post mature level of the samples (i.e. TOC values reported may contain EOM).



Figure 4.11 Plot of S2 versus present-TOC indicating kerogen types of the cutting sample in this study sorted by exploration wells.

4.3 Thermal maturation

The level of thermal maturation is important for the generation of hydrocarbon. Thermal maturity describes the impact of time and heat during burial of sediment and converts kerogen into petroleum. Several parameters have been used to evaluate the level of organic maturity. For this study, parameters used for the evaluation of the maturation are: vitrinite reflectance (%Ro), Tmax and Production Index (PI) from Rock-Eval pyrolysis, *thermal alteration* scale (*TAS*), and biomarkers.

4.3.1 Vitrinite reflectance

Vitrinite reflectance (%Ro) is widely used to indicate thermal maturity. %Ro is a measure of the amount of light reflected by vitrinite particles in the source rock, which is based on the change in the reflectance of polished vitrinite particles with increasing time and temperature, but not affected significantly by pressure. Reflectance increasing is caused by the progressive aromatization of the kerogen with accompanying loss of hydrogen in the form of hydrocarbon gases, in which the end product of the process is graphite (Peters and Cassa, 1994).

<u>Result</u>

Eighteen cutting samples from 9 explorations well, except Dong Mun-2 well, were measured by Core Laboratories (Core Lab), Malaysia. Seven samples cannot determine vitrinite reflectance, no determination possible (NDP), because there was no vitrinite particles found in the plate (polish block) that can be taken for %Ro measurement. These samples include CNB1, CNB2, DM13, KSB1, KSB2, KPL1 and PL1.

Based on vitrinite reflectance criteria, 11 cutting samples are post mature, more than 1.35 %Ro. The ranges of vitrinite reflectance values for each unit are summarized in Table 4.7 and Figure 4.12. Histograms showing the %Ro variation for each unit with mean Ro values and standard deviations are shown in Appendix C.



Figure 4.12 Vitrinite Reflectance results from this study and previous studies sorted by exploration wells.

4.3.2 Thermal alteration scale (TAS)

The color of the spore and pollen grains present is used as an indicator of thermal maturation level; thermal alteration index (TAI), spore color index (SCI) and Thermal alteration scales (TAS). Organic matter such as spore and pollen under the microscope in transmitted light, generally change color from yellow to brown to black with increasing burial depth (Peters and Moldowan, 1993). Batten (1980) had discussed a utilization of sporomorph color change for evaluating hydrocarbon potential of rocks and created a simple 7-point scale, as shown in Table 4.8. This scale is called the TAS scales, which is compared with the TAI and SCI scales in Figure 4.13 (Traverse, 2007).

	Average _	Vitrin	ite reflectance (%Ro)		TAS		Tmax	Produc	ction index (PI)
mple	depth	Number of	Mean	Maturity	Scale	Maturity level	ς Ω	Maturity	٦	Maturity
2	(ft.)	reading	Vitrinite (%)	level		material seven	5	level		level
NB1	9,540	r	QN	L	Ŋ	Late mature	411	Immature	0.24	Early mature
NB2	10,615	4	QN	I	Ŋ	Late mature	380	Immature	0.43	Late mature
DR1	3,650	13	1.735	Post mature	5-5/6	Late mature	341	Immature	0.41	Late mature
DR2	4,410	,	×.	ł	ŗ	¢	323	Immature	0.45	Late mature
M11	7,800	4	1.738	Post mature	1	la '	357	Immature	0.58	Late mature
M12	8,180	ţ.	ı	È	ţ.	¢.	375	Immature	09.0	Late mature
M13	8,700	r	QN	ı	ı	r	327	Immature	0.58	Late mature
M21	7,805	1	1	1	1	10	360	Immature	0.57	Late mature
SB1	930	r	ND	I.	5-5/6	Late mature	354	Immature	0.42	Late mature
SB2	1,680	x	ND	ĩ	5-5/6	Late mature	345	Immature	0.43	Late mature
SB3	2,985	24	2.035	Post mature	5/6-6	Late to Post mature	364	Immature	0.29	Peak mature
PL1	7,470	x	ND	ı	5/6-6	Late to Post mature	344	Immature	0.37	Peak mature
PL2	026,7	4	2.004	Post mature	5/6-6	Late to Post mature	335	Immature	0.38	Peak mature
VS1	5,625	r	Ţ	Ŀ	ŗ	19	431	Immature	0.36	Peak mature
NS2	6,275	40	2.125	Post mature	6-6/7	Post mature	361	Immature	0.46	Peak mature
۲ 1	4,144	1	ND	1	Ŷ	Post mature	340	Immature	0.31	Peak mature
0L2	4,331	2	1.843	Post mature	5-5/6	Late mature	340	Immature	0.23	Early mature
p1	6,700	10	2.009	Post mature	5/6-6	Late to Post mature	449	Mature	0.37	Peak mature
P2	6,850	24	2.083	Post mature	5/6-6	Late to Post mature	425	Immature	0.48	Late mature
P3	8,050	30	2.120	Post mature	5/6-6	Late to Post mature	426	Immature	0.47	Late mature
p4	8,415	48	2.163	Post mature	9	Post mature	425	Immature	0.59	Late mature
W1	11.442	10	2.185	Post mature	6-6/7	Post mature	373	Immature	0.38	Peak Mature

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	1, 1900).	
TAS scale	Color of palynomorgh	The maturity level
1	Colorless, pale yellow,	Chemical change negligible; organic
	yellowish green	matter immature, having no source
		potential for hydrocarbon
2	Yellow	Some chemical change, but organic
		matter still immature
3	Light brownish yellow,	Some chemical change, marginally
	yellowish orange	mature but not likely to have potential
		as a commercial source
4	Light medium brown	Mature, active volatilization, oil
		generation
5	Dark brown	Mature, production of wet gas and
		condensate, transition to dry gas phase
6	Very dark brown-black	Over-mature; source potential for dry gas
7	Black (opaque)	Traces of dry gas only

Table 4.8 Palynomorph colors change for evaluating hydrocarbon potential of rocks (Batten, 1980).

ORGANIC THERMAL MATURITY	COLOR OF FOSSIL SPORES/ POLLEN	MUNSELL PROD. NO.		APPI COR TO S	ROXIM RELAT OTHE CALES	ATE TON R	COAL RANK	EXINITE FLUORESCENCE: AMOUNT AND COLOR
	. OLLEN	TRIPLET NO.	TAS	TAI	SCI	VITRINITE REFLECT- ANCE		
		23,678 FFFFCC	1	1	1	0.2%	Peat	High to Medium; blue-green
IMMATURE		20,520 FFFF66 19,688 FFFF00	1.5 2 2.5	1+ 2-	2 3	0.3%	Lignite	High to Medium; green-white
		20,856 (no match)	3	2	4		Subbituminous	High to Medium:
MATURE		23,002 FFCC00	3.5 4	2+	5 6	0.5%	Bituminous, High Vol. C Bituminous, High Vol. B	white-yellow
MAIN PHASE OF LIQUID		21,322 CC9900	4.5	3-	7	0.9%	Bituminous, High Vol. A	High to Low; yellow
GENERATION		20,060 CC9933 23,177 556600	5 5.5	3 3+	8	1.3%	Bituminous, Medium Vol.	Low: dark yellow to orange-brown
DRY GAS OR		21,913 663300	6.5	4-	9	2.0%	Bituminous, Low Vol.	0077523 00
BARREN		19,365 000000	7	4		2.5%	Semi-anthracite	No Fluorescence of Spores/Pollen Exines
	BLACK & DEFORMED	-			10	2000/04/08 40	Anthracite	

Figure 4.13 TAS scale compared to other thermal maturation parameters (Traverse, 2007).

<u>Result</u>

Except Dong Mun-1 and Dong Mun-2, sixteen cutting samples from eight exploration wells were measured for TAS by Core Laboratories (Core Lab), Malaysia and the TAS results are shown in Table 4.7. TAS values of samples range between 5-6/7. This value indicates the maturity level in the range of late mature to post mature, which could generate wet gas and dry gas, respectively.

4.3.3 Tmax and production index (PI) from Rock-Eval pyrolysis

Tmax and PI value from Rock-Eval pyrolysis are thermal maturation parameters. Tmax is the temperature at which the maximum amount of S2 hydrocarbons liberate and dependent on the kerogen type in the source rock. Tmax values correlate directly with vitrinite reflectance values. PI is the ratio of already generated hydrocarbons (S1) to potential hydrocarbon (S2), which is calculated from the ratio S1/(S1+S2). Tmax values from too small S2 peaks (<0.2 mg HC/g rock) and S2<S1 are unreliable (Peters, 1986).

<u>Result</u>

Tmax values for cutting samples are summarized in Table 4.7 and Figure 4.14. Almost all cutting samples have Tmax less than 440° C indicating that a majority of the samples are immature. Except PP1 sample has Tmax 449° C, which indicates mature source rock.

PI values for cutting samples are summarized in Table 4.7 and Figure 4.15. Most samples have PI values between 0.29-0.60 which indicate that the samples have the maturity level in the range of peak mature to late mature. Except CNB1 and PL2 samples which have PI values less than 0.25 that indicate early mature level.

In this study, PI values correspond with vitrinite reflectance (Ro) and thermal alteration scale (TAS) result, while Tmax values do not correspond with Ro and TAS. Results of Ro and TAS suggest the samples are of late mature to post mature. However, Tmax of PP1 sample correspond with PI values. Tmax results of Dao Ruang-1, Phu Lop-1, Phu Wiang-1 from previous studies agree with this study, suggesting immature level. When considering the depth and age of the samples, Tmax values in this study are unreliable. Furthermore, Tmax values from too small S2 peak (<0.2 mg HC/g rock) and S2<S1 are unreliable (Peters, 1986). In addition, Peters (1986) had suggested that sample which has high PI but low Tmax may be caused by weathering or migrated hydrocarbon.

PI result of Dao Ruang-1 well from previous study agrees with this study. But, PI of Phu Lop-1 and Phu Wiang-1 wells from previous studies do not conform to this study, which they indicated the maturity level in the range of immature to early mature. Results of Phu Lop-1 and Phu Wiang-1 from previous study include very low S1 (0-0.06 mg HC/g rock) when compare to S2 (0.13-1.00 mg HC/g rock) (TOTAL Khorat Limited, 1994) and (Amerada Hess Exploration (Thailand) Co Ltd, 1998).



Figure 4.14 Tmax results from this study sorted by exploration wells.



Figure 4.15 PI results from this study sorted by exploration wells.

4.3.4 Biomarkers maturity parameters

Biomarkers or biological markers are molecular fossils that derived from formerly living organisms. They are complex molecules, which mainly consist of carbon, hydrogen, and other elements. They are found in crude oils and extracts of petroleum source rocks. Biomarkers are used to indicate the origin of organic matter in source rocks, determine depositional conditions, and assess thermal maturity level. Because they keep all or most of their original carbon skeletons of the original natural product and this structural similarity reveals more information about their origins than other compounds (Peters et al., 2005b). Biomarker parameters can be archived from GC-MS data.

Biomarkers maturity parameters are based on measuring the relative concentrations of reactant (A) and product (B) in the following reaction;

A
$$\stackrel{R1}{\underset{R2}{\longleftarrow}}$$
 B

The ratio of the concentration of B to the sum of A and B (B/(A+B) ratio) can range from 0 to 1 or 0 to 100% with increasing thermal maturity. R1 and R2 represent the rates of the forward and reverse reactions, respectively (Peters and Moldowan, 1993). For this study, two biomarker groups are used for the evaluation of the maturation, terpanes (m/z 191) as shown in Figure 4.16 and steranes (m/z 217) as shown in Figure 4.17. Biomarker maturity parameters results are summarized in Table 4.9.



Figure 4.16 Example of terpanes (m/z 191) chromatogram from the DM12 sample.

C ₁₉ Tri	C ₁₉ Tricyclic Terpane
C ₂₀ Tri	C ₂₀ Tricyclic Terpane
C ₂₁ Tri	C ₂₁ Tricyclic Terpane
C ₂₂ Tri	C ₂₂ Tricyclic Terpane
C ₂₃ Tri	C ₂₃ Tricyclic Terpane
C ₂₄ Tri	C ₂₄ Tricyclic Terpane
C ₂₄ Tetra	C ₂₄ Tetracyclic Terpane
Ts	C ₂₇ 18 a (H)-22,29,30-Trisnorhopane
Tm	C ₂₇ 17 a (H)-22,29,30-Trisnorhopane
C ₂₉ Hop	C ₂₉ 17 α (H),21 β (H)-Hopane
C ₃₀ Hop	C ₃₀ 17 α (H),21 β (H)-Hopane
Moretane	C ₃₀ 17 β (H),21 α (H)-Moretane
C ₃₁ S/R	$C_{\scriptscriptstyle 31}\alpha\beta\text{-}Homohopane$ (22S) and $C_{\scriptscriptstyle 31}\alpha\beta\text{-}Homohopane$ (22R)
Gammacerane	C30 Gammacerane
C ₃₂ S/R	$C_{\scriptscriptstyle 32}\alpha\beta\text{-}Homohopane$ (22S) and $C_{\scriptscriptstyle 32}\alpha\beta\text{-}Homohopane$ (22R)
C ₃₃ S/R	$C_{\scriptscriptstyle 33}\alpha\beta\text{-}Homohopane$ (22S) and $C_{\scriptscriptstyle 33}\alpha\beta\text{-}Homohopane$ (22R)
C ₃₄ S/R	$C_{{}_{34}}\alpha\beta\text{-}Homohopane$ (22S) and $C_{{}_{34}}\alpha\beta\text{-}Homohopane$ (22R)
C ₃₅ S/R	$C_{\scriptscriptstyle 35}\alpha\beta\text{-}Homohopane$ (22S) and $C_{\scriptscriptstyle 35}\alpha\beta\text{-}Homohopane$ (22R)



Figure 4.17 Example of steranes (m/z 217) chromatogram from the DM12 sample.

4.3.4.1 C₃₁22S/(22S+22R) homohopane isomerization ratio

Homohopane isomerization ratio is used as a biomarker maturity parameter. It is measured from the m/z 191 mass chromatogram. 22S/(22S+22R) homohopane ratio describes the conversion of the biological 22R to the geological 22S configuration of homohopane molecules, so this ratio increased from zero to about 0.6 at equilibrium during maturation. Values in the range 0.50 to 0.54 have barely entered oil generation, whereas ratios from 0.57 up to 0.62 indicate that the oil window has been reached (Seifert and Moldowan, 1986). Homohopane isomerization ratio can be calculated from any or all of the C₃₁-C₃₅ homohopanes. This study calculates from C₃₁ homohopane.

<u>Result</u>

From Table 4.9, most cutting samples have C_{31} 22S/(22S+22R) homohopane ratios in the range 0.55 to 0.63, which indicate the oil window has been reached. The exception is homohopane ratio of PW1 sample (0.53) that indicates early mature level. Homohopane isomerization ratios values do not correspond with Ro and TAS, indicating late mature to post mature. Peters et al. (2005b) suggest this ratio is highly specific for immature to early oil generation. Therefore, this parameter is not significant for this study.

ample	Average depth (ft.)	C ₃₁ 22S/(22S+22R)	Ts/(Ts+Tm)	moretane/(moretane +hopane)	C ₂₉ 20S/(20S+20R)	C ₂₉ ββ/(ββ+αα)
CNB1	9,540	0.55	0.56	ND	0.26	0.39
CNB2	10,615	0.60	0.49	0.08	0.39	0.43
DR1	3,650	0.58	0.55	0.06	0.43	0.47
DR2	4,410	0.56	0.55	ND	0.28	0.44
DM11	7,800	0.60	0.59	0.06	0.47	0.52
DM12	8,180	0.59	0.59	0.07	0.46	0.53
DM13	8,700	0.60	0.84	0.09	0.41	0.54
DM21	7,805	0.59	0.57	0.06	0.46	0.52
KSB1	930	0.63	0.64	0.10	0.20	0.32
KSB2	1,680	0.56	0.56	0.12	0.26	0.34
KSB3	2,985	0.57	0.57	0.07	0.41	0.49
KPL1	7,470	0.59	0.55	0.12	0.35	0.45
KPL2	7,970	0.61	0.56	0.12	0.30	0.41
NS1	5,625	0.58	0.59	0.08	0.21	0.34
NS2	6,275	0.56	0.54	0.10	0.17	0.35
PL1	4,144	0.58	0.56	0.10	0.33	0.42
PL2	4,331	0.58	0.60	0.08	0.33	0.39
PP1	6,700	0.60	0.58	0.10	0.30	0.41
PP2	6,850	0.62	0.54	0.11	0.36	0.48
PP3	8,050	0.57	0.58	0.09	0.37	0.49
PP4	8,415	0.59	0.57	0.08	0.21	0.39
PW1	11 442	0.53	0.51	0.07	0.26	037

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4.3.4.2 Ts/(Ts+Tm)

The ratio of Ts ($C_{27}18\alpha$ (H)-22,29,30- trisnorneohopanes) and Tm ($C_{27}17\alpha$ (H)-22,29,30- trisnorhopane, Ts/(Ts+Tm), is used for maturity indication. During catagenesis, Tm is less stable than Ts, so this ratio value increases with organic maturity (Seifert and Moldowan, 1986). Ts/(Ts+Tm) ratio can be calculated from the peak area of Ts and Tm in m/z 191 mass chromatogram. Samples are mature when the values are in the range of 0.35-0.95 (Peters et al., 2005b). In addition, the ratio also may be influenced by source lithology, in which carbonate source rocks have significantly lower ratio than shale source rocks. However, source lithology should not affect Ts/(Ts+Tm) ratios of Huai Hin Lat Formation samples in this study because samples were selected from shale and claystone intervals.

<u>Result</u>

From Table 4.9, cutting samples have the Ts/(Ts+Tm) ratio in the range of 0.49-0.84. The results suggest that the samples are peak mature to late mature level. The Ts/(Ts+Tm) ratios are plotted with the C_{31} 22S/(22S+22R) homohopane ratios in Figure 4.18 which shows that most samples are peak mature level, except CNB2 and DM13 which are early mature and late mature level respectively.



Figure 4.18 Level of maturity classified by Ts/(Ts+Tm) ratio plotted against C_{31} 22S/(22S+22R) ratio.

4.3.4.3 Moretane/(hopane + moretane) ratio

The ratio of $17\beta(H), 21\alpha(H)$ -moretanes and $17\alpha(H), 21\beta(H)$ -hopanes are used as maturity parameter, moretane/(hopane + moretane). It is measured from the m/z 191 mass chromatogram. Moretanes are thermally less stable than hopanes, and the abundance of moretanes decreases relative to the corresponding hopanes with increasing thermal maturity. This ratio decreases with thermal maturity from ~0.8 in immature source rocks to <0.15 in mature source rocks to a minimum of 0.05 (Seifert and Moldowan, 1986). The C₂₉ and C₃₀ compounds are used for moretane/(hopane + moretane) ratio (Peters et al., 2005b). This study calculates from C₃₀ compounds.

<u>Result</u>

From Table 4.9, cutting samples studied have low moretane/(hopane + moretane) ratio (0.06-0.12) that suggests the samples are of mature level. The exception is samples from CNB1 and DR2, which moretane peak cannot be identified. These ratios values do not correspond with Ro and TAS, indicating late mature to post mature. Peters et al. (2005b) suggested that this ratio is highly specific for immature to early oil generation. So, this parameter is not significant for this study.

4.3.4.4 C_{29} 205/(20S+20R) and $\beta\beta/(\beta\beta+\alpha\alpha)$ sterane ratio

 C_{29} 20S/(20S+20R) and $\beta\beta/(\beta\beta+\alpha\alpha)$ sterane ratio are thermal maturity parameter, which is measured in m/z 217 mass chromatogram. 20S/(20S+20R) ratio can be calculated from the peak area of C_{29} 20S and C_{29} 20R steranes. C_{29} 20S and C_{29} 20R steranes are isomerization at C-20 in the C_{29} 5 α ,14 α ,17 α (H)-steranes. This ratio increases from zero to about 0.5 with increasing thermal maturity (0.52-0.55 at equilibrium) (Seifert and Moldowan, 1986). Isomerization at C-14 and C-20 in the C_{29} 20S and 20R regular steranes cause an increase in $\beta\beta/(\beta\beta+\alpha\alpha)$ ratio from near-zero values to about 0.7 (0.67-0.71, equilibrium) with increasing thermal maturity (Seifert and Moldowan, 1986).

<u>Result</u>

From Table 4.9, cutting samples have the 20S/(20S+20R) ratio in the range of 0.17-0.47, and $\beta\beta/(\beta\beta+\alpha\alpha)$ ratio in the range of 0.32-0.54. Plot of 20S/(20S+20R) versus $\beta\beta/(\beta\beta+\alpha\alpha)$ for the C₂₉ steranes is particularly effective in order to describe the thermal maturity of source rocks. The plot can be used to check one maturity parameter versus another. From Figure 4.19, differences in the maturity of Huai Hin Lat Formation are immature, early mature and peak mature levels with a predominance of early mature level. Samples from Dong Mun-1 and Dong Mun-2 are of mature level. Three samples are of immature level; KSB1, NS1 and NS2. Both ratios values do not correspond with Ro and TAS, indicating late mature to post mature. Peters et al. (2005b) suggest this ratio is highly specific for immature to mature range. So, this parameter is not significant for this study.



Figure 4.19 Cross-plot of C₂₉ sterane 20S/(20R+20S) ratio versus $\beta\beta/(\beta\beta+\alpha\alpha)$ ratios for the cutting samples analyzed.

4.4 Organic matter input and depositional environment

Biomarkers can provide information about organic facies and depositional environment. In this study, organic facies and depositional environment were interpreted with the use of pristane (Pr), phytane (Ph), terpane (m/z 191) and sterane (m/z 217) distributions. In addition, non-biomarker parameters, such as n-alkane distribution, Pr/Ph, Pr/nC_{17} and Ph/nC_{18} can be used to identify the source of organic matter and depositional environment.

4.4.1 n-Alkane distribution

The distribution of n-alkanes in extract from source rocks can be used to the organic matter source indicator, measured in GC-FID and GC-MS (m/z 85). The short chain n-alkanes ($<C_{20}$) are characteristic of microbial input, which medium boiling point n-alkanes (nC_{11} - nC_{20}) are considered to indicate algal and/or bacterial origin for the organic material. The long chain n-alkanes ($>C_{20}$), high boiling point n-alkane, has been commonly attributed to the contribution of terrestrial waxes, especially in the C_{25} - C_{33} range (Peters and Moldowan, 1993).

Terrigenous source material inputs, associated with leaf waxes, are indicated by a strong predominance of high molecular weight odd-numbered alkanes (nC_{27} , nC_{29} and nC_{31}). Marine algae synthesize lower molecular weight n-alkanes with maximum at nC_{17} and without any odd or even chain length preference. Freshwater algae produce longer chain length n-alkanes, with predominance similar to that in higher land plants (Gonzalez-Vila, 1995).

Carbon preference index (CPI) is the ratio obtained from n-alkanes distribution, which divide the sub of the odd carbon-numbered alkanes to the sum of the even carbon numbered alkanes. CPI is specifically used for maturity indication, but also affected by source of organic matters and biodegradation (Tissot and Welte, 1984). CPI values above or below 1.0 indicate immature stage of oil or extract, while values close to 1.0 indicates mature level (Peters and Moldowan, 1993). In very reducing environments, reduction of n-fatty acids, alcohols from waxes, and phytol is prevalent over decarboxylation, which results in predominance of even-carbonnumber n-alkane molecules over odd molecules (CPI<1) and a predominance of phytane over pristane. In less reducing environments, decarboxylation results in a majority of odd n-alkanes (CPI>1) and a predominance of pristane over phytane. Moreover, CPI values less than 1.0 indicate carbonate facies, while CPI values higher than 1.0 indicate lacustrine environment or siliciclastic source rock (Tissot and Welte, 1984). CPI can be expressed as follows;

$$CPI = 2(C_{23}+C_{25}+C_{27}+C_{29})/[C_{22}+2(C_{24}+C_{26}+C_{28})+C_{30}]$$

GC-FID chromatogram may also indicate if there is any biodegradation, in which case the unresolved complex mixture (UCM) or "humpogram" of the compounds rises above the baseline and the relative concentration of n-alkanes decreases compared to isoprenoids. (Sutton et al., 2005).

In oils of the Jianghan basin, central China, the n-alkanes with odd-to-even dominance in the nC_{11} to nC_{17} range could be derived directly from marine algae organic matter (Fowler et al., 1986). The crude oils from the Xifeng oilfeld show an n-alkane distribution with maxima at nC_{19} , nC_{20} and nC_{21} , which n-alkane distribution suggests a mixed organic matter source from aquatic organisms and land plant with the latter being dominant (Duan et al., 2008). The n-alkanes patterns of extract from Zhunonai Lake and Lunpori oil shale are dominated by long chain n-alkanes with a marked odd over even preference in the nC_{23} to nC_{31} range, indicating higher terrestrial plants organic matter input (Wang et al., 2011).

<u>Result</u>

Table 4.10 presents the results from the GC-FID and GC-MS (m/z 85). The examples of gas chromatograms of the alkane fraction from GC-FID and GC-MS (m/z 85) are shown in Figure 4.20 and 4.21. Mostly, they are dominated by the n-alkane series in the range nC_{13} - nC_{33} , extending up to C_{34} in KSB1, NS1, and PL2 samples and to C_{35} in DM21, KSB2, KSB3, KPL1, KPL2 and PP1. PP4 sample contains n-alkanes in the range of nC_{12} - nC_{34} . In PP1 and PP2 samples, n-alkanes in the range of nC_{12} - nC_{35} are the dominant peaks. This n-alkane distribution suggests a mixed organic matter source from aquatic organisms and land plant.

			,			8
Sample	Average depth (ft)	Maximum peak heidht	Dominant n-alkanes series	Distribution	CPI	Biodegraded
	(11)	11212114	222	100.000		
CNB1	9,540	nC ₁₉	nC ₁₃ – nC ₃₃	Unimodal	1.38	Yes
CNB2	10,615	nC ₁₈	nC ₁₃ – nC ₃₃	Unimodal	1.01	Yes
DR1	3,650	nC ₁₈	nC ₁₃ – nC ₃₃	Unimodal	1.11	Yes
DR2	4,410	nC ₂₀	nC ₁₃ – nC ₃₃	Unimodal	1.53	Yes
DM11	7,800	nC ₂₁	nC ₁₃ – nC ₃₃	Unimodal	1.00	Yes
DM12	8,180	nC ₂₂	nC ₁₃ – nC ₃₃	Unimodal	0.99	Yes
DM13	8,700	nC ₂₀	nC ₁₃ – nC ₃₃	Unimodal	1.13	Yes
DM21	7,805	nC ₂₂	nC ₁₃ – nC ₃₅	Unimodal	1.12	Yes
KSB1	930	nC ₁₉	nC ₁₃ – nC ₃₄	Unimodal	1.03	Yes
KSB2	1,680	${ m nC_{18}}$ and ${ m nC_{28}}$	nC ₁₃ – nC ₃₅	Bimodal	1.33	Yes
KSB3	2,985	nC ₂₀	nC ₁₃ – nC ₃₅	Unimodal	1.18	Yes
KPL1	7,470	nC_{18} and nC_{22}	nC ₁₃ – nC ₃₅	Bimodal	1.45	Yes
KPL2	7,970	nC_{18} , nC_{25} and nC_{31}	nC ₁₃ – nC ₃₅	Trimodal	0.80	Yes
NS1	5,625	nC ₁₉	nC ₁₃ – nC ₃₄	Unimodal	2.17	Yes
NS2	6,275	nC ₁₆	nC ₁₃ – nC ₃₃	Unimodal	1.19	Yes
PL1	4,144	nC ₁₈	nC ₁₃ – nC ₃₃	Unimodal	1.13	Yes
PL2	4,331	nC_{18} and nC_{23}	nC ₁₃ – nC ₃₄	Bimodal	1.01	Yes
PP1	6,700	nC_{18} and nC_{26}	nC ₁₃ – nC ₃₅	Bimodal	1.03	Yes
PP2	6,850	nC_{16} and nC_{24}	nC ₁₂ – nC ₃₅	Bimodal	1.01	Yes
PP3	8,050	nC ₁₄	nC ₁₂ – nC ₃₅	Unimodal	1.00	Yes
PP4	8,415	nC_{16}	nC ₁₂ – nC ₃₄	Unimodal	1.11	Yes
PW1	11,442	nC ₁₈	nC ₁₃ – nC ₃₃	Unimodal	1.09	Yes

Table 4.10 *n*-alkane distribution and CPI results from cutting samples studied.

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Figure 4.20 Example of GC-FID chromatogram and UCM from the DM11 sample.



Figure 4.21 Example of m/z 85 chromatogram from the DM11 sample.

Extracts from KSB2, KPL1, PL2, PP1 and PP2 samples show bimodal n-alkane distributions with the highest peaks at nC_{18} (or nC_{16}) and nC_{28} (or nC_{22} or nC_{23} or nC_{24}). In addition, extract from KPL2 sample show trimodal n-alkane distribution, with the highest peaks at nC_{18} , nC_{25} and nC_{31} . These characters indicate higher terrestrial plants organic matter input.

From Table 4.10, nine samples (CNB2, DM11, DM12, KSB1, PL2, PP1, PP2, PP3 and PW1) have CPI values close to 1.0 indicating mature level, while other samples have CPI above or below 1.0 indicating immature stage. When considering the burial depth and age of sample, samples should not be in immature stage. These results may be affected by depositional environment, in which most samples that have CPI more than 1.0 indicate less reducing environments during deposition. Exceptions are DM12 and KPL2 samples which have a CPI less than 1.0, indicating more reducing depositional environments than other samples. Moreover, the UCM is present in all extract chromatogram, which indicates a degree of biodegradation is present.

4.4.2 Pristane/Phytane ratio (Pr/Ph)

Pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$) are regular isoprenoid hydrocarbons, which both of them were derived from the phytol side chain of chlorophyll molecule (Miles, 1989). The phytol can be transformed into pristane of phytane depending on the depositional environment. So, pristane/phytane ratio (Pr/Ph) can be used to indicate the oxic/anoxic conditions of their depositional environment (Didyk et al., 1978). Anoxic or reducing condition in sediment promotes cleavage of the phytol side chain to yield phytol, which undergoes reduction to dehydrophytal and phytane. On the other hand, oxic or oxidizing conditions promote the competing conversion of phytol to pristine by oxidation of phytol to phytenic acid, decarboxylation to pristene and then reduction to pristane, as shown in Figure 4.22 (Peters et al., 2005b). Normally, pristane (Pr) and phytane (Ph) peaks in chromatogram appear as double peaks next to n-C₁₇ and n-C₁₈ normal alkanes, respectively.



Figure 4.22 Scheme of the conversion of phytol to pristane and phytane (Peters et al., 2005b)

Ratio values of more than 3.0 are considered to indicate terrestrial organic matter input under oxidizing environment, oxic. Whereas a ratio value of <1.0 indicates the sediments were deposited in reducing depositional environment, anoxic. Pr/Ph ratio values between 1.0 and 3.0 suggest intermediate conditions, suboxic (Didyk et al., 1978). Examples are shale cutting samples from the Madbi Formation in the Masila Basin, Yemen with Pr/Ph ratios between 1.64 to 2.38, suggesting these samples were deposited under suboxic conditions (Hakimi et al., 2010). Moreover, Peters et al. (2005b) suggest Pr/Ph <0.8 indicates anoxic, commonly saline to hypersaline conditions associated with evaporated and carbonate deposition. However, thermal maturity and type of organic matter deposited can affect Pr/Ph ratio (Didyk et al., 1978).

<u>Result</u>

From Table 4.11, the Pr/Ph ratios for most samples studied are in range from 1.03 to 1.84, which suggest that these samples were deposited under suboxic conditions. Except samples from Dong Mun-1 (DM11, DM12, and DM13) and Dong Mun-2 (DM21) have values in range from 0.69 to 0.80, which can be interpreted to deposition under anoxic and hypersaline conditions.

4.4.3 Pristane/nC₁₇ and Phytane/nC₁₈

Pristane/nC₁₇ and Phytane/nC₁₈ ratio have been used as indicators of source rock types, depositional environments, approximate organic matter maturation and level of biodegradation (Peters et al., 2005b). By increasing maturity, n-alkanes are generated faster than isoprenoids. Generally, isoprenoid hydrocarbons are more resistant to biodegradation than normal alkanes, so the early effect of microbial degradation can be monitored by the ratios of biodegradable to the less degradable compounds. Thus, the ratio of the Pr/nC_{17} is provided as a rough indication to the relative state of biodegradation. Moreover, this ratio decreases as weathering proceeds (Moustafa and Morsi, 2012).

<u>Result</u>

From Table 4.11, the ratio of Pr/nC_{17} for the samples ranged between 0.47 and 6.39, and the ratio of Ph/nC_{18} ranged between 0.41 and 3.84. The cross plot of Pr/nC_{17} and Ph/nC_{18} for cutting samples are shown in Figure 4.23. The results indicate clearly of source to be terrestrial organic matters deposited under oxidizing condition, except NS2 which shows mixed source organic matter deposited under reducing condition with less effect of biodegradation/or higher mature stage.



Figure 4.23 Plots of Pr/nC_{17} versus Ph/nC_{18} ratio for the analyzed samples sorted by exploration wells.

Sample name	Average depth (ft.)	Pr/Ph	Pr/nC ₁₇	Ph/nC ₁₈
CNB1	9,540	1.10	2.24	0.95
CNB2	10,615	1.19	1.84	1.12
DR1	3,650	1.34	1.42	0.81
DR2	4,410	1.08	2.27	1.04
DM11	7,800	0.78	1.53	0.70
DM12	8,180	0.69	1.47	0.79
DM13	8,700	0.80	2.71	1.37
DM21	7,805	0.80	3.05	2.36
KSB1	930	1.04	3.11	1.89
KSB2	1,680	1.09	3.60	1.59
KSB3	2,985	1.03	1.85	0.98
KPL1	7,470	1.33	3.72	2.84
KPL2	7,970	1.34	3.51	1.84
NS1	5,625	1.43	2.26	0.99
NS2	6,275	1.43	0.47	0.41
PL1	4,144	1.73	2.46	1.42
PL2	4,331	1.78	3.79	2.75
PP1	6,700	1.77	6.39	3.84
PP2	6,850	1.84	2.41	1.71
PP3	8,050	1.32	3.29	3.60
PP4	8,415	1.43	2.94	2.88
PW1	11,442	1.54	1.88	1.16

Table 4.11 Pr/Ph, Pr/nC_{17} and Ph/nC_{18} ratio from cutting samples studied area.

4.4.4 Gammacerane index

Gammacerane is C_{30} pentacyclic triterpene, each ring contains six carbon atoms, measured in m/z 191 mass chromatogram. Gammacerane is eluted after C_{31} homohopane 22S and 22R doublet. Gammacerane indicates as stratified water column in marine and non-marine source rock depositional environments and is associated with increasing salinity of the depositional environment (Peters and Moldowan, 1993). The gammacerane index is shown as the ratio of gammacerane/(gammacerane + C_{30} $\alpha\beta$ hopane) ratios.

Gammacerane index less than 0.1 indicates freshwater depositional conditions such as the northern Qaidam oil in China (Duan et al., 2006), while gammacerane index with a range of 0.1-1.0 suggests saline environment of deposition such as the western Qaidam oil (Duan et al., 2006) and hydrocarbon from Barssarin Formation in Kirkuk and Taq Taq Oil Fields, Northern Iraq (Baban and Ahmed, 2008). Gammacerane index more than 1.0 indicates high salinity depositional environment such as the Cenomanian-Turonian black shales of the Dereköy and Ballik Formations in SW Turkey (Kara-Gülbay et al., 2010).

<u>Result</u>

From Table 4.12, most cutting samples studied contain small amounts of gammacerane, with gammacerane index less than 0.100. The results indicate a low salinity lacustrine depositional environment, except DM13 and KSB3 samples have gammacerane index higher than other samples, 0.284 and 0.125 respectively, suggesting higher salinity environment of deposition. In CNB1 and DR1 samples gammacerane peak cannot be identified.

4.4.5 C₃₁ 22R homohopane/C₃₀ hopane ratio

The C_{31} 22R homohopane/ C_{30} hopane ratio (C_{31} 22R/ C_{30} hopane) is used to distinguish between marine and lacustrine source rock depositional environments. This ratio is generally higher than 0.25 for marine environments and lower for lacustrine environments (Peters et al., 2005b).

The $C_{31}22R/C_{30}$ hopane ratio higher than 0.25 suggests marine depositional environment such as crude oil and asphaltites from Southeast Anatolia, Turkey (Kara-Gülbay and Korkmaz, 2012) and the Cenomanian-Turonian black shales of the Dereköy and Ballik Formations in SW Turkey (Kara-Gülbay et al., 2010) that both fields have $C_{31}22R/C_{30}$ in range of 0.26-0.44. The ratio less than 0.25 indicates lacustrine environment such as the Aptian bituminous limestone in the Kale Gümüşhane area, NE-Turkey ($C_{31}22R/C_{30}$ hopane 0.16-0.19) (Kara-Gülbay and Korkmaz, 2012).

<u>Result</u>

From Table 4.12, the C₃₁22R/C₃₀ hopane ratios of cutting samples studied are varying from 0.176 to 0.588. The result can be divided into two groups. In the lacustrine environment group (CNB2, DR1, DR2, DM11, DM12, KSB2, KPL1 and KPL2), the ratio varies from 0.176 to 0.246. For the marine environment group (CNB1, DM13, DM21, KSB1, KAB3, NS1, NS2, PL1, PL2, PP1, PP2, PP3, PP4 and PW1), the ratios range between 0.269 and 0.588.

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Sample	Average depth	Gammacerane	C 22P/C honono
name	(ft.)	Index	
CNB1	9,540	ND	0.273
CNB2	10,615	0.054	0.176
DR1	3,650	0.038	0.246
DR2	4,410	ND	0.238
DM11	7,800	0.044	0.228
DM12	8,180	0.043	0.241
DM13	8,700	0.284	0.536
DM21	7,805	0.045	0.280
KSB1	930	0.086	0.357
KSB2	1,680	0.036	0.240
KSB3	2,985	0.125	0.588
KPL1	7,470	0.053	0.203
KPL2	7,970	0.064	0.226
NS1	5,625	0.056	0.269
NS2	6,275	0.031	0.285
PL1	4,144	0.046	0.378
PL2	4,331	0.041	0.369
PP1	6,700	0.036	0.347
PP2	6,850	0.042	0.334
PP3	8,050	0.082	0.492
PP4	8,415	0.064	0.336
PW1	11,442	0.058	0.426

Table 4.12 Gammacerane index and C_{31}/C_{30} hopane ratio from cutting samples studied.

(ND = no data due to lack of peak)

4.4.6 Homohopane index

The extended hopanes or homohopanes (C_{31} - C_{35}) distribution is applied as an indicator of redox conditions in marine sediments based on a homohopane index (Peters and Moldowan, 1993). High C_{35} homohopanes indicate highly reducing marine conditions during deposition, on the other hand low C_{35} homohopane concentrations are typically observed in oxidizing freshwater conditions during deposition (Peters et al., 2005b). Moreover, homohopane distributions are affected by thermal maturity which C_{35} homohopane decrease and C_{31} homohopane increase with increasing maturity. Homohopanes are measured from m/z 191 mass chromatogram. Homohopane index can be expressed as follows;

Homohopane index = $C_{35}\alpha\beta(S+R)/(\Sigma C_{31}-C_{35}\alpha\beta S+R)$

The low C_{35} homohopane indices (<0.1) indicate a probable freshwater depositional environment such as Triassic and Jurassic source rocks in the Ordos basin, north-central China (Hanson et al., 2007) and the source rock from Lower Carboniferous coal in the Norwegian Barents Sea (van Koeverden et al., 2010). The high index (>1.0) probable indicating a reducing marine carbonate evaporitic environment such as Syrian oils (Abboud et al., 2005).

The C_{35}/C_{34} homohopane ratio can be used to define the source facies of oil. Crude oils from coal/resin source rocks show lower C_{35}/C_{34} homohopanes (<0.6) than marine shale, carbonate, or marine source rocks, consistent with more oxic depositional conditions. Crude oils from marine carbonate source rocks show high C_{35}/C_{34} homohopane (>0.8) that deposited under anoxic conditions (Peters et al., 2005b).

<u>Result</u>

From Table 4.13, samples extraction of CNB2, DM13, KSB3, PL1, PL2, PP2, PP3, PP4 and PW1 have high homohopane index ratio, where they range from 0.103-0.155 that indicate reducing marine environment. Both CNB1 and DR2 samples were absent of C_{35} homohopane. The homohopane index in seven samples which were more than 0.20 indicating a high reducing marine environment compared to other sample extractions; KSB1, KSB2, KPL1, KPL2, NS1, NS2 and PP1. Extraction of DR1, DM11, DM12 and DM21 samples have low homohopane index (0.027-0.072), indicating more terrigenous organic matter input.

Sample	Average depth (ft.)	Homohopanes - index	% of total C ₃₁ -C ₃₅ homohopanes					
name			C ₃₁	C ₃₂	C ₃₃	C ₃₄	C ₃₅	C ₃₅ /C ₃₄
CNB1	9,540	0.000	62.02	37.98	0.00	0.00	0.00	-
CNB2	10,615	0.103	44.98	19.59	13.54	11.58	10.31	0.891
DR1	3,650	0.072	48.49	22.55	11.94	9.80	7.22	0.737
DR2	4,410	0.000	100.00	0.00	0.00	0.00	0.00	-
DM11	7,800	0.032	62.60	21.31	8.97	3.86	3.25	0.841
DM12	8,180	0.027	54.45	23.58	15.28	4.03	2.67	0.663
DM13	8,700	0.117	48.51	18.91	12.97	7.92	11.69	1.476
DM21	7,805	0.040	60.03	22.88	9.25	3.85	4.00	1.039
KSB1	930	0.497	24.55	12.16	8.66	4.90	49.72	10.147
KSB2	1,680	0.374	32.01	14.70	8.80	7.07	37.42	5.294
KSB3	2,985	0.128	40.42	21.77	15.46	9.52	12.82	1.346
KPL1	7,470	0.513	23.83	13.96	6.53	4.43	51.26	11.570
KPL2	7,970	0.321	31.95	19.26	8.60	8.13	32.06	3.942
NS1	5,625	0.216	38.36	20.66	11.84	7.58	21.57	2.844
NS2	6,275	0.349	33.05	15.67	9.52	6.88	34.87	5.065
PL1	4,144	0.151	36.82	21.79	14.90	11.34	15.15	1.336
PL2	4,331	0.155	39.73	21.74	14.02	9.04	15.48	1.711
PP1	6,700	0.214	37.68	18.76	13.20	9.00	21.37	2.374
PP2	6,850	0.118	42.36	20.71	15.37	9.76	11.80	1.209
PP3	8,050	0.130	38.45	21.69	16.04	10.80	13.02	1.206
PP4	8,415	0.150	41.65	21.56	13.30	8.46	15.03	1.777
PW1	11,442	0.134	41.80	21.83	13.62	9.31	13.44	1.444

Table 4.13 C₃₁-C₃₅ homohopanes compositions of extraction from cutting samples studied.



(c) Decreasing trend from C_{31} to C_{34} , but increase in C_{35} homohopane (d) Decr

 C_{31} - C_{35} homohopanes distributions for all samples are shown in Figure 4.24(a). Sample extractions of CNB2, DR1, DM11, DM12 and DM21 samples have similar homohopane distributions and there is a decrease from C_{31} to C_{35} homologue, as shown in Figure 4.24(b), suggesting terrigenous organic matter input. Moreover, this distribution pattern may be affected by thermal maturity, in which higher homologue cracked to lower ones leading to relative increase in the concentration of C_{31} homohopane (Peters and Moldowan, 1991).

In different distributions, homohopane distributions decrease from C_{31} to C_{34} and increase from C₃₄ to C₃₅, which they can be divided into two groups. In the first group, C₃₅ homohopane is less in quantity than C₃₁ homohopane. This group includes samples KSB3, NS1, PL1, PL2, PP1, PP2, PP3, PP4 and PW1, as shown in Figure 4.24(c). In the second group, C_{35} homohopane is more abundant than C_{31} homohopane, as seen in samples DM13, KSB1, KSB2, KPL1, KPL2, NS1 and NS2, and shown in Figure 4.24(d). Both groups show elevated C₃₅ homohopanes compared to the C₃₄ homohopanes that can indicate marine source rock deposited under anoxic conditions. However, this distribution characteristic may be affected by thermal maturity, which C35- and C31-homohopane indices decrease and increase, respectively, with increasing maturity (Peters and Moldowan, 1991). Although most samples show high C35 homohopane but no evidence has been presented to indicate the sediments were deposited under hypersaline conditions. Moreover, the cutting samples contain small amounts of gammacerane that indicate a low salinity environment of deposition.

The C_{35}/C_{34} homohopane ratios of cutting samples have values in range from 0.663 to 11.570, as shown in Table 4.13. The ratio higher than 0.6 suggests a reducing marine environment (Peters et al., 2005b).

4.4.7 Tricyclic terpane ratios

The tricyclic terpane ratios can be useful in order to distinguish marine, carbonate, and lacustrine organic matter (Peters et al., 2005b). The ratios can expressed as C_{19}/C_{23} , C_{22}/C_{21} and C_{24}/C_{23} tricyclic terpane ratios.

A predominance of C₁₉ tricyclic terpanes reflects terrigenous organic matter, while predominant C₂₃ tricyclic terpanes indicate marine organic matter. Hydrocarbon from marine organic matter has low C₁₉/C₂₃ tricyclic terpane ratios whereas hydrocarbon from mainly terrigenous source has ratios of about 1 or greater (Moldowan et al., 1985). Moreover, marine carbonates are distinguished from other source rocks by their high C₂₂/C₂₁ and low C₂₄/C₂₃ tricyclic terpane ratio; in contrast, lacustrine rocks are generally represented by their low C₂₂/C₂₁ and high C₂₄/C₂₃ tricyclic terpane ratio (Peters et al., 2005b).

The Fort Worthe Basin oils had reported a range for C_{19}/C_{23} ratios of 0.02-0.51 thus suggesting a limited terrigenous input (Hill et al., 2007). The C_{19}/C_{23} tricyclic terpane ratios of oil from south east Anatolia, Turkey were less than 1, indicating the oils contain predominantly marine organic matter (Kara-Gülbay and Korkmaz, 2012).

The Aptian bituminous limestone samples in the Kale Gümüşhane area, NE-Turkey have low C_{22}/C_{21} (0.22-0.23) and high C_{24}/C_{23} (0.49-0.53) tricyclic terpane ratios, which is an indicator of a lacustrine environment and received both algal/bacterial and terrigenous organic matter input (Kara-Gülbay et al., 2012). Bitumen extracts from Barssarin Formation in Kirkuk and Taq Taq Oil Fields, Northern Iraq have very low C_{19}/C_{23} tricyclic terpanes ratios (0-0.33), C_{22}/C_{21} tricyclic terpane ratios of 0.42-0.46 and C_{24}/C_{23} tricyclic terpane ratios less than 1 (0.54-0.62) that suggest marine facies and anoxic depositional condition for the source rock (Baban and Ahmed, 2008).

<u>Result</u>

From Table 4.14, most cutting samples have low C_{19}/C_{23} tricyclic terpane ratios (0.064-0.495), indicating marine organic matter input. The exceptions are samples PP3 and PP4 which contain high C_{19}/C_{23} tricyclic terpane ratios that indicate more terrigenous organic matter input than marine organic matter.

	Average depth	age depth Tricyclic terpane ratio				
Sample name	(ft.)	C ₁₉ /C ₂₃	C ₂₂ /C ₂₁	C ₂₄ /C ₂₃		
CNB1	9,540	0.407	0.426	0.396		
CNB2	10,615	0.264	0.426	0.589		
DR1	3,650	0.229	0.482	0.480		
DR2	4,410	0.180	0.548	0.418		
DM11	7,800	0.199	0.704	0.404		
DM12	8,180	0.126	0.831	0.431		
DM13	8,700	0.105	0.558	0.243		
DM21	7,805	0.132	0.732	0.467		
KSB1	930	0.270	0.546	0.394		
KSB2	1,680	0.309	0.464	0.614		
KSB3	2,985	0.222	0.577	0.522		
KPL1	7,470	0.064	0.791	0.876		
KPL2	7,970	0.135	0.659	0.527		
NS1	5,625	0.413	0.350	0.498		
NS2	6,275	0.291	0.486	0.441		
PL1	4,144	0.266	0.583	0.521		
PL2	4,331	0.186	SITY 0.779	0.542		
PP1	6,700	0.170	0.624	0.537		
PP2	6,850	0.405	0.380	0.549		
PP3	8,050	0.770	0.324	0.515		
PP4	8,415	0.949	0.442	0.441		
PW1	11,442	0.495	0.527	0.447		

Table 4.14 Tricyclic terpane ratios from cutting samples studied.

The C_{22}/C_{21} and C_{24}/C_{23} tricyclic terpane ratios from cutting samples studied can be divided into three groups. The first group has high C_{22}/C_{21} and low C_{24}/C_{23} tricyclic terpane ratios, which indicate marine source organic matter. This group includes samples CNB1, DR2, DM11, DM12, DM13, DM21, KSB1 KPL2, PL1, PL2 and PW1. In the second group, with low C_{22}/C_{21} and high C_{24}/C_{23} tricyclic terpane ratios in samples CNB2, KSB2, KPL1, NS1, PP2 and PP3 suggesting lacustrine source organic matters. In the last group, C_{22}/C_{21} tricyclic terpane ratios are the same as C_{24}/C_{23} tricyclic terpane ratios in samples DR1, KSB3, NS2, PL1 and PP4, which may suggest contribution from both marine and lacustrine organic matter.

4.4.8 C₂₇-C₂₈-C₂₉ regular steranes

The distributions of steranes, C_{27} - C_{28} - C_{29} regular steranes, indicate distinguished different source rocks or organic facies of different facies of the same source rock (Peters and Moldowan, 1993). The relative abundance of C_{27} - C_{28} - C_{29} steranes was converted to a percentage value and plotted in a ternary diagram, which peak area measurement was made in m/z 217 mass chromatogram. C_{29} steranes derive from terrestrial higher plants. The lacustrine environment is usually characterized by a higher relative concentration in C_{28} steranes. The presence of higher C_{27} steranes content suggests a marine influenced system. In addition, some C_{28} and C_{27} steranes may derive from fresh water plankton and/or algae (Volkman and Maxwell, 1986).

The relative contents of C_{27} , C_{28} and C_{29} regular steranes in the oils from the western Qaidam Basin, NW China are in the range of 39.0-52.7%, 18.1-24.9% and 28.8-39.8%, respectively, indicated this oil contains relatively large amounts of algalderived C_{27} steranes. For the crude oil from the northern Qaidam Basin, NW China, the relative contents of C_{27} , C_{28} and C_{29} regular steranes are in the range of 34.6-38.3%, 14.8-21.5% and 40.7-50.6%, respectively. The C_{29} steranes are higher than concentrations of C_{27} or C_{28} steranes. So, the oils from the northern Qaidam Basin originated from terrestrial organic matter (Duan et al., 2006). Moreover, the crude oils from the Xifeng oilfield of the Ordos basin, China show a higher proportion of C_{29} sterane (44.7-50.0%) compared to C_{27} sterane (23.0-26.5%) and C_{28} sterane (26.8-30.2%) that suggests this crude oil originated from source rock with high higher plants contribution (Duan et al., 2008).
<u>Result</u>

From Table 4.15, the relative contents of C_{27} , C_{28} and C_{29} regular steranes in extract from cutting samples studied are in the range of 32.42-55.02%, 16.00-23.81% and 25.08-50.92%, respectively, which they are in the order of $C_{29}>C_{28}<C_{27}$ steranes. The distribution of $C_{27}-C_{28}-C_{29}$ regular steranes for Huai Hin Lat Formation samples are scattered over a wide area between C_{27} and C_{29} of the ternary diagram, as shown in Figure 4.25. The predominance of C_{27} and C_{29} steranes in most of the samples is interpreted as strongly indicating a marine phytoplankton and terrestrial input respectively. Khositchaisri (2012) studied outcrops of Huai Hin Lat Formation, and reported $C_{27}-C_{28}-C_{29}$ regular sterane distribution similar to this study.

In addition, the extracts from cutting samples show the V-shaped C_{27} , C_{28} and C_{29} regular steranes distribution, which C_{28} sterane is less than both C_{27} and C_{29} steranes, as example shown in Figure 4.26. This characteristic indicates high thermal maturity (Stout and Wang, 2008). Lu et al. (1989) suggested that secondary cracking in thermal maturation may alter the distribution of C_{27} - C_{28} - C_{29} steranes because C_{29} and/or C_{28} steranes show lower thermal stability than C_{27} steranes. Ro and TAS results of cutting samples indicated late mature to post mature.

Sample	Average	C ₂₇ -C ₂	₈ -C ₂₉ regula	ar steranes	Regular Steranes/
name	depth (ft.) %C ₂₇	%C ₂₈	%C ₂₉	17 α -hopanes
CNB1	9,540	37.49	20.96	41.55	0.935
CNB2	10,615	43.24	21.78	34.97	0.589
DR1	3,650	51.30	16.00	32.70	0.476
DR2	4,410	45.62	17.35	37.03	0.510
DM11	7,800	44.27	23.15	32.57	0.684
DM12	8,180	43.28	23.81	32.92	0.679
DM13	8,700	41.88	17.67	40.45	0.456
DM21	7,805	48.97	20.56	30.47	0.834
KSB1	930	32.42	17.38	50.20	0.730
KSB2	1,680	33.80	17.56	48.64	0.588
KSB3	2,985	37.10	20.87	42.04	0.201
KPL1	7,470	55.02	19.90	25.08	0.752
KPL2	7,970	39.77	18.38	41.85	0.419
NS1	5,625	34.70	17.08	48.22	0.670
NS2	6,275	32.21	16.87	50.92	0.732
PL1	4,144	34.09	17.45	48.46	0.364
PL2	4,331	33.91	16.11	49.98	0.381
PP1	6,700	33.31	21.92	44.77	0.440
PP2	6,850	38.93	23.05	38.03	0.485
PP3	8,050	35.51	22.49	42.00	0.270
PP4	8,415	35.48	18.00	46.52	0.503
PW1	11,442	37.30	17.88	44.82	0.447

Table 4.15 C_{27} - C_{28} - C_{29} regular steranes, regular Steranes/ 17 α -hopanes and diasterane/sterane from cutting samples studied.

C27-C28-C29 Steranes Ternary Diagram



Figure 4.25 Ternary plots of the relative amounts of C_{27} - C_{28} - C_{29} regular steranes of this study and sorted by exploration wells.



Figure 4.26 Example of V-shaped C_{27} , C_{28} and C_{29} regular steranes distribution from the DM12 sample.

4.4.9 Regular steranes/17 α -hopanes

The regular steranes/17 α -hopanes ratio has been thought to be an indicator for organic matter composition (Moldowan et al., 1985). The ratios can be expressed as ratios;

$(C_{27}+C_{28}+C_{29} \text{ regular steranes}/C_{29}+C_{30} \text{hopanes}+C_{31}+C_{32}+C_{23} \text{homohpanes})$

High concentrations of sterane and high sterane/hopane ratios (\geq 1) suggest aquatic algae and have been observed in many marine and evaporitic sediment. In contrast, low concentrations of steranes and low steranes/hopanes are more indicative of terrigenous and/or microorganism reworked organic matter (Tissot and Welte, 1984).

The freshwater lacustrine oils in the northern Qaidam have steranes/hopanes ratios around 0.1, but the saline lacustrine oils of the western Qaidam have this ratios in excess of 1.0 (Duan et al., 2006). The sterane concentration of the crude oil and asphaltites samples from South East Anatolia, Turkey are high, and high sterane/hopanes ratios were determined (1.17-2.23) that indicate that samples were derived from marine organic matter (Kara-Gülbay and Korkmaz, 2012).

<u>Result</u>

From Table 4.15, the regular steranes/17 α -hopanes ratios in extract from cutting samples studied are in the range of 0.201-0.935, less than 1.0, suggesting a terrigenous organic matter.

CHAPTER V

DISCUSSION

This study analyzed source rocks for the petroleum geochemical properties of cutting samples to determine the source potential for petroleum, type of organic matter, thermal maturity and depositional environment of the Huai HIn Lat Formation. Twenty two cutting samples from ten exploration wells were selected from shale and claystone intervals based on gamma ray and resistivity log of the wells. Samples used in this study are from exploration wells that used water-based mud to avoid contamination. The results are presented in Chapter IV and will be discussed in this chapter.

Ten exploration wells in this study can be separated into three petroleum provinces; Chum Phae Area, Khon Kaen-Ubon Area and Phu Phan Anticlinorium, as shown in Figure 4.1. The cutting sample depths of each well from west to east are shown in Figure 4.2.

5.1 Petroleum potential

From results of thermal maturity level in this study, Huai Hin Lat Formation samples are within late mature to post mature stage, based on vitrinite reflectance (%Ro) and thermal alteration scale (TAS), as shown in Figures 5.1 and 5.2. These results influence interpretation on hydrocarbon potential and kerogen typing of samples.

From TOC data, organic richness from the laboratory is present-day TOC that is lower than original TOC (TOC₀). The measured TOC values can be converted to TOC_0 with correction factor base on the type of kerogen and level of maturity. TOC_0 of samples are shown in Table 4.3 and Figure 4.5. The TOC_0 results of 22 samples are considered having very low to very high organic richness (poor to excellent source rock potential). From three petroleum provinces in this study, Phu Phan Anticlinorium has more organic richness than Chum Phae and Khon Kaen-Ubon Areas. Howevers, Chum Phae and Khon Kaen-Ubon Areas have only data from 4 wells; Kaset Sombun-1, Dao Ruang-1, Chonnabot-1 and Phu Wiang-1, which do not cover all the area. In Phu Phan Anticlinorium province, the north central part has high to very high organic contents when compared with eastern and westerns parts. Black shale from Phu Phar-1 well is a very good to excellent potential source rock.



Figure 5.1 Vitrinite reflectance (%Ro) results of cutting samples from each exploration well from west to east in this study.



Figure 5.2 Thermal alteration scale (TAS) results of cutting samples from each exploration well from west to east in this study.

The present-day TOC values were plotted with the EOM values in Figure 5.3. The graph shows that EOM values in most samples analyzed are relatively high compared with their TOC contents. High EOM could be a result of generated free hydrocarbon in the rock. This is supported by the thermal maturity result, suggesting the cutting samples are late mature to post mature level. In addition, high EOM may be a migrated hydrocarbon from other stratigraphic locations. In the Asgard field, the Norwegian Sea, immature source rocks in Kimmerridge Clay Formation have high EOM values (Kalio et al., 2015). Kalio et al. (2015) concluded that the presence of the high EOM values is an indication that hydrocarbon must have migrated from lower sections into the reservoir unit.



Figure 5.3 Relationship between present-day TOC and EOM values obtained from this study.

In addition, no samples in this study have Rock-Eval S2 values more than 5.0 mg HC/g rock that indicates poor to fair hydrocarbon potential. These results suggest that most samples are of late mature to post mature stage, which is supported by the PI values. Moreover, Rock-Eval pyrolysis result show S1 peak higher than S2 peak in all samples, as shown in Figure 5.4 as an example.





Kerogen types, based on HI values, of samples in each wells are shown in Figure 5.5. In general HI values indicate that Huai Hin Lat Formation samples contain mixed kerogen type II, II/III and III indicating both oil and gas potential. From Figure 5.5, the upper part of Huai Hin Lat Formation is composed of kerogen type II or type II/III, while the lower part is composed of kerogen type III or type IV. In Phu Phan Anticlinorium area, the main kerogen in the western part is type II, while the main kerogen in the eastern part is type II/III. Kaset Sombun-1, Dao Ruang-1, Chonnabot-1 and Phu Wiang-1 contain of kerogen type II/III. However, the interpretation of kerogen type with HI values in this study may not be justified, because most samples have very low TOC contents (Table 4.6), which may cause apparent higher HI values. The exceptions are samples DM11, DM12, DM21, NS2, PP2, PP3 and PP4 that contain high TOC (>1.0 wt.%), which kerogen interpretation may be reliable.

From visual kerogen analysis, sixteen samples contain mainly inertinite (Kerogen type IV) and non-fluorescent amorphous of amorphinite (Kerogen type III/IV), which is different from HI result. Peters and Cassa (1994) described kerogen type IV as dead carbon that has little or no hydrocarbon generating capability. From Van Krevelen diagram, as shown in Figure 1.3(a), during thermal maturation, generation of hydrocarbon products caused the kerogen to become depleted in hydrogen and



Figure 5.5 Kerogen type interpreted from HI results of cutting samples from each exploration well from west to east in this study.

relatively enriched in carbon. During late mature and post mature stages all kerogen approach graphite in composition near the lower left portion of both Van Krevelenand Pseudo-Van Krevelen diagram diagrams. Elgmati et al. (2011) studied the Utica Haynesville and Fayetteville shale-gas source rocks likely initially contained Kerogen type III (gas prone material) that converted to Kerogen type IV during the process of thermal over maturation. So, the Huai Hin Lat Formation cutting samples currently may contain thermally post-mature type IV kerogen. This is supported by the thermal maturity result, suggesting the cutting samples are of post mature level.

The summary result of organic richness, potential to generate petroleum, kerogen type and thermal maturity level from this study in comparison with results from previous outcrop study of Phillips Petroleum Company (1982), Unocal Petroleum (1994) and (Khositchaisri, 2012), and previous reports on geochemistry of exploration wells including; Dao Ruang-1 (Abolins, 1993), Kham Palai-1 (Unocal Petroleum, 1994), Phu Lop-1 (Villain et al., 1994) and Phu Wiang-1 (Kaye, 1998), are shown in Table 5.1.

5.2 Organic facies

Based on nonbiomarker parameter in this study, the source organic matter input of Huai Hin Lat Formation derived from mixed organic matter sources from aquatic organisms and land plants, as shown by the n-alkane distribution dominate in the range of nC_{13} - nC_{33} . In addition, from biomarker study samples can be divided into 2 groups; terrestrial organic matter dominant and marine organic matter dominant.

Mixed organic matter source contains more terrestrial organic matter than marine organic matter include CNB1, KSB2, KSB3, KPL1, KPL2, NS1, NS2, PL1, PL2, PP1, PP2, PP3 and PP4 samples. The chromatograms in this group show characteristics of bimodal and trimodal n-alkane distribution, which indicates higher terrestrial plant organic matter input. For tricyclic terpane ratios, the cutting samples have C_{19}/C_{23} ratios of about 1 (0.770-0.949), low C_{22}/C_{21} and high C_{24}/C_{23} ratios. In addition, samples in this group comprised of C_{29} regular steranes more than C_{27} regular sterane indicating that they derived from terrestrial higher plants and were supported by regular steranes/17**Q**-hopanes ratio of <1.0.

Lat Formation in this	study compare with	previous studies.			
	Sample	Organic richness (TOC ₀)	Potential to generate petroleum (Rock-Eval S2)	Kerogen type	Thermal Maturity level
This study	Cutting	Very low to very high	Poor to Fair		Late mature to post
Abolins (1993)	Dao Ruang-1 cutting	Very low to low	Poor		mature Late Mature
Unocal Petroleum	Kham Palai-1 cutting	Very low to low	ı	ũ	Post Mature
(1994) Villain et al (1994)	Phu Lop-1 cutting	Very low	Poor	ī	¢
Kaye (1998)	Phu Wiang-1 cutting	Very Iow	Poor	ï	ĩ
Phillips Petroleum	outcrop	Low to very high	Poor		Peak mature to post
(1982) Unocal Petroleum	outcrop	Moderate to very high	poor	Ţ	mature Post mature
(1994) Khositchaisri (2012)	outcrop	Very low to very high	Poor to Fair	≡	Late mature

Table 5.1 Summary of organic richness, potential to generate petroleum, kerogen type and thermal maturity level of Huai Hin L Mixed organic matter source contains more marine organic matter than terrestrial organic matter include CNB2, DR1, DR2, DM11, DM12, DM13, DM21, KSB1 and PW1 samples. Tricyclic terpane ratios in this group have low C_{19}/C_{23} ratio (<0.5), high C_{22}/C_{21} and low C_{24}/C_{23} ratio. From regular steranes distribution, samples consist of more C_{27} regular sterane than C_{29} regular sterane suggesting derivation from marine organisms. This results are supported with C_{35}/C_{34} homohopane ratio >0.6.

All cutting samples of Huai Hin Lat Formation contain small amounts of gammacerane, a biomarker indicative of a lacustrine depositional environment with low salinity. From data, DM13 and KSB3 samples have gammacerane index higher than other samples (0.284 and 0.125 respectively) that indicate lacustrine depositional environment with higher salinity. The results conform with previous study of Khositchaisri (2012). In addition, when considered with other biomarkers; CPI, Pr/Ph, C_{31} 22R homohopane/ C_{30} hopane ratio and homohopane index, results from this study can divide the depositional environment into two groups; less reducing lacustrine environment and reducing marine environment, as shown in Figure 5.6.

Less reducing lacustrine depositional environment are found in CNB1, CNB2, DR1, DR2, DM11, DM12, KSB2 and KPl1 samples. The extracts from this group have CPI more than 1.0, C_{31} 22R homohopane/ C_{30} hopane ratio less than 0.25 and homohopane index less than 0.1, these biomarkers indicate less reducing lacustrine environment. This is supported by Pr/Ph ratio of 1.0-2.0.

Reducing marine depositional environment are found in DM13, DM21, KSB1, KSB3, KPL2, NS1, NS2, PL1, PL2, PP1, PP2, PP3, PP4 and PW1 samples. The extractions have $C_{31}22R$ homohopane/ C_{30} hopane ratio more than 0.25 and homohopane index more than 0.1 that indicates a marine environment, supported by CPI (<1.0) of DM12 and KPL2 samples, and Pr/Ph ratio (<1.0) of DM12 and DM13 samples.

From Figure 4.25, ternary diagram of regular sterane indicate that all samples were possibly deposited in estuarine and/or marine environment. These results are supported by gammacerane index and other biomarker organic facies parameters. Khositchaisri (2012) concluded Huai Hin Lat Formation outcrop samples have



Figure 5.6 Organic facies of cutting samples from each exploration well from west to east in this study.

contribution from both continental and marine organisms, and were possibly deposited in estuarine and/or terrestrial environments (Figure 4.25). Moreover, all samples of Huai Hin Lat Formation in this study show the V-shaped of C_{27} , C_{28} , and C_{29} sterane in chromatogram, as shown in Figure 4.26. This characteristic indicates a high thermal maturity, which C_{29} and/or C_{28} steranes have lower thermal stability than C_{27} sterane, will crack during thermal maturation (Stout and Wang, 2008).

The Pr/nC_{17} and Ph/nC_{18} ratios of cutting samples in this study suggest that they were deposited under oxidizing condition, which is different from results from other biomarkers in this study and the result from Khositchaisri (2012) (Figure 5.7). The different interpretation of results may be caused by biodegradation of the cutting samples that can affect the Pr/nC_{17} and Ph/nC_{18} ratios. Unresolved complex mixture (UCM) hump present in all extracts. Generally, isoprenoid hydrocarbons are resistant to biodegradation than normal alkanes (Moustafa and Morsi, 2012) leading to higher Pr and Ph than their alkane counterparts (i.e. nC_{17} , nC_{18}).



Figure 5.7 Plots of Pr/nC_{17} versus Ph/nC_{18} ratio of samples from this study compared with those of Khositchaisri (2012).

The schematic cross section of exploration well with samples depth of each exploration well in this study can be separated into 3 lines; line A-A', B-B' and C-C', as shown in Figures 5.8, 5.9 and 5.10, respectively



Figure 5.8 a) The schematic cross section line A to A'; Dao Ruang-1 (DR), Kaset Sombun-1 (KSB), Chonnabot-1 (CNB) and Phu Wiang-1 (PW) wells.

b) The actual seismic line with wells locations.

c) Seismic cross section along line A to A'. Note that the location of KSB is projected onto the line.

d) Interpreted lithologic section of (c). Green is Khorat Group. Orange is Huai Hin Lat Formation. Yellow is Saraburi Group.



Figure 5.9 a) The schematic cross section line B to B'; Phu Phra-1 (PP), Phu Lop-1 (PL), Dong Mun-2 (DM2) and Dong Mun-1 (DM1) wells.

b) The actual seismic line with wells locations.

c) Seismic cross section along line B to B'. Note that the locations of DM2 and PP are projected onto the line.

d) Interpreted lithologic section of (c). Green is Khorat Group. Orange is Huai Hin Lat Formation. Yellow is Saraburi Group.



Figure 5.10 a) The schematic cross section line C to C'; Kham Palai-1 (KPL) and Non Sung-1 (NS) wells.

b) The actual seismic line with wells locations.

c) Seismic cross section along line C to C'.

d) Interpreted lithologic section of (c). Green is Khorat Group. Orange is Huai Hin Lat Formation. Yellow is Saraburi Group.

Cross section line A to A' runs across 2 petroleum provinces; Chum Phae Area (Kaset Sombun-1 and Dao Ruang-1 wells) and Khon Kaen-Ubon Area (Chonnabot-1 and Phu Wiang-1 wells), as shown in Figure 5.8. The cross section passes Chonnabot-1, Phu Wiang-1 and Dao Ruang-1 wells, while Kaset Sombun-1 well location is projected onto the line from about 32 km southwest of cross section line. In both petroleum provinces, we found mixed organic matter from aquatic and land plant input under lacustrine depositional environment. The exceptions are KSB3 and PW1 samples, which were possibly deposited in marine environment.

Cross section line B to B' and line C to C' are located in Phu Phan Anticlinorium. Line B to B' passes Dong Mun-1 and Phu Lop-1 wells, whereas Dong Mun-2 and Phu Phra -1 wells are projected onto a line from about 12 km and 14 km southeast of cross section line respectively (Figure 5.9). Line C to C' consists of Kham Palai-1 and Non Sung-1 wells (Figure 5.10). In Phu Phan Anticlinorium petroleum province, original organic matters are divided into 2 groups. 1) Marine organic matters source are found in Dong Mun-1 and Dong Mun-2 wells that locate in the western part of the province. 2) Terrestrial organic matters are mainly deposited in marine environment. However, DM11, DM12 and KPL1 samples are possibly deposited under lacustrine environment.

From Figure 5.6, characteristic organic facies of Dao Rung-1 well (DR1 and DR2) are similar to those of Dong Mun-1 well (DM11 and DM12) that suggest marine organic matter deposited under less reducing lacustrine environment.

Evidence from this study suggest that Phu Phan Anticlinorium, Chum Phae and Khon Kaen-Ubon Areas were possible subjected to marine regression in Triassic as evidenced by change in environment from marine to lacustrine in Kaset Sombun-1, Chonnabot-1, Phu Wiang-1, Dong mun-1 and Kham Palai-1 wells (Figure 5.6).

5.3 Limitation

The Huai Hin Lat Formation samples in this study have two limitations;

1) Each sample was combined from many cutting bags because each cutting bag was collected for every 10 feet of drilling depth and quantity of cuttings in one bag is not enough for studying petroleum geochemistry (5-10 gram/bag). One combined cutting samples has total weight of about 40-70 gram is collected from depths ranging between 30-200 feet. Therefore, the result from one combined samples in this study will represent in many feet of rocks.

2) Cutting samples have been stored in a warehouse for more than 15 years. Old cutting samples may be affected by the environment of storage places such as oxidation or biodegradation.



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CHAPTER VI

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

A total of 22 cutting samples from the Huai Hin Lat Formation in the Khorat Plateau have been studied geochemically. The cutting samples were collected from ten exploration wells; Chonnabot-1, Dao Ruang-1, Dong Mun-1, Dong Mun-2, Kaset Sombun-1, Kham Palai-1, Non Sung-1, Phu Lop-1, Phu Phra-1 and Phu Wiang-1, which can be separated into three petroleum provinces; Chum Phae Area, Khon Kaen-Ubon Area, and Phu Phan Anticlinorium. The studys conclusions are as follows:

1) Out of the three petroleum provinces, Huai Hin Lat Formation samples from Phu Phan Anticlinorium have more organic content than Chum Phae and Khon Kaen-Ubon Areas. Moreover, the north-central part of Phu Phan Anticlinorium has very high organic richness when compared with the eastern and western part of Phu Phan Anticlinorium. From Rock-Eval pyrolysis, low S2 values indicate poor to fair hydrocarbon generating potential, which is a result of high thermal maturity. Relatively high EOM compared to present-day TOC also indicate a presence of generated petroleum (as a result of high maturity) and/or migration of hydrocarbon from nearby units.

2) Based on HI values, Huai Hin Lat Formation was likely initially contained kerogen type II, II/III and III with both oil and gas potential, but were converted to kerogen type IV during the thermal maturity process (late mature to post mature level). Therefore, the Huai Hin Lat Formation samples in this study currently contain predominance of thermally post-mature kerogen type IV as shown by visual kerogen typing analysis.

3) Vitrinite reflectance and thermal alteration scale (TAS) suggest that samples from Huai Hin Lat Formation are within late mature to post mature stage. This result is supported by PI values. In addition, this result supports interpretation of hydrocarbon potential and kerogen typing. 4) Nonbiomarker and biomarker parameters in this study suggest that samples from Huai Hin Lat Formation contain mixed organic sources between terrestrial and marine organic matters deposited in less reducing to reducing environmental conditions. In addition, bimodal and trimodal distribution in n-alkane chromatogram indicates greater terrestrial higher plant organic matter input than marine organic matter.

5) Ternary diagram of C_{27} - C_{28} - C_{29} regular sterane indicates that samples of Huai Hin Lat Formation were possibly deposited in estuarine and/or marine environment. This is supported by a presence of gammacerane in all samples.

6) The presence of UCM in all samples indicates that the samples were affected by biodegradation.

In conclusion, all organic petroleum geochemical data of cutting samples suggest that the Huai Hin Lat Formation is a poor to very good potential source rock. The contain kerogen type II/III, based on HI and OI values. However, the thermal maturity of the samples is late mature to post mature, which has an influence on kerogen type interpreted from HI/OI and visual kerogen analysis. Visual kerogen typing indicated Huai Hin Lat Formation currently contains thermally post-mature kerogen type IV. From late mature to post mature stage, dry gas is the main hydrocarbon product of Huai Hin Lat Formation. Organic matter of Huai Hin Lat Formation is derived from mixed organic sources, with more higher terrestrial plant organic matter input than marine organic matter, which were possibly deposited in estuarine and/or marine environment.

6.2 Recommendation

Since, Thailand has limited domestic petroleum production and reserves, shale gas is an option to increase petroleum reserves. Shale gas is unconventional gas, which refers to natural gas that is found trapped within shale formations.

In this study, three Huai Hin Lat Formation samples from Phu Phra-1 well (PP2, PP3 and PP4) are black shale with high to very high organic richness (very good to excellent source rock potential). From seismic data, the thickness of Triassic shale of Phu Phra-1 is more than 1,500 feet (ESSO Exploration Inc, 1984). Therefore, this unit is suitable for studying the possibility of developing shale gas fields in the future.

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APPENDIX A

Cutting Sample Description





APPENDIX B

Total Organic Carbon Content

No.		1st	2nd	Avg	
	Sample name	(g/kg)	(g/kg)	(g/kg)	(wt.%)
1	CNB1	1.20	2.28	1.74	0.174
2	CNB2	1.26	1.25	1.26	0.126
3	DR1	4.60	6.00	5.30	0.530
4	DR2	2.59	1.91	2.25	0.225
5	DM11	15.23	14.79	15.00	1.500
6	DM12	12.79	13.00	12.90	1.290
7	DM13	3.12	3.42	3.27	0.327
8	DM21	13.01	13.57	13.30	1.330
9	KSB1	0.306	0.509	0.41	0.041
10	KSB2	0.633	0.662	0.65	0.065
11	KSB3	0.709	0.102	0.41	0.041
12	KPL1	0.255	0.108	0.18	0.018
13	KPL2	2.26	2.25	2.25	0.225
14	NS1	0.847	0.626	0.74	0.074
15	NS2	16.28	15.71	16.00	1.600
16	PL1	2.64	2.78	2.71	0.271
17	PL2	2.11	2.15	2.13	0.213
18	PP1	3.80	3.86	3.87	0.387
19	PP2	25.73	29.37	27.60	2.760
20	PP3	30.58	28.37	29.50	2.950
21	PP4	27.24	25.25	26.30	2.630
22	PW1	8.96	10.23	9.60	0.960

TOC content by TOC analyzer HT-1300 at Environmental Research Institute (ERIC), Chulalongkorn University.










Rock-Eval Pyrolysis Data

จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University

No.	Sample	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	S3CO (mg/g)	PC (%)	RC (%)	TOC (%)	MINC (%)	TpkS2 (°c)	Tmax (°c)
1	CNB1	0.08	0.25	0.54	0.07	0.05	0.06	0.11	1.46	449	411
2	CNB2	0.13	0.17	0.75	0.04	0.05	0.10	0.15	2.16	418	380
3	DR1	0.57	0.83	0.45	0.06	0.14	0.36	0.50	2.41	379	341
4	DR2	0.53	0.64	0.52	0.05	0.12	0.11	0.23	2.30	361	323
5	DM11	4.69	JII 3.38	0.40	0.14	0.69	0.31	1.01	1.93	395	357
6	DM12	5.77	3.87	0.46	0.09	0.82	0.32	1.14	2.17	413	375
7	DM13	1.03	0.74	0.65	0.07	0.17	0.10	0.27	3.82	365	327
8	DM21	4.84	JII 3.70	0.74	0.12	0.74	0.34	1.08	1.89	398	360
9	KSB1	0.30	0.41	0.16	0.01	0.07	0.06	0.13	1.64	392	354
10	KSB2	0.18	0.24	0.18	0.02	0.05	0.03	0.08	1.48	383	345
11	KSB3	0.12	0.29	0.35	0.01	0.04	0.10	0.15	1.35	402	364
12	KPL1	0.14	0.24	0.18	0.03	0.04	0.04	0.08	0.83	382	344
13	KPL2	0.16	0.26	0.21	0.03	0.04	0.06	0.10	1.29	373	335
14	NS1	0.20	0.35	0.35	0.08	0.06	0.11	0.17	0.28	469	431
15	NS2	0.31	0.37	0.75	0.09	0.09	1.41	1.50	1.79	399	361
16	PL1	0.32	0.72	2.20	0.17	0.16	0.07	0.23	1.08	378	340
17	PL2	0.18	0.59	1.52	0.12	0.11	0.05	0.16	0.58	378	340
18	PP1	0.33	0.57	1.00	0.08	0.11	0.15	0.26	3.10	487	449
19	PP2	1.22	1.33	1.26	0.21	0.26	1.82	2.08	3.24	463	425
20	PP3	0.98	000 1.12	1.56	0.19	0.23	1.43	1.66	3.46	464	426
21	PP4	1.06	0.73	0.70	0.12	0.18	1.52	1.69	3.10	463	425
22	PW1	0.77	1.28	1.27	0.33	0.23	0.58	0.81	3.62	411	373

Rock-Eval Pyrolysis results from cutting samples in this study.

Rock-Eval Parameters

S1 (mg/g)	:	Free hydrocarbons
S2 (mg/g)	:	Hydrocarbons evolved from kerogen at 300° C to 600° C
S3 (mg/g)	:	Organic CO ₂ generated from 300° C to 390° C
S3CO (mg/g)	:	CO from organic and mineral sources
PC (%)	:	Pyrolysable carbon
RC (%)	:	Residual carbon
TOC (%)	:	Total organic carbon
MINC (%)	:	Mineral carbon
TpkS2 ([°] C)	:	Temperature in the oven at the top of the S2 peak
Tmax ([°] C)	:	Maximum temperature at S2 peak

	No.	S1	S2	S3	S3CO	PC (%)	RC	тос	MINC	TpkS2	Tmax
Sample		(mg/g)	(mg/g)	(mg/g)	(mg/g)		(%)	(%)	(%)	(°c)	(°c)
	1	0.08	0.26	0.55	0.05	0.05	0.08	0.13	1.45	473	435
CND1	2	0.08	0.25	0.51	0.09	0.05	0.03	0.08	1.47	451	413
CNR1	3	0.08	0.25	0.56	0.06	0.05	0.07	0.12	1.45	423	385
	Average	0.08	0.25	0.54	0.07	0.05	0.06	0.11	1.46	449	411
	1	0.10	0.12	0.72	0.05	0.04	0.06	0.10	2.22	378	340
CNIDO	2	0.14	0.20	0.71	0.03	0.05	0.07	0.12	2.17	437	399
CINDZ	3	0.14	0.20	0.81	0.04	0.05	0.17	0.22	2.08	440	402
	Average	0.13	0.17	0.75	0.04	0.05	0.10	0.15	2.16	418	380
	1	0.52	0.75	0.48	0.07	0.13	0.36	0.49	2.41	368	330
004	2	0.55	0.90	0.44	0.06	0.14	0.37	0.51	2.40	371	333
DRI	3	0.64	0.85	0.43	0.05	0.14	0.35	0.49	2.41	397	359
	Average	0.57	0.83	0.45	0.06	0.14	0.36	0.50	2.41	379	341
	1	0.57	0.64	0.51	0.08	0.12	0.11	0.23	2.31	338	300
002	2	0.39	0.60	0.53	0.05	0.10	0.11	0.21	2.30	371	333
DRZ	3	0.64	0.67	0.51	0.03	0.13	0.11	0.24	2.29	375	337
	Average	0.53	0.64	0.52	0.05	0.12	0.11	0.23	2.30	361	323
	1	4.74	3.29	0.44	0.14	0.69	0.31	1.00	1.94	403	365
0.444	2	4.73	3.44	0.39	0.14	0.70	0.32	1.02	1.95	412	374
DM11	3	4.61	3.41	0.38	0.13	0.69	0.31	1.00	1.91	369	331
	Average	4.69	3.38	0.40	0.14	0.69	0.31	1.01	1.93	395	357
	1	5.97	3.90	0.46	0.11	0.84	0.32	1.16	2.15	406	368
	2	5.51	3.84	0.49	0.11	0.80	0.32	1.12	2.17	415	377
DM12	3	5.83	3.87	0.44	0.06	0.82	0.33	1.15	2.19	418	380
	Average	5.77	3.87	0.46	0.09	0.82	0.32	1.14	2.17	413	375
	1	1.02	0.73	0.67	0.07	0.17	0.08	0.25	3.87	345	307
	2	0.99	0.75	0.64	0.06	0.17	0.13	0.30	3.81	404	366
DM13	3	1.07	0.75	0.65	0.09	0.18	0.08	0.26	3.79	346	308
	Average	1.03	0.74	0.65	0.07	0.17	0.10	0.27	3.82	365	327
	1	4.84	3.62	0.74	0.13	0.73	0.34	1.07	1.91	399	361
	2	4.91	3.72	0.74	0.10	0.75	0.34	1.09	1.88	399	361
DM21	3	4.77	3.76	0.75	0.12	0.74	0.34	1.08	1.88	397	359
	Average	4.84	3.70	0.74	0.12	0.74	0.34	1.08	1.89	398	360
	1	0.25	0.35	0.17	0.01	0.06	0.07	0.13	1.63	386	348
	2	0.30	0.41	0.16	0.01	0.07	0.08	0.15	1.63	402	364
KSB1	3	0.35	0.47	0.15	0.02	0.08	0.03	0.11	1.66	387	349
	Average	0.30	0.41	0.16	0.01	0.07	0.06	0.13	1.64	392	354

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Sample	No.	51 (mg/g)	52 (mg/g)	53 (mg/g)	53CO (mg/g)	PC (%)	RC (%)	(%)	MINC (%)	l pkS2 (°c)	l max (°c)
	1	0.13	0.21	0.18	0.03	0.04	0.02	0.06	1.50	378	340
	2	0.21	0.25	0.18	0.02	0.05	0.02	0.07	1.50	371	333
KSB2	3	0.21	0.25	0.18	0.02	0.05	0.06	0.11	1.45	400	362
	Average	0.18	0.24	0.18	0.02	0.05	0.03	0.08	1.48	383	345
	1	0.09	0.23	0.38	0.01	0.04	0.05	0.09	1.44	395	357
	2	0.11	0.29	0.33	0.01	0.04	0.12	0.16	1.26	400	362
KSB3	3	0.15	0.35	0.35	0.01	0.05	0.14	0.19	1.34	411	373
	Average	0.12	0.29	0.35	0.01	0.04	0.10	0.15	1.35	402	364
	1	0.11	0.22	0.20	0.03	0.04	0.05	0.09	0.82	381	343
	2	0.16	0.25	0.18	0.02	0.04	0.05	0.09	0.81	382	344
KPL1	3	0.14	0.25	0.16	0.03	0.04	0.01	0.05	0.86	384	346
	Average	0.14	0.24	0.18	0.03	0.04	0.04	0.08	0.83	382	344
	1	0.14	0.22	0.22	0.04	0.04	0.05	0.09	1.30	366	328
	2	0.19	0.31	0.19	0.03	0.05	0.06	0.11	1.28	382	344
KPL2	3	0.16	0.25	0.23	0.03	0.04	0.07	0.11	1.29	372	334
	Average	0.16	0.26	0.21	0.03	0.04	0.06	0.10	1.29	373	335
	1	0.25	0.37	0.36	0.09	0.07	0.11	0.18	0.27	453	415
	2	0.18	0.36	0.34	0.08	0.06	0.11	0.17	0.29	499	461
NS1	3	0.17	0.33	0.36	0.06	0.06	0.11	0.17	0.27	456	418
	Average	0.20	0.35	0.35	0.08	0.06	0.11	0.17	0.28	469	431
	1	0.29	0.31	0.73	0.09	0.08	1.31	1.39	1.61	398	360
	2	0.32	0.38	0.79	0.09	0.09	1.46	1.55	1.92	342	304
NS2	3	0.33	0.42	0.72	0.10	0.09	1.47	1.56	1.84	458	420
	Average	0.31	0.37	0.75	0.09	0.09	1.41	1.50	1.79	399	361
	1	0.34	0.77	2.16	0.19	0.17	0.06	0.23	1.11	374	336
	2	0.28	0.66	2.30	0.17	0.15	0.10	0.25	1.07	374	336
PL1	3	0.35	0.73	2.14	0.16	0.16	0.06	0.22	1.07	387	349
	Average	0.32	0.72	2.20	0.17	0.16	0.07	0.23	1.08	378	340
	1	0.16	0.56	1.52	0.12	0.11	0.03	0.14	0.58	369	331
	2	0.18	0.60	1.49	0.11	0.11	0.09	0.20	0.53	375	337
PL2	3	0.19	0.61	1.55	0.13	0.12	0.03	0.15	0.62	391	353
	Average	0.18	0.59	1.52	0.12	0.11	0.05	0.16	0.58	378	340
	1	0.34	0.57	1.00	0.07	0.11	0.13	0.24	3.16	464	426
	2	0.32	0.49	1.02	0.07	0.10	0.17	0.27	3.00	537	499
PP1	3	0.34	0.64	0.97	0.10	0.12	0.15	0.27	3.15	459	421
	Average	0.33	0.57	1.00	0.08	0.11	0.15	0.26	3.10	487	449

Sample	Ne	S1	S2	S3	S3CO	PC	RC	тос	MINC	TpkS2	Tmax
	NO.	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(%)	(%)	(%)	(%)	(°c)	(°c)
	1	1.21	1.18	1.27	0.20	0.25	1.80	2.05	3.25	464	426
200	2	1.22	1.42	1.29	0.21	0.27	1.84	2.11	3.27	463	425
PPZ	3	1.24	1.38	1.22	0.21	0.27	1.82	2.09	3.21	463	425
	Average	1.22	1.33	1.26	0.21	0.26	1.82	2.08	3.24	463	425
	1	0.99	1.06	1.64	0.18	0.23	1.44	1.67	3.31	472	434
002	2	0.96	1.01	1.48	0.19	0.22	1.39	1.61	3.66	461	423
PPS	3	1.00	1.29	1.55	0.19	0.25	1.45	1.70	3.40	458	420
	Average	0.98	1.12	1.56	0.19	0.23	1.43	1.66	3.46	464	426
	1	1.01	0.71	0.75	0.12	0.17	1.51	1.68	3.09	463	425
	2	1.05	0.76	0.67	0.10	0.18	1.52	1.70	3.07	462	424
PP4	3	1.12	0.72	0.67	0.13	0.18	1.52	1.70	3.14	465	427
	Average	1.06	0.73	0.70	0.12	0.18	1.52	1.69	3.10	463	425
	1	0.70	1.16	1.26	0.30	0.21	0.55	0.76	3.55	446	408
	2	0.78	1.30	1.25	0.30	0.23	0.59	0.82	3.66	407	369
PVV1	3	0.82	1.38	1.30	0.38	0.25	0.60	0.85	3.66	379	341
	Average	0.77	1.28	1.27	0.33	0.23	0.58	0.81	3.62	411	373



APPENDIX E

GC-FID and GC-MS Chromatograms

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CNB2





DR2



DM11



DM12











KSB1



KSB2













NS1



NS2









PP2



РРЗ



PP4



PW1

VITA

Mr.Prawat Chamchoy was born in Phetchaburi in 1976. He studied at Phrommanusorn School in Phetchaburi from 1988-1993. He graduated in Bachelor Degree of Science of Chemistry from Chiang Mai University in 1998. After graduation, he has been employed under the position of scientist of Department of Mineral Resources in 1998-2002 and started at Department of Mineral Fuels in 2002. He has been studied in Master Degree of Science in Earth sciences at Chulalongkorn University since 2011.



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