ธรณีเคมีปิโตรเลียมของหมวดหินห้วยหินลาดในอำเภอน้ำหนาว จังหวัดเพชรบูรณ์ และอำเภอชุมแพ จังหวัดขอนแก่น ประเทศไทย

นางสาววิไลรัตน์ โฆษิตชัยศรี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

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ปีการศึกษา 2555

PETROLEUM GEOCHEMISTRY OF HUAI HIN LAT FORMATION IN AMPHOE NAM NAO, CHANGWAT PHETCHABUN AND AMPHOE CHUMPAE, CHANGWAT KHON KAEN, THAILAND

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ที่ราบสูงโคราชตั้งอยู่ในบริเวณภาคตะวันออกเฉียงเหนือของประเทศไทย มีการสำรวจพบแก๊สธรรมชาติและผลิตในเชิงพาณิชย์ในแอ่งตะกอนยุคไทรแอสซิก และเพอร์เมียน เชื่อกันว่าหมวดหินห้วยหินลาดและกลุ่มหินสระบุรียุคเพอร์เมียนเป็นหินต้นกำเนิดแก๊สเหล่านี้ อย่างไรก็ตาม การศึกษาทางธรณีเคมีปิโตรเลียมในพื้นที่ยังมีน้อย การศึกษานี้ได้เก็บตัวอย่างหินโผล่จากหมวดหินห้วยหินลาด และกลุ่มหินสระบุรี มาทำการวิเคราะห์คุณสมบัติทางธรณีเคมีปิโตรเลียม เพื่อประเมินศักยภาพในการเป็นหินต้นกำเนิดปิโตรเลียม โดยทำการวิเคราะห์หาค่าปริมาณคาร์บอนอินทรีย์ทั้งหมด (TOC) และปริมาณสารอินทรีย์ที่สกัดได้ (EOM) ซึ่งเป็นการประเมินเบื้องต้นถึงความสมบูรณ์ของสารอินทรีย์ในหินต้นกำเนิด การวิเคราะห์หาค่า Vitrinite Reflectance (Ro), การศึกษา nonbiomarkers และ biomarkers ด้วยเครื่องแก๊สโครมาโตกราฟี และเครื่องแก๊สโครมาโตกราฟี-แมสสเปกโตรมิเตอร์ และการวิเคราะห์ด้วยเครื่อง Rock-Eval Pyrolysis เป็นการประเมินระดับความร้อนที่เหมาะสมในการให้ปิโตรเลียม และสภาพแวดล้อมในการตกสะสมตัว นอกจากนี้ ยังทำการวิเคราะห์ชนิดของเคอโรเจนด้วยกล้องจุลทรรศน์ เพื่อหาเปอร์เซ็นต์ของเคอโรเจนชนิดต่างๆในตัวอย่างหิน ในการประเมินเบื้องต้นพบว่าหมวดหินห้วยหินลาดมีค่า TOC 0.79-13.80 wt% ซึ่งแสดงให้เห็นถึงความมีศักยภาพในการเป็นต้นกำเนิดในระดับปานกลางถึงดีมาก ในขณะที่หมวดหินน้ำดุก, หัวนาคำ และตากฟ้า มีค่า TOC อยู่ระหว่าง 0.66-0.75 wt%, 1.47-1.74 wt% และ 0.37 wt% ตามลำดับ ค่า TOC แสดงให้เห็นว่า กลุ่มหินสระบุรีมีศักยภาพในการเป็นหินต้นกำเนิดในระดับปานกลางถึงดี ในขณะที่ค่าปริมาณสารอินทรีย์ที่สกัดได้ในทุกตัวอย่างมีค่ามากกว่า 200 ppm ซึ่งเป็นระดับที่สามารถพิจารณาเป็นหินต้นกำเนิดปิโตรเลียมได้ สำหรับการวิเคราะห์ค่าระดับความร้อนที่เหมาะสมในการให้ปิโตรเลียม ตัวอย่างหินมีค่า Ro ระหว่าง 0.898-1.935% ซึ่งแสดงให้เห็นถึงระดับความร้อนอยู่ในช่วงที่สามารถให้ปิโตรเลียม (น้ำมัน) ได้ในช่วงสุดท้ายถึงผ่านการให้ปิโตรเลียม(น้ำมัน) แล้ว ค่าอัตราส่วนของ Ts/(Ts+Tm), C_{31} 22S/(22S+22R), Pr/nC_{17} และ Ph/nC_{18} รวมถึงค่า CPI สนับสนุนว่าตัวอย่างอยู่ในช่วงที่สามารถให้ปิโตรเลียมได้ จากการศึกษาชนิดและสัดส่วนของเคอโรเจนในตัวอย่าง พบว่าประกอบด้วยเคอโรเจนชนิด III เป็นส่วนใหญ่ นอกจากนี้ค่าอัตราส่วน Pr/Ph, Pr/nC_{17}, Ph/nC_{18} และไดอะแกรมสามเหลี่ยมของ C_{27}-C_{29} regular sterane ชี้ให้เห็นว่าสารอินทรีย์มาจากสิ่งมีชีวิตจากบนบกและทะเล ที่มีการตกสะสมตัวภายใต้สภาวะไร้ออกซิเจน การพบ gammacerane ในทุกตัวอย่าง ยังชี้ให้เห็นว่ามีสภาพแวดล้อมในการตกสะสมตัวในทะเลสาบแบบปิดมาเกี่ยวข้องด้วย ผลที่ได้จากการศึกษาครั้งนี้ สรุปได้ว่า ในชุดหินที่ศึกษา หมวดหินห้วยหินลาดและหมวดหินหัวนาคำมีโอกาสสูงในการเป็นหินต้นกำเนิด ปิโตรเลียมของที่ราบสูงโคราช

ภาควิชา ธรณีวิทยา ลายมือชื่อนิสิต

สาขาวิชา โลกศาสตร์ ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

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KEYWORDS: PETROLEUM SOURCE ROCK/ PETROLEUM GEOCHEMISRY / HUAI HIN LAT FORMATION / KHORAT PLATEAU

WILAIRAT KHOSITCHAISRI: PETROLEUM GEOCHEMISTRY OF HUAI HIN LAT FORMATION IN AMPHOE NAM NAO, CHANGWAT PHETCHABUN AND AMPHOE CHUMPAE, CHANGWAT KHON KAEN, THAILAND. ADVISOR: KRUAWUN JANKAEW, Ph.D., 127 pp.

Khorat Plateau is located in the northeast of Thailand where natural gas has been discovered and commercially produced from Triassic and Permian Basin. Huai Hin Lat Formation and Permian Saraburi Group are believed to be the petroleum source rocks of the gases. However, petroleum geochemical studies in this area are relatively scarce. This study includes collecting outcrop samples from Huai Hin Lat Formation and Saraburi Group and analyzing them for their geochemical properties to evaluate their potentials to be the sources of petroleum. Total organic carbon (TOC) content and extractable organic matter (EOM) were determined as the preliminary source richness evaluation. Then, vitrinite reflectance measurement, studies of nonbiomarkers and biomarkers by Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS), Rock-Eval pyrolysis were done to evaluate their thermal maturity and depositional environment. Moreover, visual kerogen analysis was done to determine the percentages of different kerogen types in samples. Huai Hin Lat Formation has TOC value of 0.79-13.80 wt% which indicates fair to excellent source potential while Nam Duk, Hua Na Kham and Tak Fa Formations have TOC values of 0.66-0.75 wt%, 1.47-1.74 wt% and 0.37 wt%, respectively. These TOC values suggest that Saraburi Group has fair to good source potential. Extractable organic matter (EOM) of all samples exceed 200 ppm suggesting that sufficient quantities of petroleum can be generated from these rocks. Therefore, they can be considered petroleum source rock. In term of thermal maturity, Ro values of samples are 0.898-1.935% which indicates a range of maturity level of late mature to post mature. Ts/(Ts+Tm), C_{31} 22S/(22S+22R), Pr/$n$$C_{17}$ and Ph/$n$$C_{18}$ and CPI values also support that samples are mature. Visual kerogen reveals that samples contain predominantly Type III kerogen. Pr/Ph, Pr/$n$$C_{17}$, Ph/$n$$C_{18}$ and ternary diagram of C_{27}-C_{29} regular steranes all suggest that samples are of mixed organic sources between terrigenous and marine organic matters deposited in a reducing environment. Presence of gammacerane in all sample studied further suggests lacustrine environment of deposition. In conclusion, from results in this study Huai Hin Lat and Hau Na Kham Formations are likely the source of petroleum found in the Khorat Plateau area.

Department: Geology Student's Signature ....
Field of Study: Earth Sciences Advisor's Signature ....
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CHAPTER I

INTRODUCTION

Petroleum resources are an important energy source of the country. Each year, the demand for petroleum has increased. The quantity of petroleum produced in Thailand is not enough, so the budget to pay for import petroleum is increasing continuously. Thailands need for petroleum exploration and alternative energy sources have increased continuously in order to reduce the need to import, and to have adequate energy sources for domestic use in the future.

Khorat Plateau is a plateau in the northeastern part of the country with an area of about 150,000 square kilometers (Department of Mineral Resources, 2007). The Khorat Plateau includes the Permo-Carboniferrous, Triassic, Mesozoic and Tertiary basin sediments (Booth, 1998). The Khorat Plateau has seen exploration since the discovery of petroleum in 1960. It was found that gas accumulated in 4 fields, which compose of Nam Phong, Sin Phu Horm, Dong Mun and Si That Fields. The Nam Phong and Sin Phu Horm Fields have been put for commercial production, while the Dong Mun Field is expected to have enough potential for future development (Department of Mineral Fuels, 2008).

In the past, the search for petroleum in the Khorat Plateau was focused on the Triassic sandstone. But recently, it has been found that Permian carbonate rocks of Pha Nok Khao Formation can be gas reservoirs (Coordinating Committee for Geoscience Programs in East and Southeast Asia [CCOP], 2002). Researchers believe that Permian shale in the Saraburi Group and organic-rich Triassic shale are the possible source rocks for these gases (Porwal and Jain, 2008). However, current available geochemical data of these rocks is not enough to prove that they are the source for petroleum discovered and produced from the Khorat Plateau. We believe that more studies on petroleum geochemistry of these potential source rocks will delineate the most probable source rocks for petroleum in the Khorat Plateau.

This study includes (1) determination of the amount of total organic carbon (TOC) to indicate quantity of organic matter in the rock, (2) analyzing for biomarkers using Gas Chromatography (GC) and Gas Chromatography – Mass Spectrometer (GC-MS), (3) determining vitrinite reflectance (Ro) values of the source rocks to assess their thermal maturity for the petroleum generation (4) analyzing the type of kerogen and maturity level by rock-eval pyrolysis method, and (5) determination of kerogen types under microscope.

1.1 Area of study

Selected outcrop samples of Huai Hin Lat Formation and Saraburi Group were collected from Changwat Nakhon Ratchasima, Changwat Phetchabun and Changwat Khon Kaen in the Khorat Plateau. The locations are shown as stars in Figure 1.1.

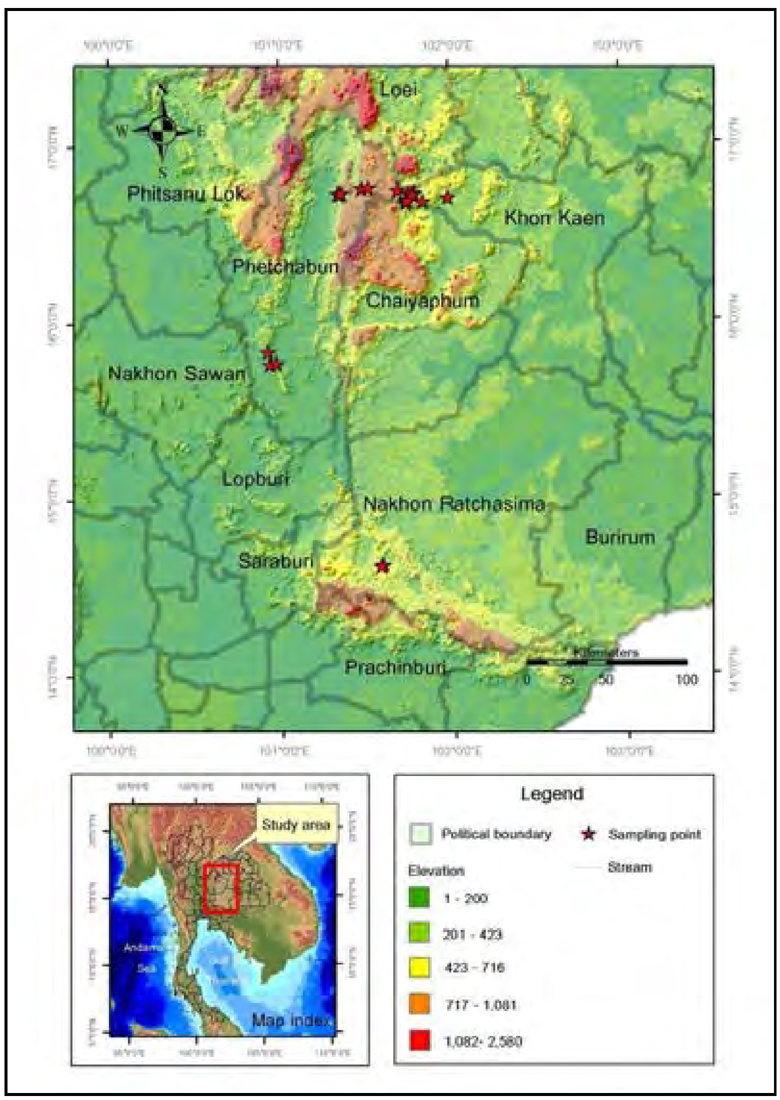

Figure 1.1 Map shows locations of samples collected for this study.

1.2 Objective

To evaluate petroleum source rock potential of the Huai Hin Lat Formation in the Khorat Plateau by analyzing the organic geochemical properties of the source rock and determining thermal maturity in relation to petroleum generation.

1.3 Expected results

1.3.1 Organic geochemical characteristics of Huai Hin Lat Formation.

1.3.2 Petroleum source rock potential of Huai Hin Lat Formation.

1.4 Theory

Source rocks are sedimentary rocks that constitute, may become, or are able to generate petroleum (Tissot and Welte, 1984). Source rock potential considered together three parameters including (1) quantity of organic matter, (2) type of kerogen (quality) and (3) thermal maturity level.

1.4.1 Quantity of organic matter

Primary screening parameter for assessment of petroleum source rock potential is TOC (total organic carbon) analysis. The higher the amount of organic matter represents the greater potential to be a good source rock. Peters and Cassa (1994) classified TOC content for shale into 5 potential levels and Gehman (1962) suggested that organic content of shale is four times of that of limestone given the same hydrocarbon content. As a result, the classification of the limestone uses the criteria TOC value of a quarter of that of the shale as shown in Table 1.1.

Table 1.1 Classification of potential source rock in shale and limestone based on TOC values (Peters and Cassa, 1994; Gehman, 1962).

TOC (wt.%)		**Potential (Quantity)**
In shale	**In limestone**	
< 0.5	< 0.12	Poor
0.5-1.0	0.12-0.25	Fair
1.0-2.0	0.25-0.50	Good
2.0-4.0	0.50-1.0	Very good
>4.0	>1.0	Excellent

1.4.2 Quality of organic matter

Kerogen is an organic matter which is insoluble in any organic solvent. It has highly complex molecules. The study of kerogen can be done in 2 ways. The first way is using an optical microscope to classify the type of kerogen and find the ratio among the quantity of each kerogen type. The second way is utilizing data from Rock-Eval pyrolysis. Rock-Eval pyrolysis uses the programmed temperature heating in a pyrolysis oven in an inert atmosphere (helium). Normally, pyrolysis process provides data recorded in three peaks (mg HC/ g rock) as following (Milner, 1996) and shown in Figure 1.2,

S_1 peak represents the quantity of free hydrocarbon C_1-C_{23} in the rock generated under the temperature of 300^oC.

S_2 peak represents the amount of hydrocarbon generated from the thermal cracking of kerogen or C_{24+} bitumen under the temperature of up to 550^oC.

S_3 peak represents carbon dioxide released during the pyrolysis under the temperature of 300-390^oC.

S_1, S_2, and S_3 peaks can be used to determine the kerogen type by calculating hydrogen index (HI) as S_2/TOC x 100 and oxygen index (OI) as S_3/TOC x 100 and plot the these values in the Pseudo-van Krevelen diagram (Figure 1.3).

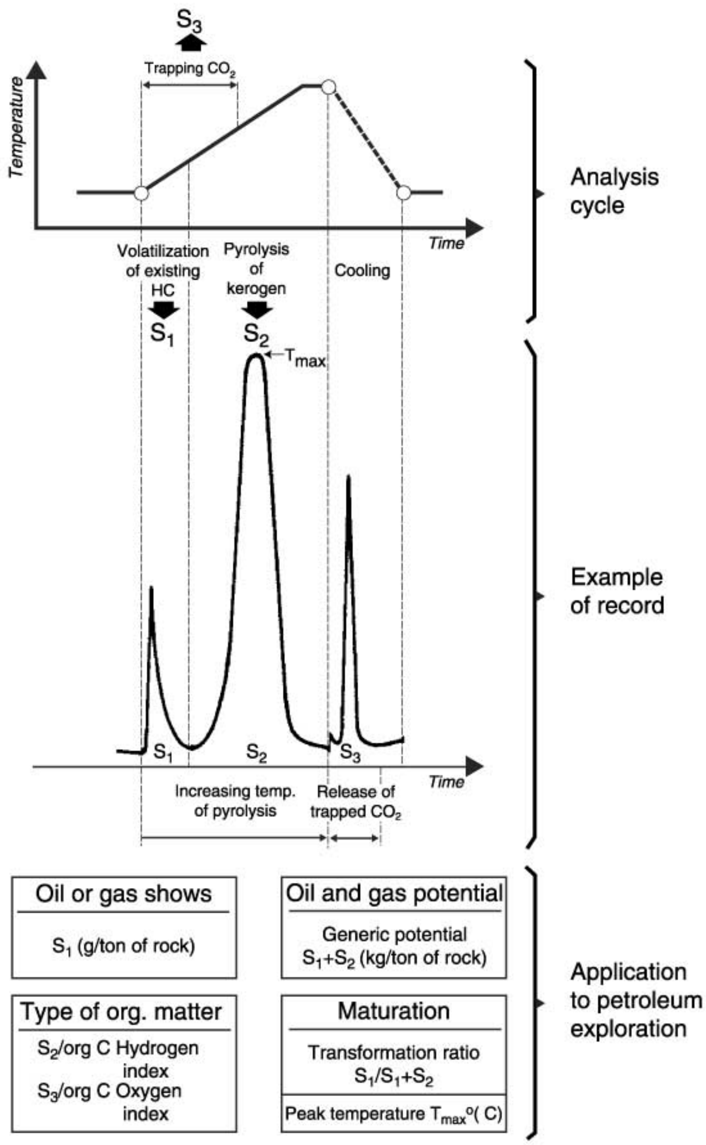

Figure 1.2 Diagram shows temperature cycle of Rock-Eval pyrolysis method and example of recorded results (S_1, S_2, S_3, Tmax) (Tissot and Welte, 1978).

Kerogen is classificated into four types which are defined by the value of atomic hydrogen/carbon (H/C) and oxygen/carbon (O/C) or the value of hydrogen index (HI) and oxygen index (OI) as follows (Peters and Cassa, 1994).

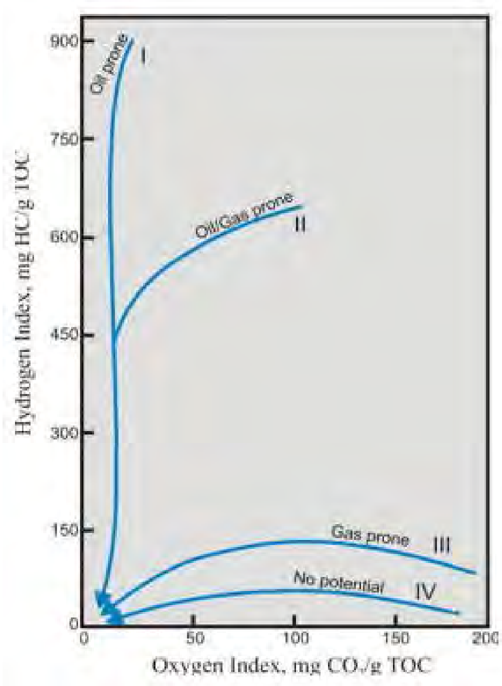

Figure 1.3 Modified Van Krevelen diagram (Pseudo-van Krevelen diagram) using HI and OI in classifying kerogen types (Slatt, 2002).

Type I kerogen mainly consists of liptinite macerals. It derives principally from lacustrine algae and forms only in anoxic lacustrine and several other unusual marine environments. This kerogen type is oil prone and has high atomic H/C ($\geq$1.5) and low atomic O/C (<0.1).

Type II kerogen is a gas-oil prone kerogen which has moderate atomic H/C value (1.2-1.5) and low atomic O/C compared to kerogen types III and IV. It is mainly derived from plankton and deposited in anoxic marine environments.

Type III kerogen has low atomic H/C (<1.0) and high atomic O/C ($\leq$0.3). It is mainly derived from terrestrial higher plants debris. Type III kerogen is gas prone and mostly found in marine source rocks which had deposited sediment from continental area.

Type IV kerogen can be derived from organic debris which have been reworked or oxidized. This type of kerogen is neither gas prone nor oil prone because it has almost no potential left. It has very low atomic H/C (0.5-0.6) and low to high atomic O/C (≤0.3).

1.4.3 Thermal maturation

The increase in temperature and pressure due to increasing burial depth of the source rock causes the change in the organic matters contained in the rock as the maturation progresses. From this process, organic matters change to kerogen and later condensates, oil and gas are generated from kerogen. If the temperature and depth of burial are still increasing, oil and condensate will eventually crack to gas. The temperature at which the source rock will generate petroleum is indicated by thermal maturity.

1.4.3.1 Vitrinite reflectance (Ro)

Vitrinite reflectance is a technique for identifying the thermal maturity level of petroleum source rock. Vitrinite reflectance measured light reflected by polished vitrinite particles in the sample in terms of percentage. Classification of maturity levels based on Ro values are shown in Table 1.2.

1.4.3.2 Rock-Eval pyrolysis

Tmax value can be used to identify the level of maturity of the source rock. It is the temperature of the highest value of S_2 peak from the pyrolysis method mentioned in Section 1.4.2. Maturity classification using Tmax value is also shown in Table 1.2.

Low hydrogen index (HI), calculated from S_2/TOC x 100, together with low oxygen index (OI), calculated from S_3/TOC x 100, could be used to suggest high level of thermal maturity and vice versa.

Production index (PI) is calculated as $S_1/(S_1+S_2)$ and can be used to identify the level of maturity. Thermal maturity levels based on PI are shown in Table 1.2 as well.

Table 1.2 Classification of thermal marturity by Tmax, %Ro and PI (modified from Peters and Cassa, 1994; Bacon et al., 2000).

Stage of Thermal Maturity of Oil		**Tmax for**			**Ro (%)**	**Production Index (PI: $S_1/(S_1+S_2)$)**
		Type I	**Type II**	**Type III**		
Immature		<440	<435	<445	0.20-0.60	<0.10
Mature	Early	440	435	445	0.60-0.65	0.10–0.25
	Peak	445	440	450	0.65-0.90	0.25–0.40
	Late	450	460	470	0.90-1.35	>0.40
Postmature		>450	>460	>470	>1.35	–

1.5 Previous works

Petroleum surveys in Khorat Plateau have been conducted since 1962. The surveys can be divided into 4 periods (Booth, 1998). The first period (1962-1972) was the finding of a small amount of gas in Kuchinarai-1 well drilled by Union Oil Company of Thailand Ltd.

The second period (1979-1984) was the finding of gas in 8 wells in the structural traps of Nam Phong Formation (Ismail, 2008) as well as in Phu Horm-1 and Chonnabot-1 wells. However, the flow tests had not been conducted at that time. After this period, the petroleum in this area had been used for commercial purposes since 1988. These findings have shown more possibility to find petroleum and/or source rocks which may be present in the area.

The third period (1990-1994) involved the usage of more conventional tools, to find the petroleum and assess the geological data. The 2-D seismic data had been used in the exploration and 12 more wells were drilled. However, only Dong Mun-1 well had enough potential for commercial usage.

The fourth period (since 1996) began with finding natural gas of Si That-2 well with an amount adequate to be considered for commercial usage.

According to petroleum surveys and commercial petroleum usage in the area, little of the petroleum geochemical data is found (or record). The studying of geochemical properties and biomarker derivatives play significant roles in the understanding of the source potential. They have been applied in other Tertiary basins of Thailand (such as Lawwongngam and Philp, 1993; Jankaew, 2002) and source rocks from Sirikit Oil Field in the Phitsanulok Basin (Klaingglom et al., 2005).

Based on geological survey along highway no. 12 (Lom Sak to Chum Phae road), Sattayarak (1987) proposed that source rocks of the petroleum in the Khorat Plateau may be (1) shale and grey to dark limestone of Triassic Huai Hin Lat Formation in Ban Huai Sanam Sai, Amphoe Nam Nao and (2) dark limestone and shale of Permian Saraburi Group. Huai Hin Lat Formation, or Pre-Khorat Facies, is the unit of the rock of the Late Triassic period (Carnian-Norian) at the western edge of the Khorat Plateau (Chonglakmani and Sattayarak, 1978).

The petroleum system in Khorat Plateau had been studied by Porwal and Jain (2008) in blocks L39/48 and L22/55 using 1-D thermal modeling which had found that the main source rock was possibly the Huai Hin Lat Formation and the secondary sources were possibly Nam Duk Formation in Saraburi Group. They suggested that Huai Hin Lat Formation is an oil-prone source rock and the onset of petroleum generation was in Middle Cretaceous period while peak oil generation was in Tertiary. Porwal and Jain (2008) further suggested that Nam Duk Formation of Saraburi Group may have enough potential for high quantity gas generation if there is an appropriate thermal maturity. For the upper clastics, Pha Nok Khao and Si That Formations, there was the study of TOC contents and thermal alteration index (TAI) which showed that they can possibly be the potential source rock for gas (Pradidtan, 1995; Chinoroj and Cole, 1995).

Thongboonruang (2008) summarized geochemical data of source rock from 4 wells; Phulop-1 well, Khumpalai-1 well, Daoruang-1 well and Phuwiang-1 well, and reported that they have fair to excellent levels of organic richness with type III/IV kerogen and have thermal maturity for petroleum generation in the level of late mature to post mature.

CHAPTER II

GEOLOGY OF STUDY AREA

2.1 Geology of the Khorat Plateau

The Khorat Plateau is the large plateau with the area of approximately 200,000 km^2 which covers in Southeast Asia (Smith and Stokes, 1997). In Thailand, the plateau covers the area from Sankampheang Range and Dongrek Mountains at the border of Cambodia in the south and Phetchabun and Dong Phayayen Mountain Ranges in the west to Mekong River at the border of Laos in the northeast (latitude of 14°N-19°N and longitude of 101°E-106°E) which is approximately 150,000 km^2 (Department of Mineral Resources, 2007). Extensive outcrops of Mesozoic rocks can be found in the area of the plateau (Figures 2.1 and 2.2). The morphological structure of the plateau is called 'sauce-pan morphology' (Piyasin, 1995). It is characterized by a rolling surface and undulating hills. The western and the southern margins of the plateau are rimmed by an escarpment of mostly steeply dipping sediments which forms cuestas rising with the elevation of 600-1,000 m (above msl). The average elevation of the plateau is about 130-250 m (above msl) and slopes gradually towards the Mekong River.

The geological structure of the Khorat Plateau consists of Khorat Group spreading across the whole area while the Saraburi Group and the Huai Hin Lat Formation can only be found in the western part of the plateau as shown in Figure 2.1 (Chantong, 2007). For Saraburi Group and Huai Hin Lat Formation, the detail will be discussed in Sections 2.2.3 and 2.2.4, respectively. The Khorat Group comprises siltstone, sandstone, claystone and conglomerate. The age of these sediments ranges from Late Triassic to Cretaceous and Tertiary, and the thickness of these sediments is approximately 4,000 m. It overlies the eroded surface of upper Paleozoic rocks. The Quaternary basalt rarely covers the southern part of the plateau.

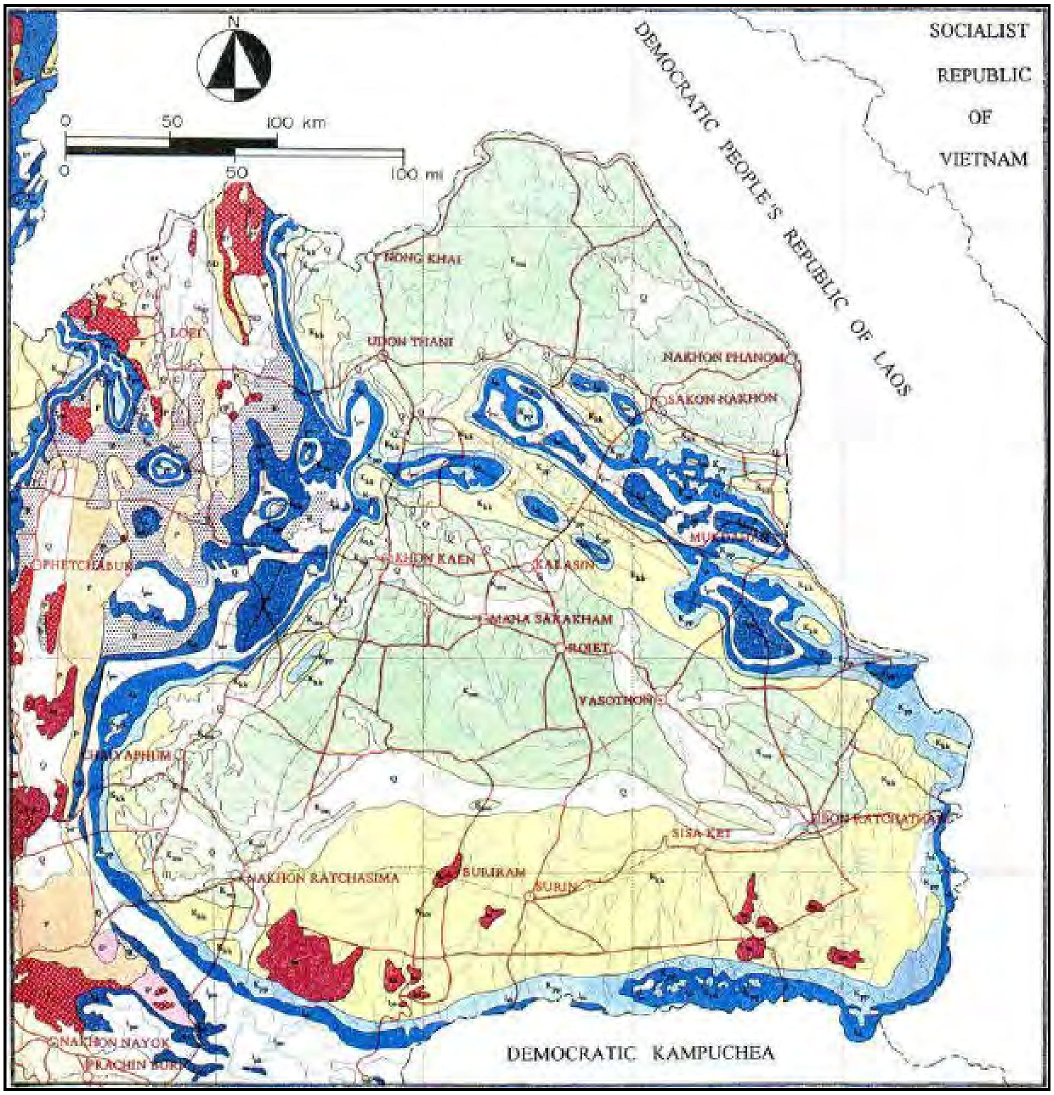

Figure 2.1 Geological map of Northeast Thailand (Department of Mineral Resources, 1987).

Figure 2.2 The explanation of the geological map of Northeast Thailand (Department of Mineral Resources, 1987).

Basin development history in the Khorat Plateau has 4 major events which have an effect on the litho-stratigraphic units, details of these events are listed as follow (Chantong, 2007);

1. Collision of the South China and Indochina blocks in Late Carboniferous period. Saraburi Group deposited over the Carboniferous rocks after this event.

2. Indosinian Orogeny in Permain to Triassic. Half–graben evolution possibly formed during Indosinian Orogeny I which deposit sediment of Haui Hin Lat Formation, then followed by Indosinian Orogeny II.

3. Collision of the Burma and Shan Thai blocks in Cretaceous.

4. Himalayan Orogeny event in Tertiary period.

2.2 Stratigraphy of the Khorat Plateau

According to stratigraphy of the Khorat Plateau and petroleum system by Chantong (2007) as shown in Figure 2.3, the details of related petroleum system are described below.

The uppermost unit of the Late Tertiary age represented in the section is Tha Chang Formation. Khorat Group comprises of rocks from the age of Late Triassic to Cretaceous in the section. The underlying Late Triassic Huai Hin Lat Formation, Kuchinarai Group and the overlying Early Cretaceous to Middle Eocene Mahasarakham and Phu Tok Formation are excluded from this group. Triassic Huai Hin Lat Formation is a unit of interest for this study. The detail of the stratigraphic sequence from the oldest to the youngest is summarized below by DMF (2006).

2.2.1 Basement

The basement of the section consists of the oldest Early Carboniferous rocks from Na Mo Group and Pak Chom Group.

2.2.2 Si That Formation

Si That Formation is the “Lower Clastics” of the Late Carboniferous-Early Permian. It consists of grey to dark grey shale interbedded with limestone, dolomite, and siltstone with some conglomerate in the lower part.

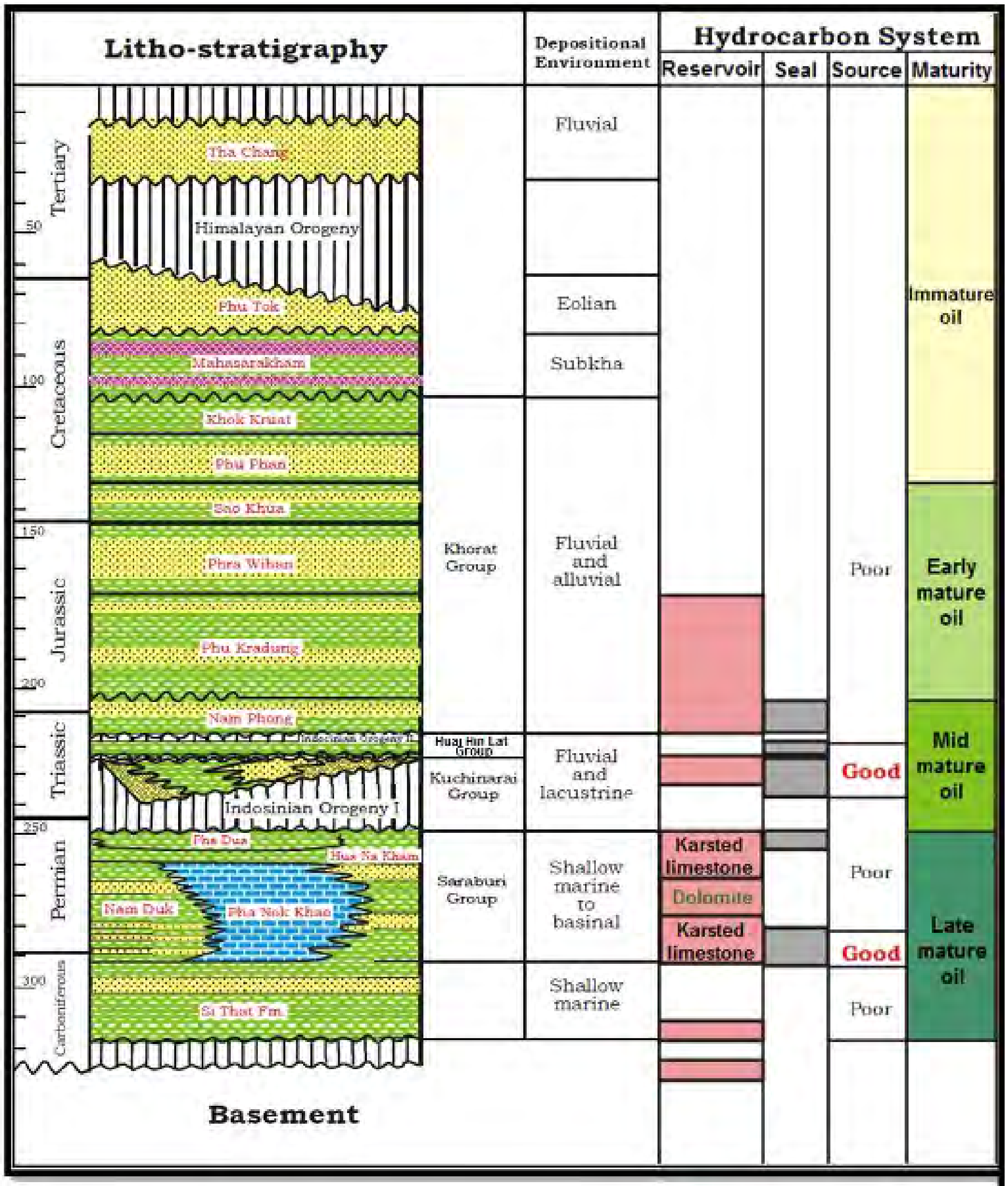

Figure 2.3 Stratigraphy and petroleum system of the Khorat Plateau (Chantong, 2007).

2.2.3 Saraburi Group

The age of the Saraburi Group ranges from Late Carboniferous to Late Permian. It is a carbonate sequence mainly consisting of limestones, dolomites, and clastic sediments of shale, sandstone and siltstone. The Permian limestones of

Saraburi Group have been exposed along the western border of the Khorat Plateau. The group components indicate that the sediment was deposited in various environments ranging from shelf platform to deep basin. Saraburi Group can be divided into 4 formations in ascending order as follows:

2.2.3.1 Nam Duk Formation

Nam Duk Formation deposited from Early to Middle Permian age. It consists of pelagic shale, dark grey sandstone, find-grained limestone with chert interbedded in limestone. The depositional environment of the formation as indicated by the rock sequence is deep sea basin.

2.2.3.2 Pha Nok Khao Formation

Pha Nok Khao Formation deposited from Early to Middle Permian age. Grey limestone and dolomite with grey shale and black chert are rock components in Pha Nok Khao Formation

2.2.3.3 Hua Na Kham Formation

Hua Na Kham Formation is the “Upper Clastics” of the Late Permian conformably overlying the Pha Nok Khao Formation. It consists of intercalated light to dark grey siltstone, sandstone, claystone and limestone. The fossils including fusulinid in limestone indicates that the sedimentary sequence was deposited in a shallow platform marginal marine environment.

2.2.3.4 Pha Dua Formation

Dark shale, siltstone and thin-bedded fine-grained clastic are rock components in Pha Dua Formation

2.2.4 Huai Hin Lat (Kuchinarai) Formation

The Huai Hin Lat Formation unconformably overlies the Permian limestone. The formation mainly consists of conglomerate containing pebbles of limestone, grey to dark sandstone, siltstone, grey mudstone, calcareous shale, dark shale and grey mudstone. This formation is the basement of the Khorat Group. It can be divided into two large sequences, the upper and the lower one. The lower sequence consists of Pho Hai and Sam Khaen Members while the upper sequence consists of Dat Fa, Phu Hi and I Mo Members as shown in Figure 2.4. Details of these five members as described by Chonglakmani and Sattayarak (1978) are as follows;

2.2.4.1 Pho Hai Member is the oldest member in Huai Hin Lat Formation. It is characterized by volcanic rocks such as tuff, agglomerate, rhyolite and andesite intercalated with sandstone and conglomerate. It angular conformably overlies the Permian shale and siltstone. In some areas, it unconformably overlies the fusulinid-bearing Permian limestone.

2.2.4.2 Sam Khaen Member is the most widely distributed unit of the Huai Hin Lat Formation. It is mainly consists of limestone and conglomerate including some intercalated of finer sediment. The lower contact is at the base of conglomerate bed and on the top of the Permian strata. In some areas, the lower contact is on top of the volcanic rocks of Pho Hai Member. The red color of the matrix in the basal conglomerate indicates that it was formed under a warm terrestrial environment.

2.2.4.3 Dat Fa Member consists of calcareous and argillaceous limestone. It is made of grey-black carbon rich well-bedded shale characterized by numerous argillaceous limestones. This member conformably overlies the Sam Khaen Member with the lower contact at the top of the basal conglomerate of Sam Khaen Member while the upper contact is at the base of sandstone or conglomerate of the Phu Hi Member. Grey to black shale and calcilutite of Dat Fa member were deposited in a lacustrine condition with quiet water and restricted environment. This facies of thin and well-bedded shale and black shale containing high organic content with grey sandstone, shale and argillaceous limestone containing terrestrial flora.

2.2.4.4 Phu Hi Member is the lower half of the unit intercalated with conglomerate bed. It conformably overlies the Dat Fa Member with the lower contact at the top of the grey shale and limestone of the Dat Fa Member while the upper contact is at the base of Nam Phong Formation. The Phu Hi Member is mainly consists of grey calcareous shale and limestone intercalated with red shale and siltstone. It was deposited in the deltaic to transitional environments during the filling-up phase of the lake basin by terrigenous sediments and later developed into fluvial environment in the Nam Phong Formation.

2.2.4.5 I Mo Member is the youngest member of Huai Hin Lat Formation. It can be found in the northwestern part of the Khorat Plateau. I Mo Member is characterized by diorite and igneous rocks intercalated with well-bedded shale, sandstone and limestone. It has neither upper contact nor exposition in the plateau.

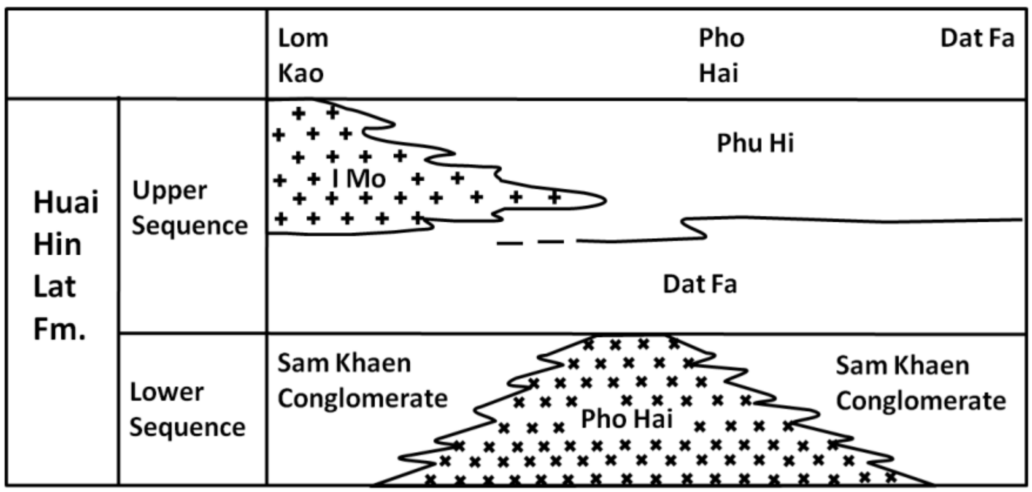

Figure 2.4 Five members of Huai Hin Lat Formation (Chonglakmani and Sattayarak, 1978).

2.2.5 Khorat Group

The Khorat Group overlies the Huai Hin Lat Formation. Sattayarak divide Khorat Group into 7 formations from the oldest to youngest as Huai Hin Lat, Nam Phong, Phu Kradung, Phra Wihan, Sao Khua, Phu Phan and Khok Kruat Formations, respectively. Details of all formations are described as follows (except Huai Hin Lat Formation which is already described in Section 2.2.4);

2.2.5.1 Nam Phong Formation

Interbedded siltstone, sandstone and conglomerate characterize the Nam Phong Formation. This formation conformably overlies the Huai Hin Lat Formation.

2.2.5.2 Phu Kradung Formation

Phu Kradung Formation overlies the Nam Phong Formation. However, in case that Nam Phong Formation is not presented it overlies the Permian rocks. This formation consists of siltstone, greenish grey sandstone, mudstone and conglomerate containing caliche pebbles.

2.2.5.3 Phra Wihan Formation

Phra Wihan Formation is characterized by cross-bedded white quartz sandstone with thin-bedded and dark grey interbedded siltstones.

2.2.5.4 Sao Khua Formation

Sao Khua Formation is in the age of Early Cretaceous and characterized by thick-bedded siltstone, mudstone and sandy conglomerate.

2.2.5.5 Phu Phan Formation

Phu Phan Formation consists of thick and cross-bedded pebbly sandstone. Fragments of dinosaur bones were also found in the formation (Department of Mineral Fuels, 2006).

2.2.5.6 Khok Kruat Formation

Khok Kruat Formation is characterized by siltstone, sandstone, caliche siltstone and conglomerate.

2.2.6 Mahasarakham Formation

Mahasarakham Formation is in the age of Late Cretaceous. It consists of siltstone, sandstone and evaporites (potash, gypsum and rock salt) with the thickness of about 200 m. Sediments in this formation were deposited in the Sakon Nakorn and Khorat Basins.

2.2.7 Phu Tok Formation

Phu Tok Formation consists of small cross-bedded and reddish fine-grained sandstones. The sandstones were deposited by stream and wind.

2.2.8 Tha Chang Formation

Tha Chang Formation is the uppermost rock unit before the deposition of the overlying Quaternary sediments. This formation overlies the Himalayan Unconformity with the thickness of more than 20 m. It is composed of semi-consolidated to consolidated, mudstone and conglomerate.

2.3 Petroleum system of the Khorat Plateau

2.3.1 Source rock

Possible potential source rocks in the Khorat Plauteau are the Triassic Huai Hin Lat Formation and Permian Saraburi Group. The previous reports about the geochemical data show that the Huai Hin Lat Formation has fair to excellent source potential with kerogen type I/III (Sattayarak at el., 1989). The Permian Saraburi Group has fair to good organic richness with kerogen type III-gas prone and type I/III-oil and gas prone (Pradidtan, 1995; Chinoroj and Cole, 1995). The thermal maturity of the Huai Hin Lat Formation and Permian Saraburi Group are in the stage of mature to late mature (Thongboonruang, 2008). Results from petroleum concession survey had reported that Huai Hin lat Formation is possible to be an oil-prone or gas-prone source rock (Sattayarak, 1985).

2.3.2 Reservoir rock

Permian carbonate of Pha Nok Khao Formation is the only sequence which has been proven to be of commercial reservoir quality by the drilling in the Khorat Plateau (Chantong, 2007). The reservoir porosity occurred from dolomitization process and fracture in limestone is important factors that make limestone act as petroleum reservoir. The porosity of the Permian carbonate ranges 0-18% while the matrix porosity is about 4%.

Besides the Pha Nok Khao Formation, the average porosity of sandstones of the Nam Phong, Phu Kradung and Phra Wihan Formations are 4.9%, 6.4% and 5.9%, respectively. They indicate a fair quality reservoir potential (DMF, 2006).

2.3.3 Seal

The seal in the Khorat Plateau consists of Permian shale and limestone, Triassic shale and limestone, clay and shale of Nam Phong Formation and Phu Kradung Formation.

2.3.4 Trap

In the Khorat Plateau, the geological structures and stratigraphic petroleum traps were successfully tested and DMF (2006) summarized that the traps consist of the following;

2.3.4.1 The angular unconformity between the Permian Saraburi Group and the Triassic Huai Hin Lat Formation.

2.3.4.2 The Permian reefal limestones in the foreslope.

2.3.4.3 The structure of half-graben under the Khorat group which consists of Permian and Triassic sediments.

2.3.4.4 The anticline of Triassic and Khorat rocks which formed in the Early Tertiary.

CHAPTER III

METHODOLOGY

The method in this research can be summarized as a flow chart as shown in Figure 3.1.

Literature review of the source rock geochemistry, petroleum geochemistry, and general geology of the Khorat Plateau were carried out. 20 outcrop samples of the Huai Hin Lat Formation and Saraburi Group in the Khorat Plateau were collected for this study. Sample locations are listed in Table 3.1. The detail of collected outcrop samples including bedding attitude is in Section 3.1. The twenty samples were grinded down with a planetary ball mill. The grinded samples were divided into five parts for; (1) analyzing total organic carbon (TOC) with TOC analyzer HT-1300, (2) biomarkers study of extractable organic matter, (3) vitrinite reflectance measurement with CRAIC CoalPro microspectrophotometer, (4) rock-eval pyrolysis and (5) kerogen typing.

Finally, the results from all parts were used for interpretation, discussion and conclusion.

3.1 Sample collection

The field work was carried out during 12th-16th November 2011 to collect outcrop samples of the Huai Hin Lat (HHL) Formation and Saraburi Group.

Sampling locations were limited to the area of HHL Formation and Saraburi Group and base on geologic maps of the area by the Department of Mineral Resources (DMR) (published in 2007 for Changwat Nakhon Ratchasima and 2009 for Changwat Phetchabun and Changwat Khon Kaen).

Total of 11 samples from Huai Hin Lat Formation and 9 samples from Saraburi Group were collected. Samples collected include shales, black shales, mudstones, argillaceous limestones and limestones. Each sample contains rocks collected from several spots within 25 meters radius. Locations of samples collected are summarized in Table 3.1 and details of the samples collected are as follows.

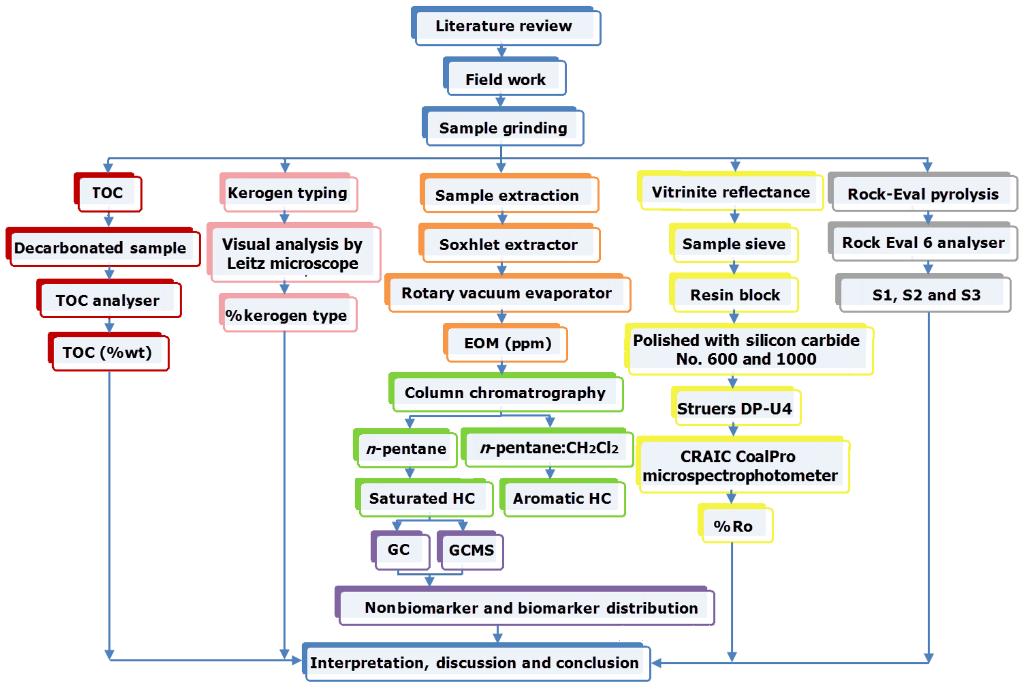

Figure 3.1 Flow chart shows methods of study.

Table 3.1 Sampling locations.

Sample name	Location				
	Latitude (N)	**Longitude (E)**	**Area**	**Amphoe**	**Changwat**
HHL 1	14^o 37' 45.701"	101^o 35' 28.389"	Ban Sap Phu	Pakchong	Nakhon Ratchasima
HHL 2	16^o 45' 37.130"	101^o 29' 6.100"	Ban Huai Rahong	Lom Sak	Phetchabun
HHL 3	16^o 40' 32.597"	101^o 44' 28.182"	Ban Huai Sanam Sai	Nam Nao	
HHL 4	16^o 40' 31.715"	101^o 44' 28.473"			
HHL 5	16^o 41' 4.679"	101^o 45' 5.340"			
HHL 6	16^o 41' 30.671"	101^o 44' 44.696"			
HHL 7	16^o 43' 35.579"	101^o 45' 28.658"	Ban Khok Yao		
HHL 8	16^o 43' 17.347"	101^o 46' 59.826"	Tad Yai Waterfall		
HHL 9	16^o 43' 49.216"	101^o 47' 25.627"	Ban Dong Sakran	Phu Pha Man	Khon Kaen
HHL 10	16^o 44' 41.700"	101^o 41' 43.765"	Wat Wang Thong Samakkhi Tham	Nam Nao	Phetchabun
HHL 11	16^o 42' 19.806"	101^o 59' 21.344"	Ban Nonchat	Chumpae	Khon Kaen
ND 1	16^o 43' 48.565"	101^o 20' 40.669"	Ban Pakchong	Lom Sak	Phetchabun
ND 2	16^o 43' 43.562"	101^o 21' 8.720"			
HNK 1	16^o 43' 53.354"	101^o 21' 56.629"	Ban Pakchong	Lom Sak	Phetchabun
HNK 2	16^o 45' 53.501"	101^o 31' 34.179"	Khao Pha Daeng		
TF 1	15^o 45' 54.528"	100^o 56' 25.262"	Ban Sap Mai Daeng	Bueng Samphan	Phetchabun
TF 2	15^o 46' 28.345"	100^o 58' 40.292"	Ban Nong Man		
TF 3	15^o 50' 9.762"	100^o 55' 37.658"	Ban Sap Charoen		
NML	16^o 40' 58.671"	101^o 50' 28.328"	Ban Wang Pha Dam	Phu Pha Man	Khon Kaen
SB	14^o 37' 9.160"	101^o 34' 43.541"	Ban Nong Song Hong	Pakchong	Nakhon Ratchasima

Location: Amphoe Pakchong, Changwat Nakhon Ratchasima

Two samples were collected at this location (Figure 3.2).

1.1 Argillaceous limestone (HHL1) of Huai Hin Lat Formation on rural road no. 2235. Attitude of bedding is 281/44. The bed thickness is from 1 to 15 centimeters (Figure 3.3).

1.2 Limestone (SB) of Sap Bon Formation in Saraburi Group on rural road no. 2231. Attitude of bedding is 24/21.

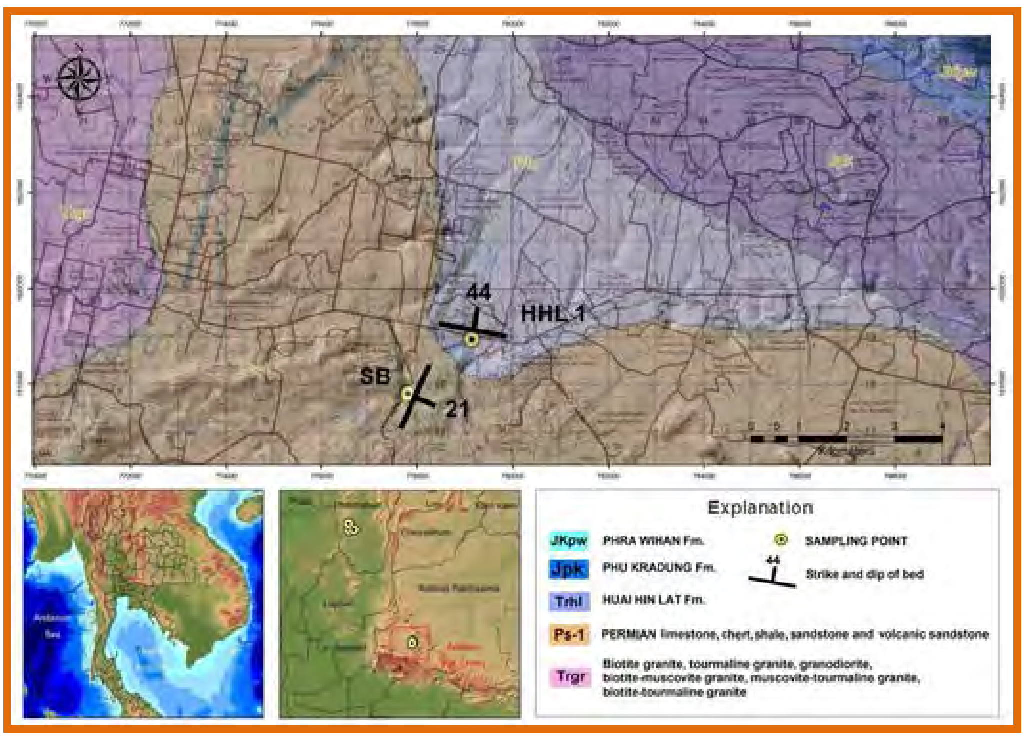

Figure 3.2 Sampling locations in Amphoe Pakchong, Changwat Nakhon Ratchasima plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2007).

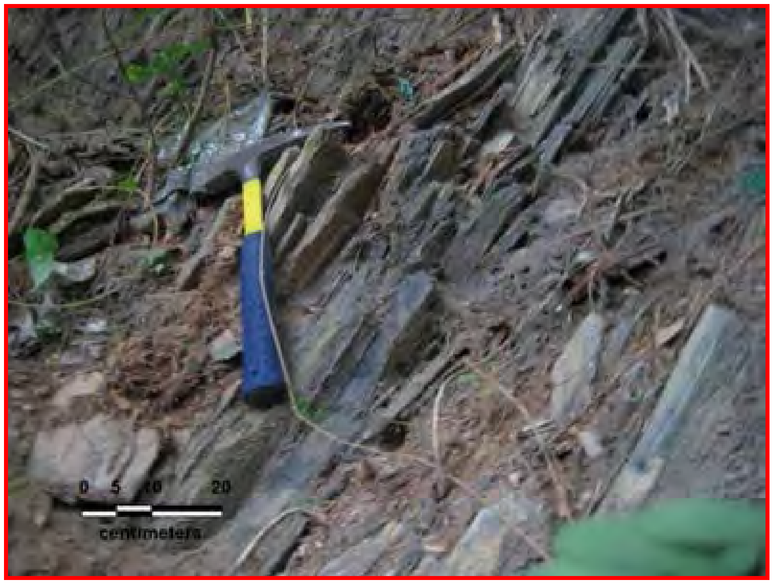

Figure 3.3 Argillaceous limestone (HHL1) of Huai Hin Lat Formation (looking east).

Location: Amphoe Bueng Samphan, Changwat Phetchabun

At this location, three samples of Tak Fa Formation from the Saraburi Group were collected (Figure 3.4).

2.1 Limestone (TF1) on rural road no. 3004

2.2 Limestone (TF2) located approximately 350 meters south of rural road no. 3004. The attitude of bedding is 148/35.

2.3 Argillaceous limestone (TF3) on rural road no. 225. Attitude of bedding is 160/62. This argillaceous limestone is found interbedded with shale layer.

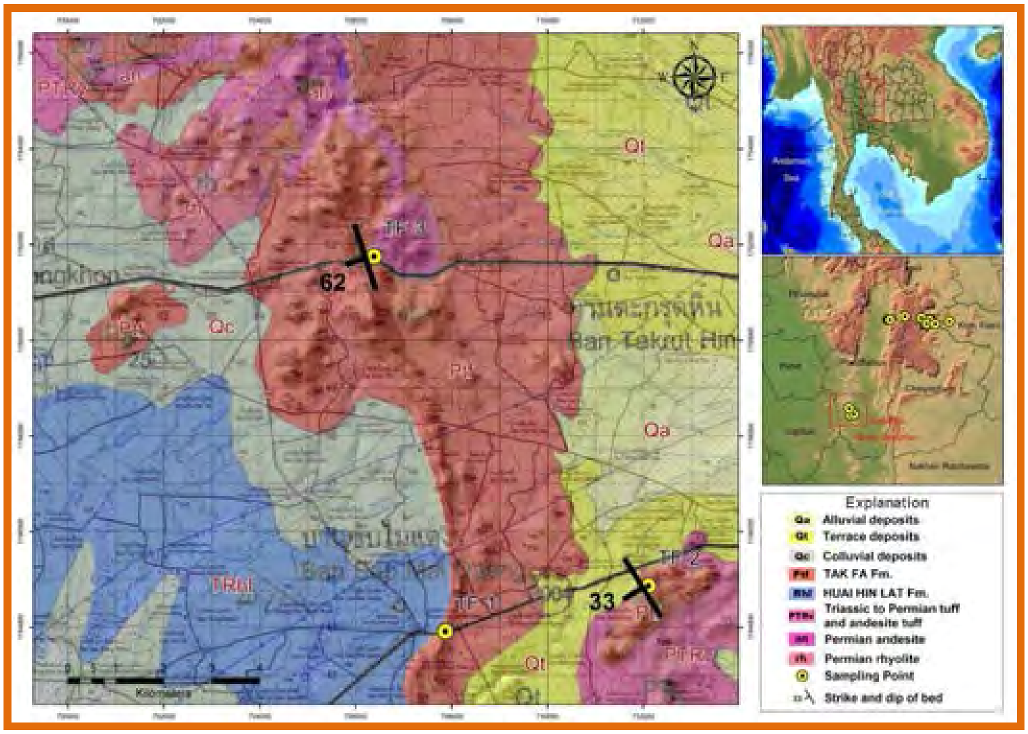

Figure 3.4 Sampling locations in Amphoe Bueng Samphan, Changwat Phetchabun plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2009).

Location: Amphoe Lom Sak, Changwat Phetchabun

At this location, five samples on highway no. 12 at Amphoe Lom Sak, Changwat Phetchabun were collected (Figure 3.5).

3.1 Shale (ND1) of Nam Duk Formation. Shale is interbedded with siltstone and sandstone (Figure 3.6). Attitudes of bedding are 190/70 and 175/75.

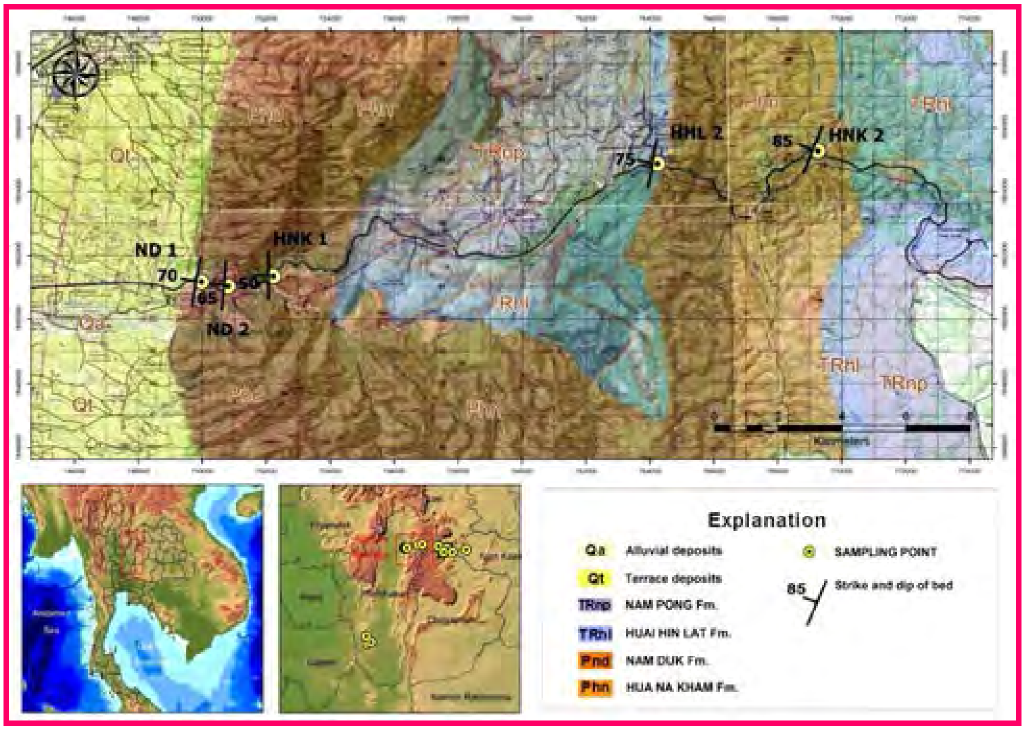

Figure 3.5 Sampling locations in Amphoe Lom Sak, Changwat Phetchabun plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2009).

Figure 3.6 Outcrop of Nam Duk Formation (ND1), looking NE.

3.2 Calcareous shale (ND2) of Nam Duk Formation. Attitude of bedding is 185/65.

3.3 Dark shale (HNK1) of Hua Na Kham Formation (Figure 3.7). Attitude of bedding is 180/50. This shale has a darker color than the calcareous shale of ND2.

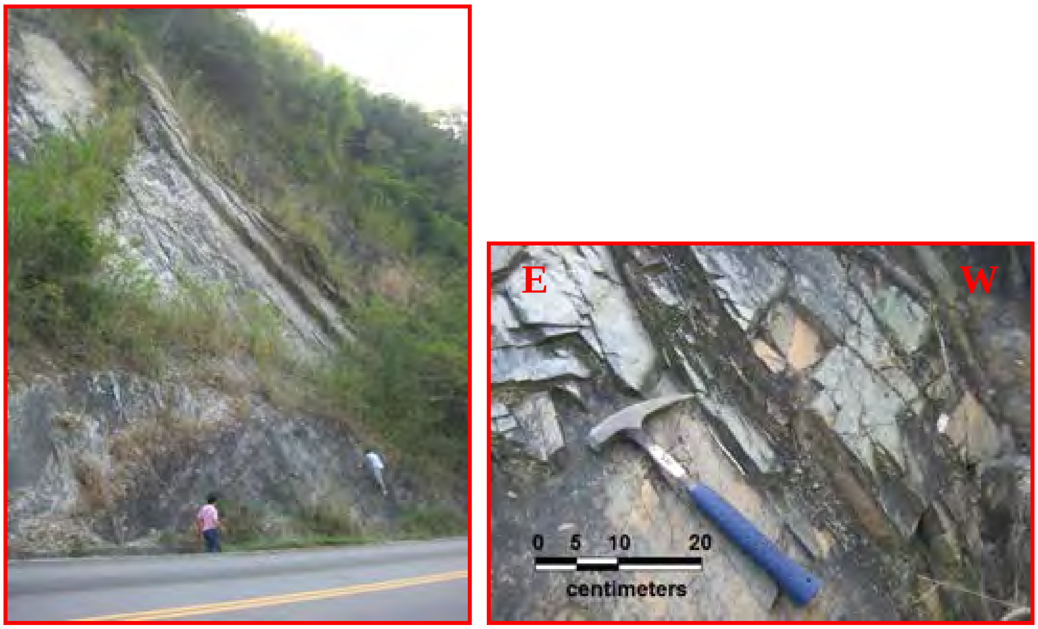

Figure 3.7 Dark shale (HNK1) exposure is approximately 80 meters high on road side no. 12.

3.4 Shale (HHL2) of Huai Hin Lat Formation. Attitude of bedding is 190/75 (Figure 3.8).

3.5 Shale (HNK2) of Hua Na Kham Formation. The attitude of bedding is 22/85 (Figure 3.9).

Figure 3.8 Alternating beds of shale (6 centimeters thick) and sandstone (10 centimeters thick), looking east.

Figure 3.9 Shale (HNK2) exposure is approximately 15 meters high on road side no. 12.

Location: Amphoe Nam Nao, Changwat Phetchabun

At this location, seven samples on rural road no. 2216 in Amphoe Nam Nao, Changwat Phetchabun were collected (Figure 3.10). All of the samples are from Huai Hin Lat Formation.

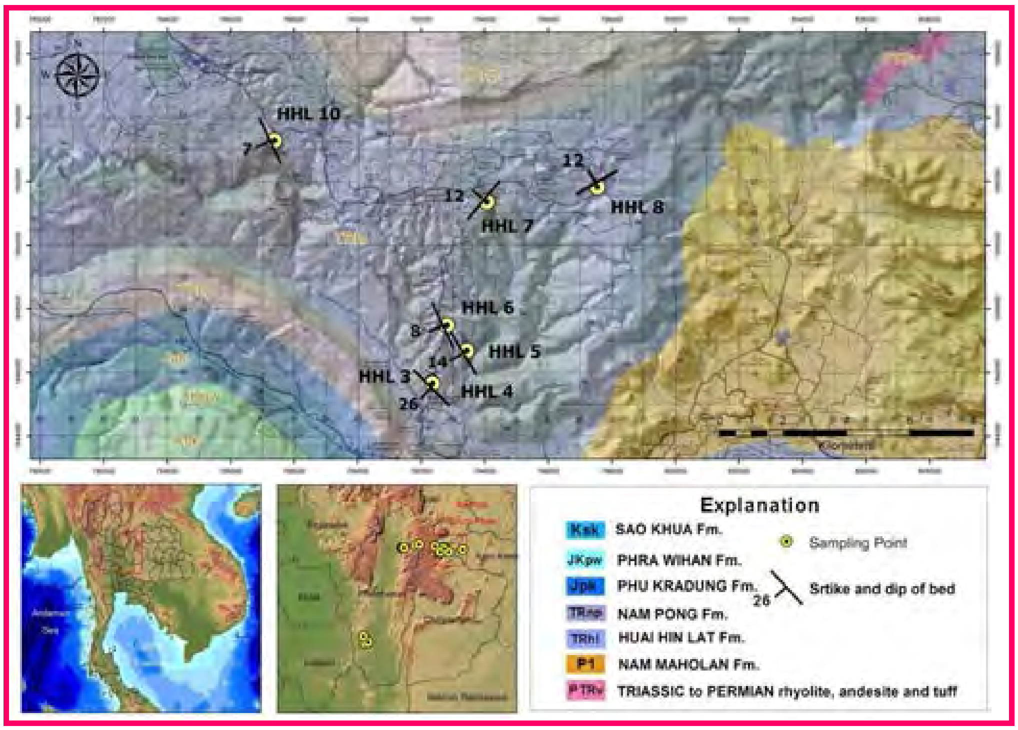

Figure 3.10 Sampling locations in Amphoe Nam Nao, Changwat Phetchabun plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2009).

4.1 Coal (HHL3) of Huai Hin Lat Formation. Coal outcrop is approximately 3-4 meters in height and 10 meters in width. Attitude of bedding is 153/39 (Figure 3.11).

Figure 3.11 Coal outcrop of HHL3 from Huai Hin Lat Formation, looking west.

4.2 Shale (HHL4) of Huai Hin Lat Formation. This outcrop is located south of coal outcrop (HHL3). Attitude of bedding is 135/26 (Figure 3.12).

4.3 Shale (HHL5) of Huai Hin Lat Formation. Attitude of bedding is 149/14.

4.4 Sample HHL6 is shale of Huai Hin Lat Formation located northwest of shale (HHL5) outcrop. Mud cracks were observed on the surface of the shale loose block (Figure 3.13). Attitude of bedding is 155/8 (Figure 3.14).

4.5 Shale (HHL7) of Huai Hin Lat Formation at Tad Mok Waterfall. Attitude of bedding is 220/12 (Figure 3.15). The range of bed thickness is from 10 centimeters to a few meters.

4.6 Mudstone (HHL8) of Huai Hin Lat Formation at Tad Yai Waterfall. This outcrop is approximately 80 meters high. Attitude of bedding is 240/12 (Figure 3.16).

4.7 Shale (HHL10) of Huai Hin Lat Formation. Attitude of bedding is 155/7 (Figure 3.17).

Figure 3.12 Shale outcrop is approximately 4 meters high and 70 meters wide, looking east.

Figure 3.13 Mud crack on surface of shale loose block.

Figure 3.14 Shale outcrop (HHL5) from Huai Hin Lat Formation, looking west.

Figure 3.15 Horizontal bedding of shale at the Tad Mok waterfall.

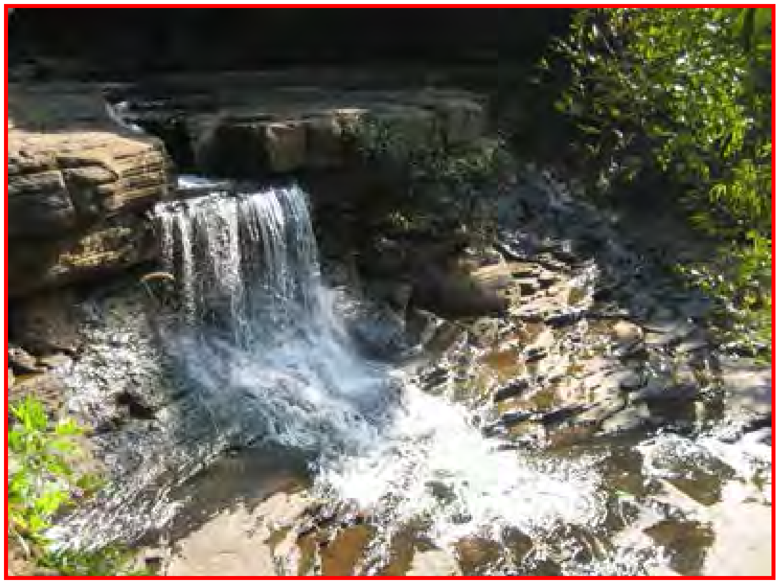

Figure 3.16 Tad Yai waterfall showing near horizontal bedding of mudstone outcrop.

Figure 3.17 Shale exposure is approximately 6 meters high and 15 meters in width (looking south).

Location: Amphoe Phu Pha Man, Changwat Khon Kaen

Two samples were collected at this location (Figure 3.18).

5.1 Shale (HHL9) of Huai Hin Lat Formation on rural road no. 2216. Attitude of bedding is 245/14 (Figure 3.19). Bed thickness is from 5 to 20 centimeters.

5.2 Limestone (NML) of Nam Maholan Formation. Attitude of bedding is 190/38.

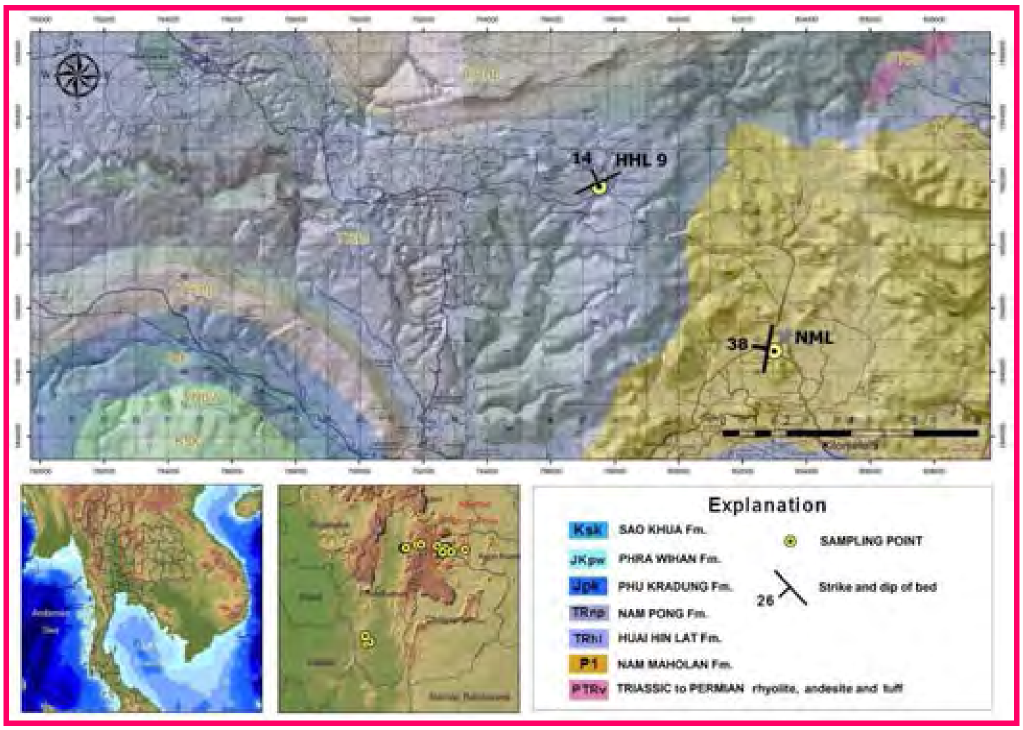

Figure 3.18 Map show sampling locations in Amphoe Phu Pha Man, Changwat Khon Kaen plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2009).

Location: Amphoe Chumpae, Changwat Khon Kaen

Only one sample of limestone (HHL11) from the Huai Hin Lat Formation was collected, the location is shown in Figure 3.20.

Figure 3.19 Shale of Huai Hin Lat Formation at Bann Dong Sakran, looking west.

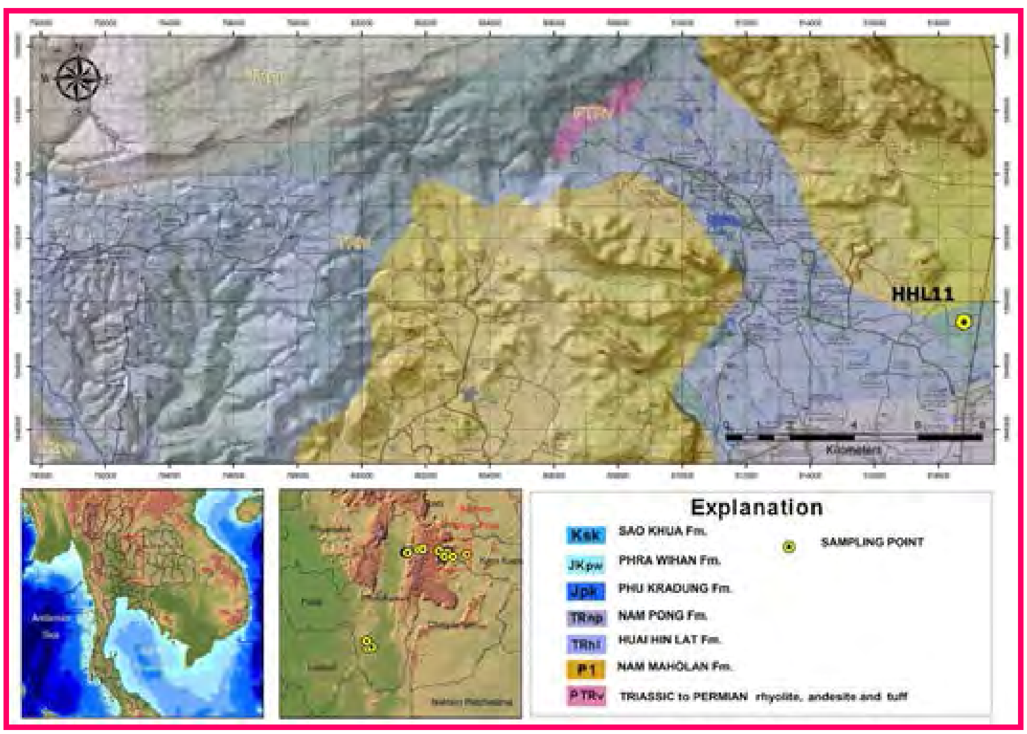

Figure 3.20 Sampling locations in Amphoe Chumpae, Changwat Khon Kaen plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2009).

3.2 Sample preparation

Samples were crushed with agate ball mill (planetary ball mill). After finishing grinding each sample, the ball mill was washed before grinding the next sample. The washing procedure started with washing with distilled water followed by cleaning with acetone and dichloromethane, respectively. This procedure prevented contamination from organic matter in the sample (Jankaew, 2002).

3.3 Geochemical analysis

3.3.1 Total organic carbon (TOC)

Total organic carbon content analysis started with sample preparation by weighing the grinded samples in a porcelain crucible, the weight of each sample was 200 mg. The samples were de-carbonated by using concentrate 2 N HCl until the reaction of the de-carbonating stopped (no bubbling). Then, they were dried in the oven at 105^{o}C for 2 hours to evaporate off the HCl from the samples. After that, the samples were analyzed with the Total Organic Carbon Analyzer HT 1300 at Environmental Research Institute, Chulalongkorn University by burning in an oxygen atmosphere at 1,200^{o}C. The machine measured the amount of carbon dioxide. Then, the amount of carbon was calculated in grams per kilogram before converting to carbon percentage to sample weight.

3.3.2 Vitrinite reflectance (%Ro)

Ground rock samples were sieved to select particles with the size between 63 µm-1 mm. About 2-3 grams of sample was used for each sample. The sieved samples were poured into the resin mold with epoxide resin and hardener at a ratio of 10:1. All ingredients were mixed and left for about 24 hours until the resin blocks settled. Then, they were removed from the mold. After that, the samples were polished with silicon carbide powder nos. 600 and 1000 until the surfaces of the samples became smooth. Then, the samples were cleaned with water.

The samples were then polished using a polishing machine (Struers DP-U4) with a polishing agent (monocystalline diamonds No. 3 µm and monocystalline diamonds No. 1 µm, respectively). Both polishing agents were used for polishing each sample for about 30-45 minutes. In case that the sample surface was not smooth, polishing procedure should be repeated using polishing agent (monocystalline diamonds No. 1 µm) until the sample surface was smooth. The sample surface smoothness was checked using reflected light of CRAIC CoalPro Microspectrophotometer at Geology Department, Chulalongkorn University (CU).

This study used a standard reflectance calibration value of 0.905%Ro of Yttrium Aluminum Garnet. For each sample, 300 measurements were conducted to determine an average apparent reflectance. Ten samples were also sent to Core Laboratories (Core Lab), Indonesia for Ro measurement.

3.3.3 Extractable organic matter (EOM)

The ground samples with a weight of approximately 50.00 g were poured into cellulose thimbles and covered with cotton wool. Prior to usage the thimbles and cotton celluloses must be extracted with dichloromethane in soxhlet apparatus for at least two hours. The extraction in this analysis is solid-liquid extraction by using soxhlet extractor apparatus. 200 ml of dichloromethane solvent was poured into 1,000 ml round bottom flasks and then, 2-3 pieces of anti-bumping granules were added to help the heating to be evenly distributed. Then, the flasks were connected to soxhlet extractors after filling the ground samples into the thimble and inserted into the soxhlet apparatus. Then about 350 ml of dichloromethane solvent was poured into the soxhlet apparatus, to make sure that the solvent volume was enough for recirculation. The extraction was done at a temperature of about 43^{o}C for at least 48 hours. After the extraction was finished, the thimble and sample was removed with tongs and wrapped in aluminum foil.

The extract solution was brought to evaporate using a Rotary Vacuum Evaporator at 40°C until the solution amount decreased to about 5 ml. The solution was partially transferred into a 2-ml weighted vial. The vial was set on stand and left for solvent to evaporate off and the vial has space to transfer the remaining solution. This process may be repeated until all solution are transferred to a vial. The flask was rinsed several times with dichloromethane to make sure no extracted matter was left.

Then the sample vial was left in the fume hood to evaporate off the excess dichloromethane solvent. The sample vials were then placed in a desiccator for one night before being weighed again to determine the amount of organic matter extracted.

3.3.3.1 Separation of the extract

The preparation of column follows that of Bastow et al. (2007) and is briefly described as follows. Silica gel (70-230 mesh) was activated at 120^{o}C for at least 8 hours and then placed in a desiccator. Column used in separation was prepared from a pasteur pipette (about 22 cm long and about 5.7 mm in diameter). The column needed to be rinsed with acetone and dichloromethane before being plugged by a small amount of cotton wool. Activated silica gel, approximately 0.6 g was packed into the column. Then, the packed column was created by passing 3 bed volumes of *n*-pentane with pressurized by pipette teat.

A concentrated band was produced by feeding the sample (10-20 mg) in a minimum volume of *n*-pentane (ca. 20 µL) to the top of the packed silica column.

The column was eluted with *n*-pentane (2ml) by gravity for saturated hydrocarbon fraction. The eluted solvent was kept in a pre-weighed vial. The vial had been weighed again after solvent was completely evaporated in a fume hood. The column, which eluted with *n*-pentane, was eluted again with *n*-pentane/dichloromethane (7:3 v/v, 2ml) for aromatic hydrocarbons fraction. The eluted solvent was kept in the vial. The volume of aromatic hydrocarbons fraction was carefully decreased to approximately 1 ml before adding *n*-hexane (1ml). The saturated hydrocarbons fraction is now ready for GC and GC-MS analysis.

3.3.3.2 Gas Chromatography (GC)

The saturated hydrocarbon fractions were dissolved in *n*-pentane/hexane solvent (1:3 v/v, 2ml). The Agilent 6890N GC of the DMF laboratory at Amphoe Phra Padaeng, Changwat Samut Prakan, was used in this study. The column of GC machine was HP-5 (30 m long, 0.32 mm wide and film thickness is

0.25 µm). This analysis used helium gas for carrying injectable samples about 1.0 µl. Temperature program was set to start up at 80^{o}C for 2 minutes and then gradually increase by 5^{o}C/min from 80-295^{o}C, followed by 295^{o}C for 30 minutes. This program had a total running time of about 75 minutes.

3.3.3.3 Gas Chromatography-Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometry was used for the saturated hydrocarbon fraction analysis. Agilent Technologies 7890A (7683B series injector) GC was connected to GCxGC TOF mass selective detector (ionizing energy of 70eV, filament current 244µA, source temperature 250^{o}C, detector voltage 1700V). GC-MS analysis was carried out at the Petroleum and Petrochemical College, Chulalongkorn University.

The column used in this study was a DB5 column with 30m length, 0.25mm internal diameter and 0.25 µm film thickness. GC-MS temperature was programmed for this analysis as follows; starting at 80^{o}C for 2 minutes, increasing with the rate of 4^{o}C/min to 310^{o}C then, keeping the final temperature for 35.5 minutes. This program had a total running time of about 95 minutes.

3.3.3.4 Compound identification and calculation of biomarker parameters

Mass fragmentographic responses and relative retention times, from mass spectra in the literature, are used in identification of compounds. Most biomarker parameters calculation was based on the relative peaks from the EXTEND GC integrator of the appropriate mass chromatogram. Peak height measurement from gas chromatograms (GC traces) were used to determine ratio of pristane/phytane (Pr/Ph), pristane/nC_{17} (Pr/nC_{17}) and phytane/nC_{18} (Ph/nC_{18}). Peak heights measurement from the m/z 85 fragmentogram was used to calculate carbon preference index (CPI).

3.3.4 Rock-Eval pyrolysis

Rock-Eval pyrolysis is the method used to analyse the type of kerogen and maturity level. In this study, ten outcrop samples were analyzed using Rock-Eval 6 analyzer (standard model S/N 18-001) at Core Laboratories (Core Lab) in Indonesia while seventeen outcrop samples were analyzed using the same type of instrument at Vinci Technologies in France. The list of samples sent for analysis are show in Table 3.2.

Table 3.2 List of samples sent for Rock-Eval pyrolysis at third party laboratories.

Sample name	Rock-Eval Pyrolysis	
	Vinci Technologies in France	Core Lab in Indonesia
HHL 1	Y	Y
HHL 2	Y	Y
HHL 3	Y	-
HHL 4	Y	Y
HHL 5	Y	-
HHL 6	Y	Y
HHL 7	Y	Y
HHL 8	Y	-
HHL 9	Y	Y
HHL 10	Y	Y
ND 1	Y	Y
ND 2	Y	-
HNK 1	Y	-
HNK 2	Y	Y
TF 1	Y	-
TF 3	Y	Y
SB	Y	-

Y: sent to test

At Core Lab and Vinci Technologies, the samples were thoroughly washed with water and cleaned by dry air to remove contamination from samples surfaces. Then the outside surfaces of all samples were removed and the remaining parts are thoroughly washed with water and cleaned by dry air again before beginning the analysis.

The sample (50-70 mg/sample) were pyrolyzed in the helium atmosphere with temperature of 300^{o}C for 3 minutes and then, the temperature is increased to 650^{o}C at a rate of 25^{o}C per minute. Then volatile component from the pyrolysis process was measured. The result was shown in 3 different peaks (S_1, S_2 and S_3).

3.3.5 Kerogen typing

In this study, visual kerogen analysis was applied in kerogen typing. This analysis separates the kerogen from the rock matrix. Then the isolated organic matter (kerogen) is put on a glass slide and examined under a high powered Leitz microscope.

The kerogen composition is reported in %contribution of amorphinite, exinite, vitrinite and inertinite, respectively, which are ordered in oil yield. Ten samples were analyzed by Core Laboratories (Core Lab) in Indonesia.

CHAPTER IV

RESULT AND INTERPRETATION

4.1 Quantity of organic matter

4.1.1 Total organic carbon

Eleven outcrop samples from Triassic Huai Hin Lat Formation and nine outcrop samples from Permian Saraburi Group were analyzed for total organic carbon (TOC) by TOC analyzer HT-1300 at Environmental Research Institute, Chulalongkorn University. TOC values are shown in the Table 4.1. TOC values of Huai Hin Lat Formation were found to be in the range of 0.69-3.27%wt for shale, 12.00%wt for coal and <0.001-1.56%wt for limestone. In the Saraburi Group, the Nam Duk Formation has TOC values in the range of 0.57-0.65%wt while that of the Hua Na Kham Formation ranges from 1.28 to 1.51%wt. Limestone samples from Tak Fa Formation has the TOC value ranges from <0.001-0.32%wt TOC. Nam Maholan Formation, TOC values were very low (<0.001%wt). Sap Bon Formation has TOC value 0.005%wt.

Total organic carbon is the first screening parameter for determining the potential for petroleum generation of source rocks. Shale samples with a TOC value of less than 0.5%wt can be neglected from the consideration, while the TOC value of more than 2%wt would be considered high potential source rocks (Bordenave et al., 1993). For limestone samples, TOC value of lower than 0.12%wt can be considered as no potential (Gehman, 1962).

According to the classification of potential source rock for shale and limestone mentioned above, all of the shale samples (except that of Tak Fa Formation) could be considered as potential source rock.

Values of $\%CO_3$ from the analysis (see Table 4.1) represent contents of carbonate in the samples which can be used as a guideline for identifying the lithology of source rocks (limestone, shale or calcareous shale, etc.). This data can be used to support the lithologic identification of the samples collected, which showed that collected samples of Huai Hin Lat Formation consists of limestone, argillaceous limestone, calcareous shale, shale and coal. Samples collected from Saraburi Group, Nam Duk Formation consists of calcareous shale and shale. For Hua Na Kham Formation, the rock collected is shale. Tak Fa Formation consists of limestone and argillaceous limestone. Collected samples from Nam Maholan and Sap Bon Formations are limestone. All %CO_3 values are shown in the Table 4.1.

4.1.2 Extractable organic matter

Extractable organic matter (EOM) from a source rock (now can be referred to as "bitumen") was measured in ppm. A high EOM value indicates that the sample tends to generate a high quantity of petroleum. Table 4.1 shows the value of EOM for each sample. It could be seen that the Huai Hin Lat Formation has the EOM value in the range of 320-3,474 ppm. In Saraburi Group, Nam Duk Formation, the value was in the range of 370-434 ppm while 2 samples from Hua Na Kham Formation had the EOM value of 266 and 768 ppm. EOM in Tak Fa, Nam Maholan and Sap Bon Formations were 352-538 ppm, 220 ppm and 1,518 ppm, respectively. Based on Continental Shelf Institute, IKU (1977), an EOM value of less than 200 ppm is considered poor and the value of more than 1,000 ppm is considered rich while an EOM value of between 200 and 1,000 ppm is considered adequate. Figures 4.1 and 4.2 show the relationship between TOC contents and EOM values of shale and limestone samples, respectively.

Figures 4.1 and 4.2 show that both shale and limestone samples of Huai Hin Lat Formation has TOC and EOM values greater than Saraburi Group, respectively. In Saraburi, Hua Na Kham has higher organic richness than Nam Duk Formation. Tak Fa Formation has greater organic richness than limestone of other formations in Saraburi Group. It is noted that EOM values in some samples analyzed are relatively high compared with their TOC contents. High EOM could be a result of migrated hydrocarbon from other stratigraphic layers.

Table 4.1 %CO_3, TOC and EOM contents for samples studied.

Sample name	UTM		lithology	%CO_3	TOC (%wt)	EOM (ppm)
	X	Y				
HHL 1	779133 E	1618930 N	Argillaceous limestone	75.86	0.88	494
HHL 2	764918 E	1854700 N	Shale	5.48	2.21	520
HHL 3	792369 E	1845694 N	Dark shale (Coal)	5.05	12.00	3,474
HHL 4	792378 E	1845667 N	Argillaceous limestone	81.32	1.56	454
HHL 5	793457 E	1846696 N	Calcareous shale	45.41	0.69	2,030
HHL 6	792834 E	1847487 N	Calcareous shale	39.08	0.98	320
HHL 7	794084 E	1851347 N	Calcareous shale	46.90	1.20	372
HHL 8	796794 E	1850824 N	Calcareous mudstone	36.97	2.67	398
HHL 9	797545 E	1851815 N	Calcareous shale	44.61	3.27	378
HHL 10	787391 E	1853289 N	Calcareous shale	43.95	2.53	408
HHL 11	818801 E	1849374 N	Limestone	99.32	<0.001	354
ND 1	749983 E	1851179 N	Shale	1.27	0.57	434
ND 2	750816 E	1851035 N	Calcareous shale	46.12	0.65	370
HNK 1	752232 E	1851353 N	Shale	4.80	1.28	266
HNK 2	769299 E	1855259 N	Shale	5.68	1.51	768
TF 1	707876 E	1743915 N	Limestone	45.99	<0.001	538
TF 2	711886 E	1744992 N	Limestone	99.60	<0.001	352
TF 3	706387 E	1751748 N	Argillaceous limestone	88.90	0.32	534
NML	803035 E	1846646 N	Limestone	71.70	<0.001	220
SB	777803 E	1617791 N	Limestone	99.46	0.005	1,518

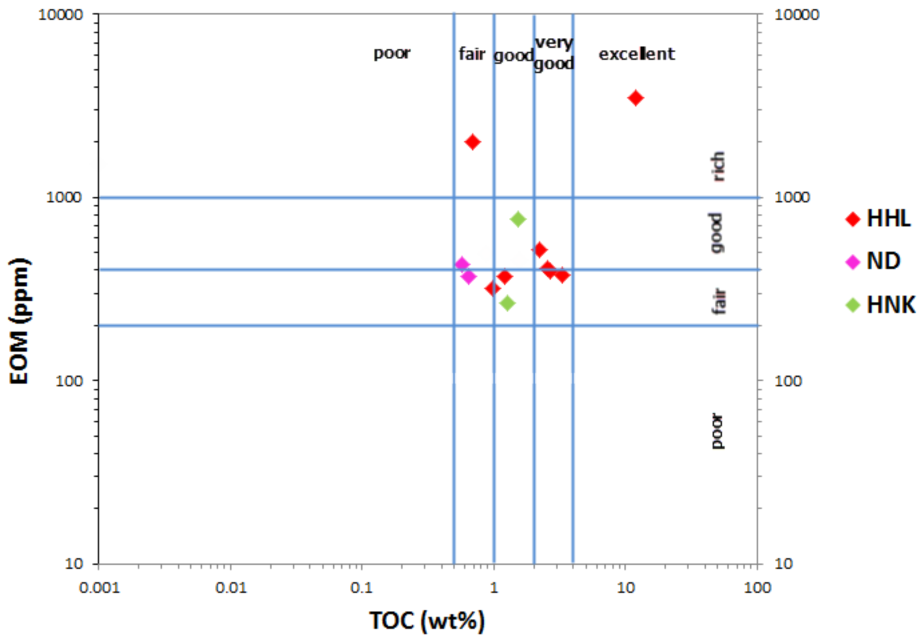

Figure 4.1 Relationship between TOC and EOM values in shale samples.

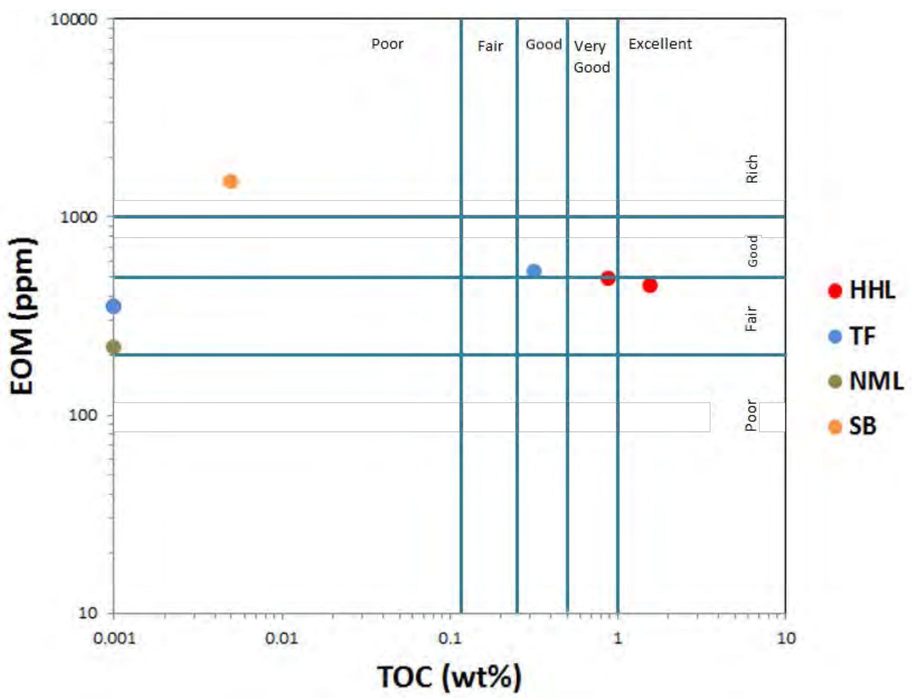

Figure 4.2 Relationship between TOC and EOM values in limestone samples.

4.2 Quality of organic matter

4.2.1 Kerogen typing

The study of maceral type, visual kerogen analysis, is used to identify the types of kerogen present in the source rock. Kerogen is divided to 4 types; type I, II, III and IV which represent that rock samples are oil-prone, oil and condensate prone, gas-prone or not productive, respectively.

The percentages of macerals identified are shown in Table 4.2. Huai Hin Lat Formation contains 55-75% of vitrinite in total maceral. This indicates that Huai Hin Lat Formation is gas-prone source rock. Nam Duk and Hua Na Kham Formations have 65% and 73% of vitrinite content, respectively, while Tak Fa Formation contains 93% of non fluorescent amorphous of amorphinite. The fluorescent amorphous maceral is capable of generating gas as well as has no potential to generate petroleum (Richard, 1993). Thus, Tak Fa Formation contains kerogen type III/IV.

4.2.2 Rock-Eval pyrolysis

Fifteen samples were analyzed with Rock-Eval pyrolysis technique. Data is shown in Table 4.3. Rock-Eval pyrolysis data is used to help assessing kerogen types (organic matter types) by using a graph plotted between hydrogen index (HI) and oxygen index (OI) on a Pseudo-Van Krevelen diagram which is shown in Figure 4.3.

According to the plotted data in Figure 4.3, Huai Hin Lat, Nam Duk and Hua Na Kham Formations contain kerogen type IV. Only Tak Fa Formation contains kerogen type III which is capable of generating gas if the rock is mature.

All studied samples have HI values between 0-150 which indicates that the samples have no or low potential to generate gas.

Table 4.2 Kerogen type determined by visual kerogen analysis of Huai Hin Lat Formation and Saraburi Group.

Sample Name	Amorphinite (Type I)		Exinite (Type I/II)						OPK %	Vitrinite Type III %	Semi Flusinite Type IV %	Inertinite Type IV %	Preserv.	Rec. of Organic Matter	TAS
	NF.A. %	F.A %	A %	C%	S%	R%	SB%	L%							
HHL-1	10	-	-	-	-	-	-	-	-	70	-	20	P	M	5*
HHL-2	10	-	-	-	-	-	-	-	-	60	-	30	P	G	6*
HHL-4	15	-	-	-	-	-	-	-	-	75	-	10	P	G	5/6*
HHL-6	10	-	-	-	-	-	-	-	-	70	-	20	P	G	5/6*
HHL-7	15	-	-	-	-	-	-	-	-	55	-	30	P	G	5/6*
HHL-9	10	-	-	-	-	-	-	-	-	70	-	20	P	G	5/6*
HHL-10	15	-	-	-	-	-	-	-	-	55	-	30	P	G	5/6*
ND-1	5	-	-	-	-	-	-	-	-	65	-	30	P	G	6*
HNK-2	7	-	-	-	-	-	-	-	-	73	-	20	P	G	6*
TF-3	93	-	-	-	1	-	-	-	1	5	-	1	P	G	5

NF.A: Non Fluorescent Amorphous; F.A: Fluorescing Amorphous; A: Alginite; C: Cutinite; S: Sporinite; R: Resinite; SB: Suberinite; L: Liptodetrinite;

OPK: Oil Prone Kerogen; TAS: Thermal Alteration Scale.

*: TAS Based on Palynomorph Assemblages; g: green; y: yellow; o: orange; do: dull orange; br: brown; dkbr: dark brown.

G: Good; P: Poor; M: Moderate.

Table 4.3 HI and OI values obtained from Rock-Eval pyrolysis of samples studied.

Sample ID	UTM		mg/gm rock			Corr. TOC (wt%)	HI	OI
	X	Y	S_1	S_2	S_3			
HHL 1[2]	779133 E	1618930 N	0.02	0.11	0.57	1.01	10.89	56.44
HHL 2[2]	764918 E	1854700 N	0.03	0.04	0.63	2.54	1.57	24.80
HHL 3[2]	792369 E	1845694 N	0.04	1.97	0.28	13.80	14.28	2.03
HHL 4[1]	792378 E	1845667 N	0.08	0.21	0.40	1.79	11.73	22.35
HHL 5[2]	793457 E	1846696 N	0.05	0.08	0.06	0.79	10.13	7.59
HHL 6[1]	792834 E	1847487 N	0.07	0.08	0.20	1.03	7.77	19.42
HHL 7[1]	794084 E	1851347 N	0.09	0.06	0.32	1.38	4.35	23.19
HHL 8[2]	796794 E	1850824 N	0.02	0.13	1.39	3.07	4.23	45.28
HHL 9[1]	797545 E	1851815 N	0.16	0.20	0.49	3.76	5.32	13.03
HHL 10[1]	787391 E	1853289 N	0.17	0.17	0.66	2.66	6.39	24.81
ND 1[1]	749983 E	1851179 N	0.01	0.01	0.20	0.66	1.52	30.3
ND 2[2]	750816 E	1851035 N	0.03	0.04	0.30	0.75	5.33	40.00
HNK 1[2]	752232 E	1851353 N	0.03	0.03	0.17	1.47	2.04	11.56
HNK 2[2]	769299 E	1855259 N	0.06	0.07	0.35	1.74	4.02	20.11
TF 3[2]	706387 E	1751748 N	0.11	0.30	0.21	0.37	81.08	56.76

[1]Analyzed by Core Lab in Indonesia.

[2]Analyzed at Vinci Techologies in France.

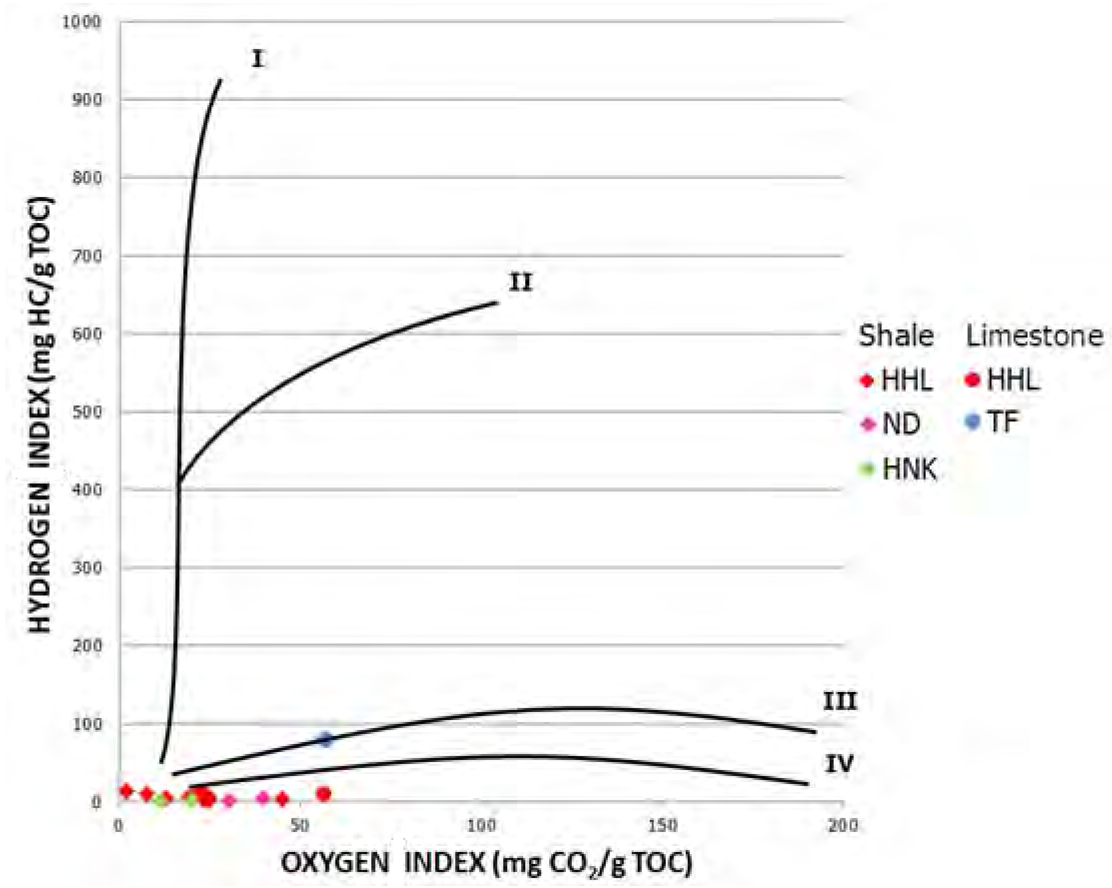

Figure 4.3 Oxygen index plotted against hydrogen index on pseudo-van Krevelen diagram to classify kerogen types of shale and limestone samples of Huai Hin Lat Formation, Nam Duk Formation, Hua Na Kham Formation and Tak Fa Formation. Most of data locate in kerogen type IV (with the exception of Tak Fa Formation).

4.3 Thermal maturation

4.3.1 Vitrinite reflectance

Vitrinite reflectance data is widely used in determining the level of thermal maturity of source rocks. Peters and Cassa (1994) defined thermal maturity level according to range of vitrinite reflectance (Ro) value as follows. Ro value in the range of 0.60-0.65% represents early mature level while the Ro value in the range of 0.65-0.90% indicates a peak mature level. Late mature level is characterized by a Ro value of 0.90-1.35% whereas a Ro value of more than 1.35% represents post mature level.

Maturity level of samples based on Ro values are shown in Table 4.4. In Table 4.4, samples from Huai Hin Lat Formation have Ro values in the range of 0.898-

1.245% while samples of Nam Duk Formation, Saraburi Group, have Ro values in the range of 1.041-1.122%. Hua Na Kham, Tak Fa, Nam Maholan and Sap Bon Formations have Ro values 1.023-1.159%, 1.021-1.578%, 1.265% and 1.395%, respectively.

Table 4.4 shows Ro values of samples analyzed by Core Lab and analyzed by me at Department of Geology, Faculty of Sciences, Chulalongkorn University. Ro values from Core Lab of Huai Hin Lat Formation are 1.05-2.04%. In Saraburi Group, Nam Duk, Hua Na Kham and Tak Fa Formations, Ro values are 2.14, 2.16 and 0.89%, respectively. When compare with data measured at Chulalongkorn University (CU) laboratory, the Ro of HHL2, ND1, HNK2 and TF3 samples are different and pointing to different levels of maturity. However, Ro values from Chulalongkorn University laboratory were used since they are based on reasonable measurements per sample (at least 50 counts) and gave reasonable histogram profiles while those from Core Lab are reported from less than 33 measurements per sample and only 2 measurements in one sample.

Since TOC values at the time of measurement are supposed to be lower than that of original state due to loss of carbon from possible petroleum generation at higher maturity level. The measured TOC values have to be converted back to the original amount of TOC based on the type of kerogen and level of maturity. The TOC values were multiplied by the correction factor which depends on the kerogen type and level of maturity as shown in Table 4.5. The corrected TOC values are slightly higher than the measured values as shown in Table 4.6.

Table 4.4 Thermal maturity level relative to petroleum generation as indicated by vitrinite reflectance (Ro) of samples studied.

Sample name	**UTM**		**Ro (%) CU**	**Maturity level**	**Ro. (%) by Core Lab**	**Maturity level**
	X	**Y**				
HHL 1	779133 E	1618930 N	1.063	Late mature	1.05	Late mature
HHL 2	764918 E	1854700 N	1.162	Late mature	2.04	Post mature
HHL 3	792369 E	1845694 N	1.118	Late mature		
HHL 4	792378 E	1845667 N	1.009	Late mature	1.31	Late mature
HHL 5	793457 E	1846696 N	1.245	Late mature		
HHL 6	792834 E	1847487 N	0.986	Late mature	1.31	Late mature
HHL 7	794084 E	1851347 N	1.216	Late mature	1.33	Late mature
HHL 8	796794 E	1850824 N	1.045	Late mature		
HHL 9	797545 E	1851815 N	1.018	Late mature	1.28	Late mature
HHL 10	787391 E	1853289 N	0.898	Peak mature	1.27	Late mature
HHL 11	818801 E	1849374 N	1.176	Late mature		
ND 1	749983 E	1851179 N	1.122	Late mature	2.14	Post mature
ND 2	750816 E	1851035 N	1.041	Late mature		
HNK 1	752232 E	1851353 N	1.023	Late mature		
HNK 2	769299 E	1855259 N	1.159	Late mature	2.16	Post mature
TF 1	707876 E	1743915 N	1.490	Post mature		
TF 2	711886 E	1744992 N	1.578	Post mature		
TF 3	706387 E	1751748 N	1.021	Late mature	0.89	Peak mature
NML	803035 E	1846646 N	1.265	Late mature		
SB	777803 E	1617791 N	1.935	Post mature		

Table 4.5 Correction factor for TOC values.

Kerogen type	%Ro		
	< 0.8	0.8-1.0	>1.0
I	1.00	2.00	2.50
II	1.00	1.33	2.00
III	1.00	1.05	1.15

Table 4.6 TOC, corrected TOC and Ro values of samples.

Sample name	UTM		TOC (%wt)	Ro (%)	Corr. TOC (%wt)	Source potential
	X	Y				
HHL 1	779133 E	1618930 N	0.88	1.063	1.01	Good
HHL 2	764918 E	1854700 N	2.21	1.162	2.54	Very Good
HHL 3	792369 E	1845694 N	12.00	1.118	13.80	Excellent
HHL 4	792378 E	1845667 N	1.56	1.009	1.79	Good
HHL 5	793457 E	1846696 N	0.69	1.245	0.79	Fair
HHL 6	792834 E	1847487 N	0.98	0.986	1.03	Good
HHL 7	794084 E	1851347 N	1.20	1.216	1.38	Good
HHL 8	796794 E	1850824 N	2.67	1.045	3.07	Very Good
HHL 9	797545 E	1851815 N	3.27	1.018	3.76	Very Good
HHL 10	787391 E	1853289 N	2.53	0.898	2.66	Very Good
HHL 11	818801 E	1849374 N	<0.001	1.176	<0.001	Poor
ND 1	749983 E	1851179 N	0.57	1.122	0.66	Fair
ND 2	750816 E	1851035 N	0.65	1.041	0.75	Fair
HNK 1	752232 E	1851353 N	1.28	1.023	1.47	Good
HNK 2	769299 E	1855259 N	1.51	1.159	1.74	Good
TF 1	707876 E	1743915 N	<0.001	1.490	<0.001	Poor
TF 2	711886 E	1744992 N	<0.001	1.578	<0.001	Poor
TF 3	706387 E	1751748 N	0.32	1.021	0.37	Poor
NML	803035 E	1846646 N	<0.001	1.265	<0.001	Poor
SB	777803 E	1617791 N	0.005	1.935	0.01	Poor

4.3.2 Tmax and PI from Rock-Eval pyrolysis

Tmax and PI values of samples are listed in Table 4.7. In most of the studied samples, Tmax values do not correspond with other indicators, except for Tak Fa Formation. Tmax of samples from Huai Hin Lat Formation (except HHL2 are 330^{o}C indicate immature) are 506-607^{o}C, which indicate post mature levels while Ro, CPI, Pr/nC_{17}, Ph/nC_{18} and Pr/Ph values suggest that this formation is mature. However, HHL1 sample has low ratio of C_{31} 22S/(22S+22R) which suggest that this sample is immature. HHL8 has a Pr/nC_{17}, Ph/nC_{18} ratios indicating that the sample is of post mature level which correspond with high Tmax value. Thermal maturity level of Huai Hin Lat Formation is possibly late mature based on Ro interpretation as Tmax values from Rock-Eval pyrolysis are less reliable due to too low S2 (<0.20mg HC/g TOC). The level of thermal maturity from Ro is supported by nonbiomarker parameter such as CPI, Pr/nC17, Ph/nC18 and Pr/Ph which suggest that samples from Huai Hin Lat Formation are mature. In Saraburi Group, both Nam Duk and Hua Na Kham Formations have low Tmax values (304-481^{o}C and 326-349^{o}C, respectively) which indicate that the samples are immature. In comparison with the interpretation from C_{31} 22S/(22S+22R) ratio, samples from Hua Na Kham have low ratios which support the stage of maturity to be immature while Tmax values of samples from Tak Fa Formation does not agree with this ratio. Tak Fa Formation has the Tmax value of 463^{o}C, which indicates mature stage and corresponds with the Ro, CPI, Pr/nC_{17}, Ph/nC_{18} and Pr/Ph values which support that this formation is mature. Tmax values obtain from too small S_2 peaks (<0.2 mg HC/g TOC) are unreliable (Peters, 1986). Because of extremely low S_2 peaks (0.01-0.21%) reported for samples studied, Tmax values reported may not be reliable and from here on given less significance. However, Peters (1986) had suggested that sample which has high PI but low Tmax may be caused by weathering or migrated hydrocarbon. This characteristic is found in HHL2, ND2, HNK1 and HNK2 samples.

Production indexes (PI) of Huai Hin Lat Formation are 0.02-0.60 which suggests that this formation has the maturity level in the range of immature to post mature. Four out of ten samples have the values of PI which correspond to Tmax suggesting the post mature level. However, Ro, Pr/nC_{17}, Ph/nC_{18} and CPI values of most samples showed that this formation is mature. In Saraburi Group, one sample from Hua Na Kham Formation (HNK2) has the highest value of PI (0.63) and only Tak Fa Formation has the PI value which is positively supported by the interpretations from other indicators. According to the PI values in the range of 0.1-0.4 mean the level of maturity are of early to late mature. That means samples from both Huai Hin Lat Formation are in a range between immature to post mature while Suraburi Group (except TF3) are post mature. Since S1 values of all sample are low (low hydrocarbon show) and S2 values of most sample are very low (<0.20mg HC/g TOC), PI values will also be affected and will be given less importance. This also affect Tmax to be inaccurate or abnormally high due to low S2 peak. Nunez-Betelu and Baceta (1994) and Worldwide Geochemistry, LLC (2001) suggested that too low organic content or S2 values are limitation of Rock-Eval pyrolysis technique.

Table 4.7 Tmax and PI from Rock-Eval pyrolysis of samples studied.

Sample ID	UTM		**mg/gm rock**			**Tmax (°C)**	**PI (S_1/S_1+S_2)**
	X	**Y**	**S_1**	**S_2**	**S_3**		
HHL 1[2]	779133 E	1618930 N	0.02	0.11	0.57	506	0.15
HHL 2[2]	764918 E	1854700 N	0.03	0.04	0.63	330	0.43
HHL 3[2]	792369 E	1845694 N	0.04	1.97	0.28	540	0.02
HHL 4[1]	792378 E	1845667 N	0.08	0.21	0.40	573	0.28
HHL 5[2]	793457 E	1846696 N	0.05	0.08	0.06	583	0.38
HHL 6[1]	792834 E	1847487 N	0.07	0.08	0.20	531	0.47
HHL 7[1]	794084 E	1851347 N	0.09	0.06	0.32	585	0.60
HHL 8[2]	796794 E	1850824 N	0.02	0.13	1.39	607	0.13
HHL 9[1]	797545 E	1851815 N	0.16	0.20	0.49	597	0.44
HHL 10[1]	787391 E	1853289 N	0.17	0.17	0.66	599	0.50
ND 1[1]	749983 E	1851179 N	0.01	0.01	0.20	481	0.50
ND 2[2]	750816 E	1851035 N	0.03	0.04	0.30	304	0.43
HNK 1[2]	752232 E	1851353 N	0.03	0.03	0.17	326	0.50
HNK 2[2]	769299 E	1855259 N	0.06	0.07	0.35	349	0.46
TF 3[2]	706387 E	1751748 N	0.11	0.30	0.21	463	0.27

[1]Analyzed by Core Lab in Indonesia.

[2]Analyzed at Vinci Techologies in France.

4.3.3 Carbon preference index (CPI) from gas chromatography

Relative abundance and distribution of *n*-alkanes identified from gas chromatogram was applied to calculate the carbon preference index (CPI) values. CPI is used to identify the level of maturity of rock samples. CPI values of samples studies are shown in Table 4.8.

CPI is the mathematical expression of abundance between odd-carbon-numbered over even-carbon-numbered *n*-alkanes and calculate as below (Scalan and Smith, 1970).

$$CPI = \frac{\sum(C25 - C33\ odd) + \sum(C23 - C31\ odd)}{2(\sum C24 - C32\ even)}$$

CPI values decrease with increasing maturity. CPI values reach equilibrium of about 1.0 at peak oil generation. CPI value of approximately 1.5, indicate top of oil generating window. While the CPI value of more than 1.5 indicates that the sample is immature.

<u>Result</u>

CPI values of Huai Hin Lat Formation were in the range of 0.92-1.13. Saraburi Group; Nam Duk, Hua Na Kham, Tak Fa, Nam Maholan and Sap Bon Formations, has CPI values 1.00-1.20. This suggests that the samples are mature, with maturity level near peak oil generation.

CPI and Ro values of all samples are shown in Table 4.8. The relationship between CPI and Ro values of samples studied is shown in Figure 4.4. According to the graph, samples from Huai Hin Lat, Nam Duk, Hua Na Kham and Tak Fa Formations are of mature level.

Table 4.8 CPI of samples studied, %Ro from CU are shown as a comparison.

Sample name	UTM		CPI	Ro (%)
	X	Y		
HHL 1	779133 E	1618930 N	1.00	1.063
HHL 2	764918 E	1854700 N	1.00	1.162
HHL 3	792369 E	1845694 N	1.07	1.118
HHL 4	792378 E	1845667 N	1.09	1.009
HHL 5	793457 E	1846696 N	1.06	1.245
HHL 6	792834 E	1847487 N	1.05	0.986
HHL 7	794084 E	1851347 N	1.13	1.216
HHL 8	796794 E	1850824 N	0.97	1.045
HHL 9	797545 E	1851815 N	1.04	1.018
HHL 10	787391 E	1853289 N	0.92	0.898
HHL 11	818801 E	1849374 N	1.00	1.176
ND 1	749983 E	1851179 N	1.13	1.122
ND 2	750816 E	1851035 N	1.15	1.041
HNK 1	752232 E	1851353 N	1.12	1.023
HNK 2	769299 E	1855259 N	1.10	1.159
TF 1	707876 E	1743915 N	1.12	1.49
TF 2	711886 E	1744992 N	1.15	1.578
TF 3	706387 E	1751748 N	1.06	1.021
NML	803035 E	1846646 N	1.20	1.265
SB	777803 E	1617791 N	1.02	1.935

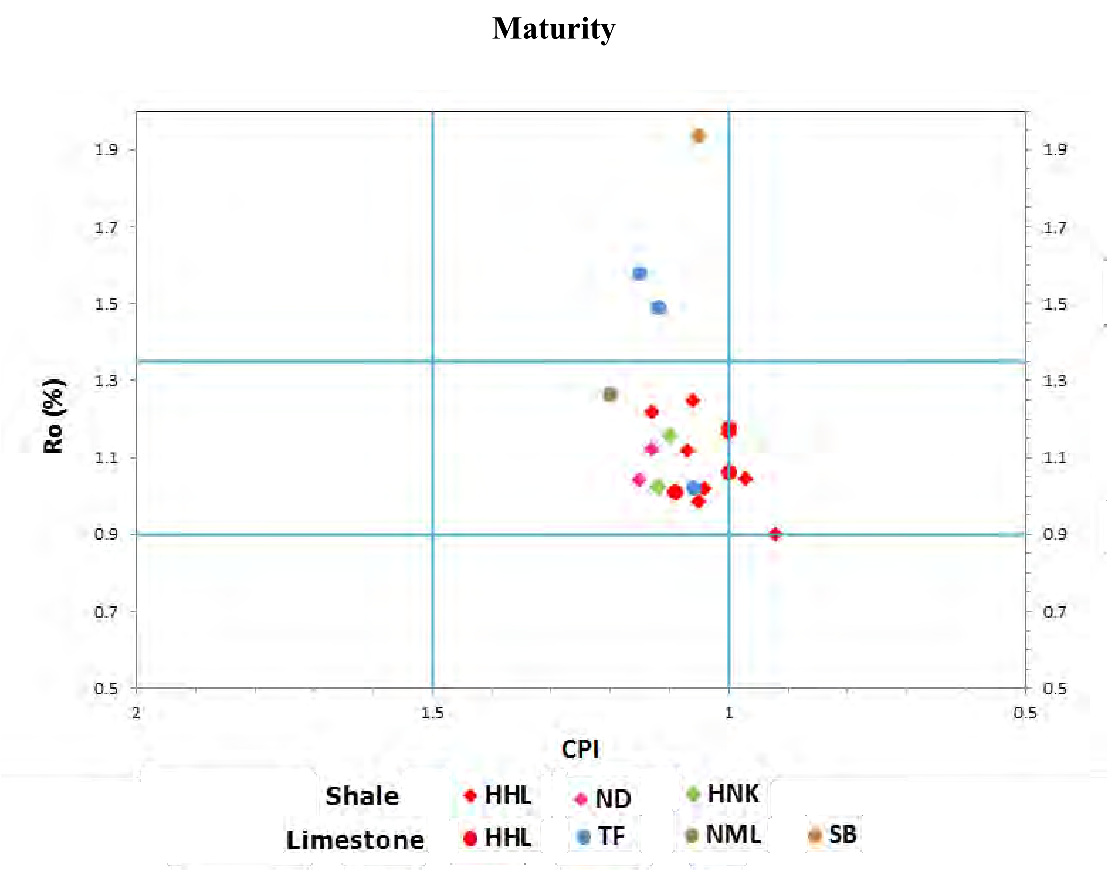

Figure 4.4 Graph plot between %Ro and CPI of all samples studied.

4.3.4 Biomarkers

Biomarkers or biological markers are compounds of organic matters which mainly consist of carbon, hydrogen and other elements which were derived from once-living organisms. They are widely used to identify depositional environments and levels of maturity because they show little or no change in an organic molecular structure from it formerly organism. Biomarker parameters can be archived from the peak area calculation from GC-MS data (Peters and Moldowan, 1993).

In this study, only ten samples with good chromatographic response from GC analysis were selected for GC-MS analysis due to budget constraint.

Various biomarkers are used to determine the properties of the studied rocks. This study utilizes some of these biomarkers. Homohopane 22S/(22S+22R) and Ts/(Ts+Tm) are biomarker parameters which are used in indicating maturity level.

4.3.4.1 Homohopane 22S/(22S+22R)

Homohopane isomerization ratio can be used to assess the level of thermal maturity for samples. This ratio was calculated using the distinctive R and S doublets peaks in m/z 191 chromatogram of C_{31}-C_{35} homohopanes (as shown in Figure 4.5). This study use peak area of C_{31} homohopanes in the calculation of this ratio. The ratio value increases with increasing thermal maturity. The ratio is effective in the range of maturity from immature to early oil generative window (0-0.55). Homohopane 22S/(22S+22R) value of 0.5 indicating that the sample barely entered oil generation (Seifert and Moldowan, 1986).

Result

Table 4.9 listed C_{31} 22S/(22S+22R) ratios of samples. Huai Hin Lat Formation has 22S/(22S+22R) ratios ranges from 0.11-0.72, which suggest that this formation is of immature to mature levels. 22S/(22S+22R) ratios of Nam Duk, Hua Na Kham and Tak Fa Formations are 0.39, 0.34 and 0.48, respectively. Samples from Saraburi Group are immature.

22S/(22S+22R) ratios of Huai Hin Lat Formation indicates level of maturity ranging from immature to mature. This is not consistent with the interpretation from Pr/nC_{17}, Ph/nC_{18} and Pr/Ph values which support that the samples from this formation are mature. However, for Hua Na Kham and Tak Fa Formations, the interpretation from 22S/(22S+22R) ratio agree with those from Pr/nC_{17}, Ph/nC_{18} and Pr/Ph ratios.

4.3.4.2 Ts/(Ts+Tm)

Ts and Tm are Trisnorneohopanes and Trisnorhopane respectively. Ts/(Ts+Tm) is the ratio used for maturity indication. This ratio can be calculated from the peak area of Ts and Tm in m/z 191 fragmentogram. The progressively increasing ratio value relates with the maturity. Samples are mature when the values are in the range of 0.35-0.95 (Peters et al., 2005).

Result

Huai Hin Lat, Nam Duk, Hua Na Kham and Tak Fa Formations have the ratios of Ts/(Ts+Tm) of 0.56-0.94, 0.58, 0.83 and 0.72, respectively which indicate the level of maturity of peak oil to late mature. All Ts/(Ts+Tm) ratios are shown in Table 4.9.

When comparing the results of Ts/(Ts+Tm) with Pr/nC_{17}, Ph/nC_{18}, Pr/Ph, CPI and Ro values, all of these values support that the rocks are mature. The Ts/(Ts+Tm) ratios are plotted with the C_{31} 22S/(22S+22R) ratios in Figure 4.6.

Table 4.9 C_{31} 22S/(22S+22R) and Ts/(Ts+Tm) calculated from peak area in m/z 191 for C_{31} homohopane, Ts and Tm.

Sample name	UTM		C_{31} 22S/(22S+22R)	Ts/(Ts+Tm)
	X	Y		
HHL1	779133 E	1618930 N	0.11	0.84
HHL2	764918 E	1854700 N	0.72	0.66
HHL4	792378 E	1845667 N	0.56	0.64
HHL6	792834 E	1847487 N	0.51	0.62
HHL7	794084 E	1851347 N	0.52	0.94
HHL9	797545 E	1851815 N	0.55	0.72
HHL10	787391 E	1853289 N	0.39	0.56
ND1	749983 E	1851179 N	0.34	0.58
HNK2	769299 E	1855259 N	0.33	0.83
TF3	706387 E	1751748 N	0.48	0.72

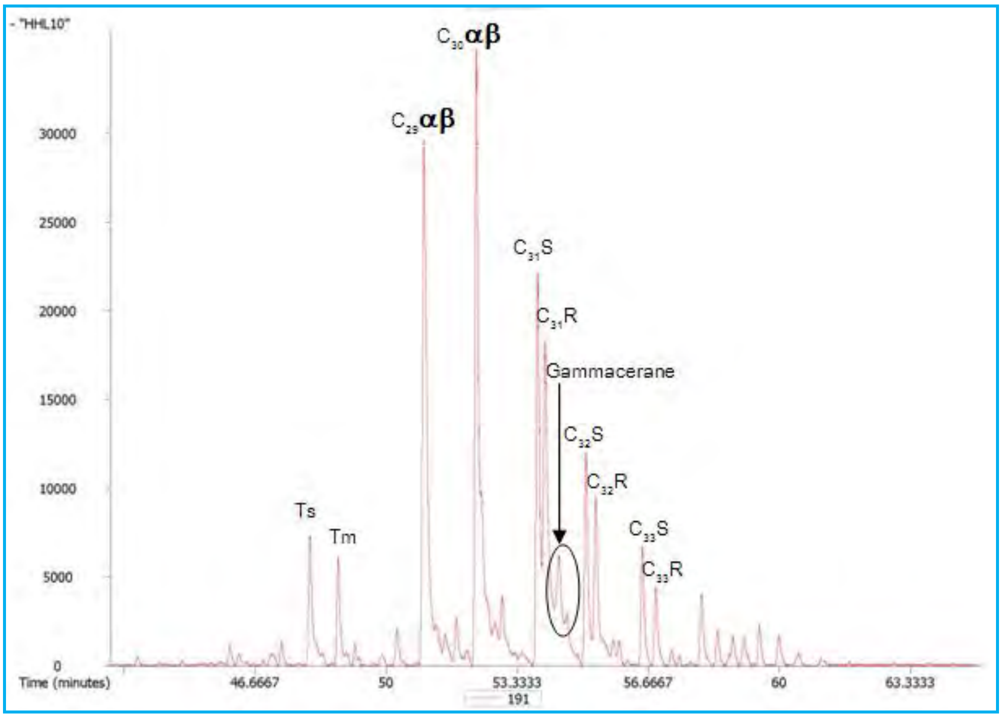

Figure 4.5 Example of mass fragmentograms (m/z 191) of HHL10 showing relative distribution of Ts, Tm $C_{29}\alpha\beta$-norhopane, $C_{30}\alpha\beta$-hopane, 22S and 22R C_{31}-C_{33} homohpanes and gammacerane.

Ts/(Ts+Tm) ratio plotted against C_{31} 22S/(22S+22R)

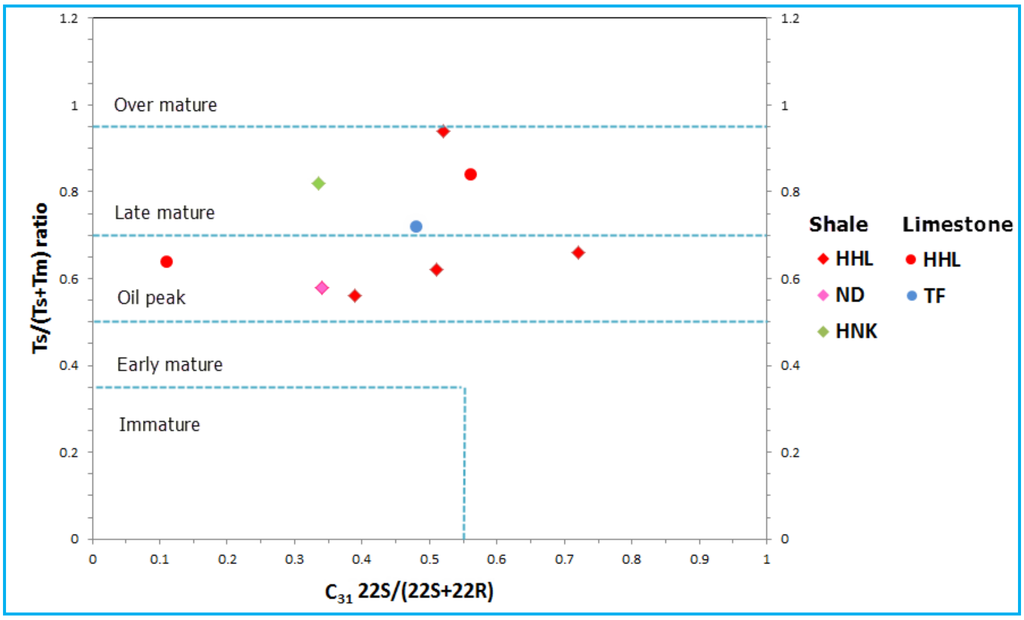

Figure 4.6 Level of maturity classified by Ts/(Ts+Tm) ratio plotted against C_{31} 22S/(22S+22R) ratio (modified from Peters et al., 2005).

4.4 Depositional environment

4.4.1 Nonbiomarkers

Pristane/Phytane (Pr/Ph) ratio and Pristane/nC$_{17}$ and Phytane/nC$_{18}$ ratios are calculated from gas chromatogram. They are used to identify the source of the organic material and/or depositional environment. Pr/Ph, Pristane/nC$_{17}$, and Phytane/nC$_{18}$ values of samples are shown in Table 4.10.

4.4.1.1 Pristane/Phytane ratio

Pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$) are regular isoprenoid hydrocarbons. Both of them were derived from side chain of chlorophyll molecule (Miles, 1989). Pristane and phytane peaks in the chromatogram were normally shown as double peaks next to C_{17} and C_{18} normal alkanes, respectively. Pr/Ph ratio is used to indicate the oxicity of their depositional environment. The ratio value of more than three indicates that the sediment may have been deposited in a more oxidizing depositional environment. On the other hand a ratio value of less than 1 indicates that the sediments were deposited in a reducing depositional environment (Dydik et al., 1978). Peters et al. (2005) suggested that Pr/Ph ratio more than 3.0 indicates terrigenous plant input deposited under oxic to suboxic conditions.

<u>Result</u>

Pr/Ph ratios are shown in Table 4.10. Pr/Ph ratios of Huai Hin Lat Formation were in the range of 0.50-1.23 except the value of HHL8 which is very high (5.07). High Pr/Ph ratio of HHL8 suggests a deposition in highly oxic environment, whereas the depositional environment of most of samples collected from Huai Hin Lat Formation was possibly anoxic and/or samples were relatively mature. For Saraburi Group; Nam Duk, Hua Na Kham, Tak Fa, Nam Maholan and Sap Bon Formations, Pr/Ph ratios are 0.82-0.96, 1.05 (except HNK2 which has high Pr/Ph ratio of 4.54 suggesting highly oxic depositional environment), 1.21-1.53, 0.58 and 0.65, respectively, which are quite low. As a result, the depositional environment of Saraburi Group was also anoxic and/or the samples were relatively mature.

4.4.1.2 Pristane/nC_{17} and Phytane/nC_{18}

Depositional environment, approximate levels of maturity and biodegradation can be identified according to the relationship between the abundance of pristane to nC_{17} and phytane to nC_{18} as shown in Figure 4.7. The mature source rock can be characterized by Pr/nC_{17} and Ph/nC_{18} values of approximately 0.1-0.5, whereas Pr/nC_{17} and Ph/nC_{18} values of more than 1.0 suggests that the source rock is immature (Leythaeuser and Schwarzkopf, 1986).

Result

Pr/nC_{17} and Ph/nC_{18} ratios are shown in Table 4.10 along with Pr/Ph ratios. Huai Hin Lat Formation has Pr/nC_{17} and Ph/nC_{18} in the range of 0.24-0.60 (except HHL8 which has high Pr/nC_{17} value suggesting oxidizing environment of deposition) and 0.23-0.52, respectively. These Pr/nC_{17} and Ph/nC_{18} ratios suggest that they were probably derived from mixed organic sources between terrigenous and marine organic matters and deposited under reducing (anoxic) environment.

Pr/nC_{17} ratios of Nam Duk Formation are 0.55-0.58 while Ph/nC_{18} ratios are 0.49-0.57. For Hua Na Kham Formation, Pr/nC_{17} ratios are 0.85 (except the Pr/nC_{17} ratio of HNK2 is 2.64) and Ph/nC_{18} ratios are 0.33-0.81. Pr/nC_{17} ratios of Tak Fa Formation are in the range of 0.43-0.46 (except TF2 with 1.04) and Ph/nC_{18} ratios are 0.33-0.37. Nam Maholan Formation has Pr/nC_{17} and Ph/nC_{18} ratios of 0.42 and 0.48, respectively. Sap Bon Formation has Pr/nC_{17} ratio of 0.36 and 0.44 for Ph/nC_{18} ratio. These Pr/nC_{17} and Ph/nC_{18} ratios of Saraburi Group suggest that these rocks were possibly mature and probably derived from mixed organic sources between terrigenous and marine organic matters and deposited under a reducing depositional environment.

Comparing with the Pr/Ph ratios, both Pr/nC_{17} and Ph/nC_{18} ratios support that these rocks were mature and deposited under reducing environment.

Table 4.10 Pr/Ph, Pr/nC_{17} and Ph/nC_{18} ratios of samples studied.

Sample name	**UTM**		**Pr/Ph**	**Pr/nC_{17}**	**Ph/nC_{18}**
	X	**Y**			
HHL 1	779133 E	1618930 N	0.96	0.24	0.23
HHL 2	764918 E	1854700 N	0.50	0.50	0.51
HHL 3	792369 E	1845694 N	0.80	0.60	0.52
HHL 4	792378 E	1845667 N	1.02	0.53	0.46
HHL 5	793457 E	1846696 N	0.77	0.45	0.43
HHL 6	792834 E	1847487 N	0.90	0.49	0.48
HHL 7	794084 E	1851347 N	1.23	0.49	0.45
HHL 8	796794 E	1850824 N	5.07	4.18	0.58
HHL 9	797545 E	1851815 N	1.18	0.55	0.50
HHL 10	787391 E	1853289 N	1.04	0.57	0.49
HHL 11	818801 E	1849374 N	0.78	0.48	0.48
ND 1	749983 E	1851179 N	0.96	0.55	0.49
ND 2	750816 E	1851035 N	0.82	0.58	0.57
HNK 1	752232 E	1851353 N	1.05	0.85	0.81
HNK 2	769299 E	1855259 N	4.54	2.64	0.33
TF 1	707876 E	1743915 N	1.21	0.46	0.39
TF 2	711886 E	1744992 N	1.53	1.04	0.37
TF 3	706387 E	1751748 N	1.41	0.43	0.33
NML	803035 E	1846646 N	0.58	0.42	0.48
SB	777803 E	1617791 N	0.65	0.36	0.44

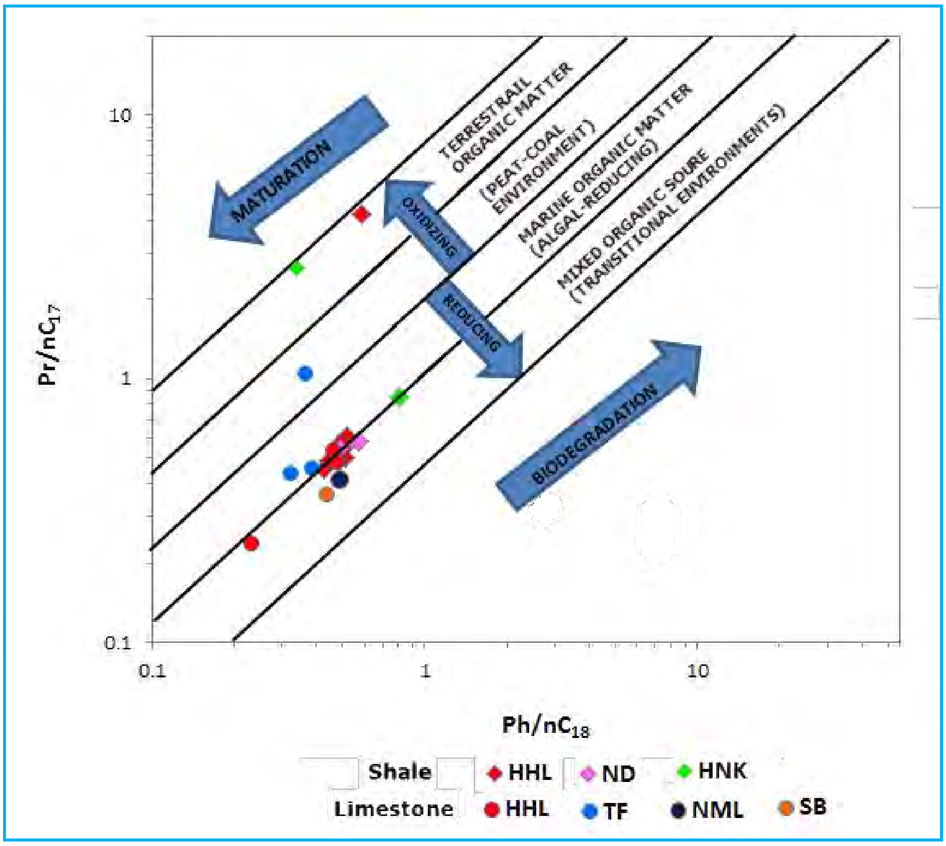

Figure 4.7 Pr/*n*C_{17} versus Ph/*n*C_{18} plot of samples studied (plot modified from Shanmugam; 1985).

4.4.2 Biomarkers

Gammacerane a biomarker that can be used as an indicator of lacustrine depositional environment. C_{27}-C_{29} regular steranes are biomarkers that can be used to specify depositional environment.

4.4.2.1 Gammacerane

Gammacerane can be identified in m/z 191 mass fragmentogram. It is eluted after C_{31}-homohopane 22S and 22R doublet as shown in Figure 4.5. Sinninghe Damste et al. (1995) and Peters et al. (2005) had suggested that abundant gammacerane possibly indicate lacustrine deposits environment.

Result

Most of the samples studied contain gammacerane, though they show lower base ion (191) and molecular ion (412) as shown in Figure 4.8. Gammacerane often used to indicate hypersaline depositional environment but also reported the deposition under lacustrine environment. Pr/Ph, Pr/nC_{17} and Ph/nC_{18} values of the samples also support that they were possibly deposited in mixed terrigenous in reducing environment.

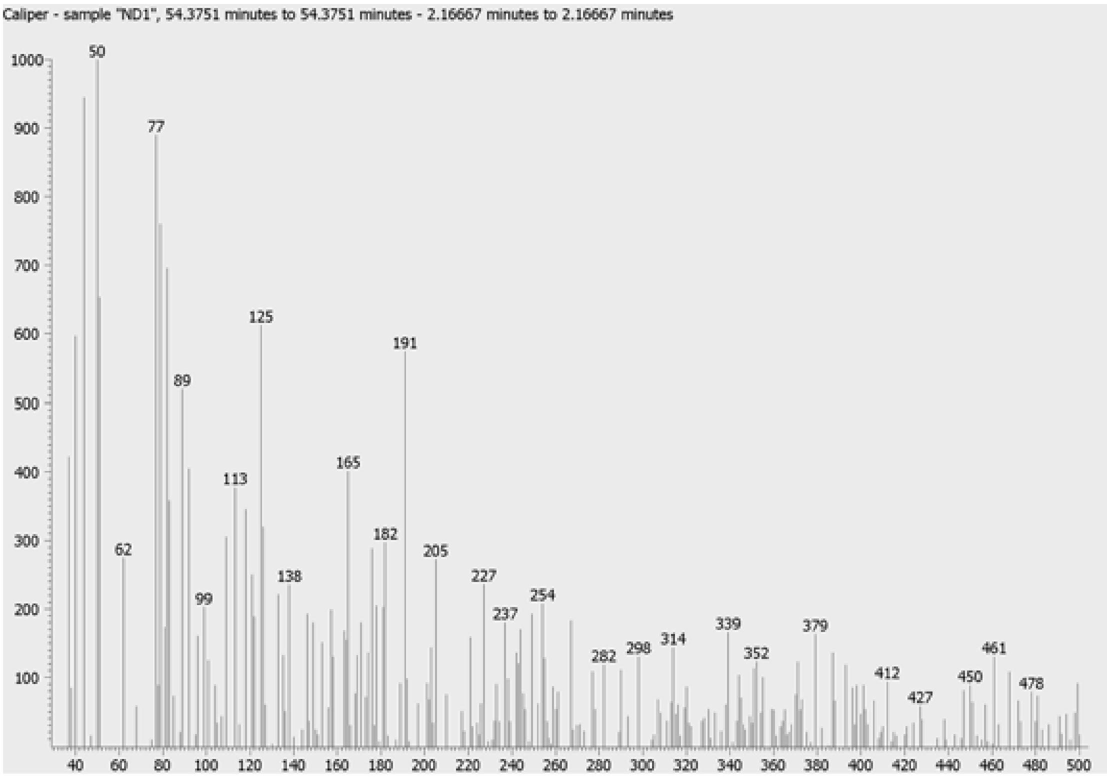

Figure 4.8 Example of mass spectra of gammacerane from ND1.

4.4.2.2 C_{27}-C_{29} regular steranes

Relative abundance of C_{27}-C_{29} steranes, which was converted to a percentage value, was normally plotted in a ternary diagram. Peak area measurement was made in m/z 217 fragmentogram. The relative proportion of each steranes in comparison to others can indicate specific depositional environments of samples (Miles, 1989). Figures 4.9 and 4.10 show ternary diagram of regular steranes distribution of samples from Huai Hin Lat Formation and Saraburi Group under studied, respectively.

Result

Because of very low concentration of steranes contain in samples studied, the peaks detected are very low making it difficult to correctly identify and quantity these regular steranes. The relative abundance of regular steranes of Huai Hin Lat, Nam Duk and Tak Fa Formations show no predominant contribution (except sample from HHL4 and HHL9) as shown in Table 4.11. From the ternary diagram (Figure 4.9), all of the Huai Hin Lat Formation samples have contributions from both continental and marine organisms which are consistent with interpretation from Pr/nC_{17}, Ph/nC_{18} ratios and the presence of gammacerane. According to Figure 4.9, most samples were possibly deposited in estuarine and/or terrestrial environments as indicated by %C_{27}-C_{29} regular steranes. These are in agreement with data from the visual kerogen analysis which indicated that they have contributions from land plants with high %vitrinite content. The sterane data of Saraburi Group as shown in Figure 4.10 indicate that samples from Nam Duk, Hua Na Kham and Tak Fa Formations were also possibly deposited in estuarine environment and/or terrestrial environments. Regular steranes distribution of samples from Saraburi Group are in agreement with interpretation from Pr/nC_{17}, Ph/nC_{18} ratios and the presence of gammacerane.

Table 4.11 %C_{27}-C_{29} regular steranes calculated from peak area in m/z 217 for sterane.

Sample name	**UTM**		**% C_{27}**	**% C_{28}**	**% C_{29}**
	X	**Y**			
HHL1	779133 E	1618930 N	34.49	21.08	44.43
HHL2	764918 E	1854700 N	26.92	22.74	50.33
HHL4	792378 E	1845667 N	12.01	30.14	57.84
HHL6	792834 E	1847487 N	29.03	47.56	23.41
HHL7	794084 E	1851347 N	42.11	34.98	22.91
HHL9	797545 E	1851815 N	19.82	20.99	59.19
HHL10	787391 E	1853289 N	33.86	23.76	42.37
ND1	749983 E	1851179 N	17.23	55.02	27.75
HNK2	769299 E	1855259 N	25.06	48.11	26.77
TF3	706387 E	1751748 N	34.66	38.84	26.50

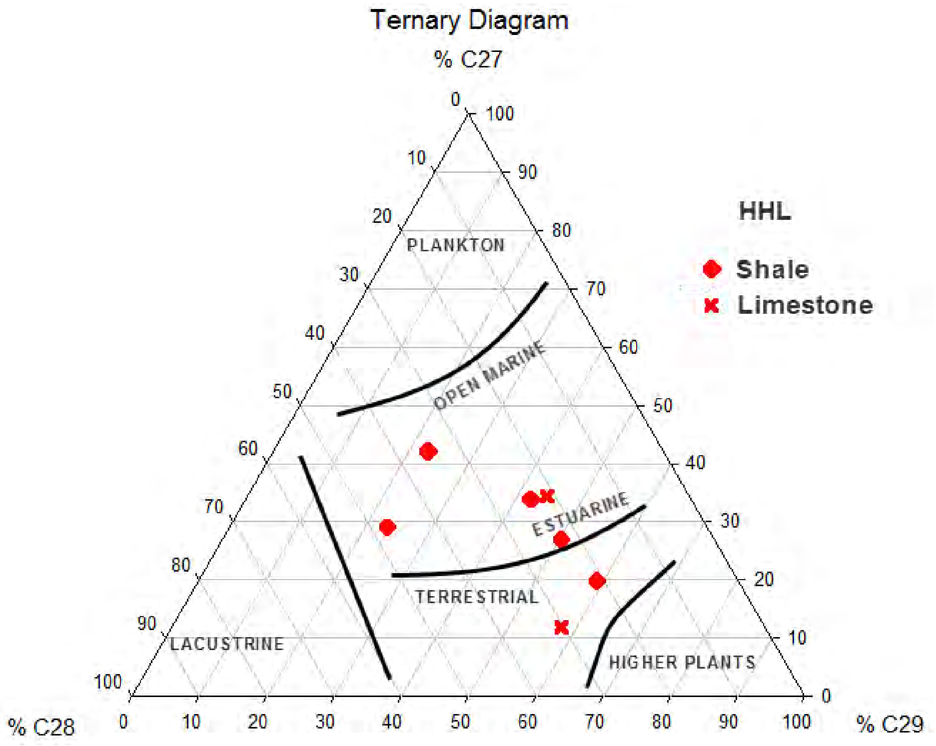

Figure 4.9 Ternary plot of C_{27}-C_{29} regular steranes of studied Huai Hin Lat Formation samples.

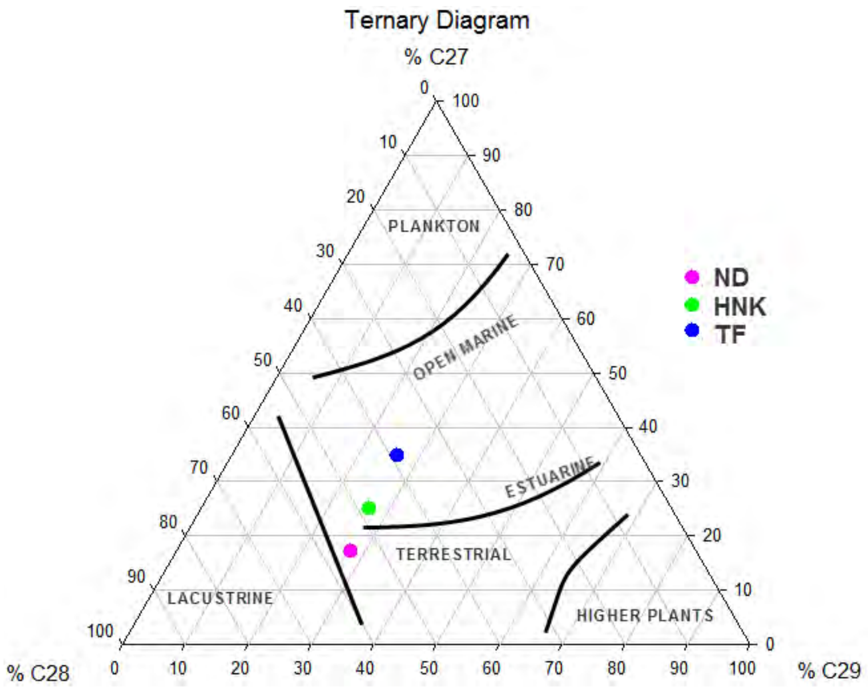

Figure 4.10 Ternary plot of C_{27}-C_{29} regular steranes of studied Saraburi Group samples.

CHAPTER V

DISCUSSION AND CONCLUSION

5.1 Discussion

This study analyzed for geochemical properties of outcrop samples from Huai Hin Lat Formation and Saraburi Group to determine their potential as petroleum source rocks, levels of maturity, type of organic matters and depositional environment.

The summary result of organic richness and thermal maturity level is shown in Table 5.1. Organic richness and thermal maturity levels from this study are compared with results from other studies including Chantong (2007) and Thongboonruang (2008), both of which utilized geochemical data from both outcrop and well cuttings from the exploration wells in the Khorat Plateau area. Thongboonruang and Chantong suggested that Huai Hin Lat Formation has fair to excellent source rock potential with thermal maturity level ranging from mature to post mature. This is supported by the result from this study. Organic richness and thermal maturity level of Saraburi Group in comparison with other studies showed that they could be considered as a potential source rock as well.

TOC content is a preliminary value used for source rock potential classification and is used in samples screening. Samples with TOC value lower than 0.50% for shale and 0.12% for limestone could be neglected from the consideration of source rock potential. TOC values of all shale samples were plotted with the EOM values in Figure 5.1. The graph shows good relationship between TOC and EOM values. Figure 5.1 shows that the studied samples could be considered fair to excellent potential source rock. Leythaeuser (1973) suggested that outcrop shale have lower TOC and EOM values than subsurface shale due to weathering process. However, based on classification of EOM values from Continental Shelf Institute (1977) which classifies samples with more than 200 ppm of EOM as having adequate quantity, all of these samples could be considered petroleum source rock. Low EOM values could also be a result of high maturity level of samples (hydrocarbon had already expelled out of the rocks).

Table 5.1 Summary of organic richness and thermal maturity level of Huai Hin Lat Formation and Saraburi Group in this study compare with Chantong (2007) and Thongboonruang (2008).

		Organic Richness	**Thermal Maturity Level**
Huai Hin Lat Formation	Outcrop samples from this study	Fair to Excellent	Late mature
	Chantong (2007)	Poor to Excellent	Mature to Post mature
	Thongboonruang (2008)	Fair to Excellent	Mature to Post mature
Saraburi Group	Outcrop samples from this study	Fair to Good	Late mature to Post mature
	Chantong (2007)	Poor to Good	-
	Thongboonruang (2008)	Fair to Excellent	Mature to Post mature

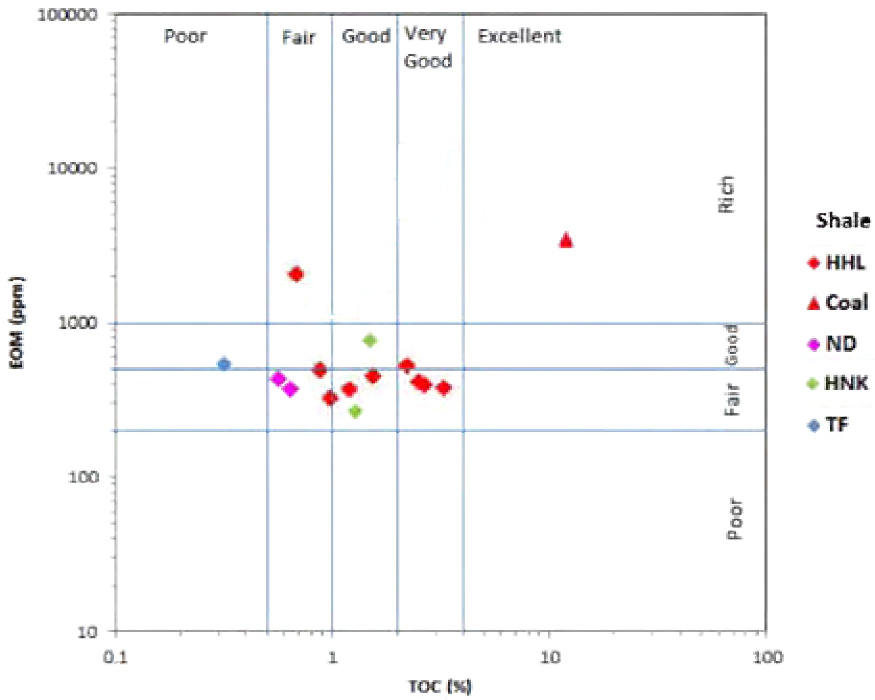

Figure 5.1 Plots of EOM and TOC of samples studied.

Bivariate plot of Ro values and Tmax, from Rock-Eval pyrolysis, both of which are thermal maturity indicators are shown in Figure 5.2. There is, however, no linear relationship between these Ro and Tmax in this figure. Tmax values indicate the maturity level ranging from immature to post mature while most of vitrinite reflectance suggests late mature to post mature level (except sample HHL10 which is of mature level).

Abnormally high Tmax values observed in this study are possibly a result of oxidation of organic matter or intense weathering of the outcrop samples (a suggestion made by Jahangard et al. (2010) in their study).

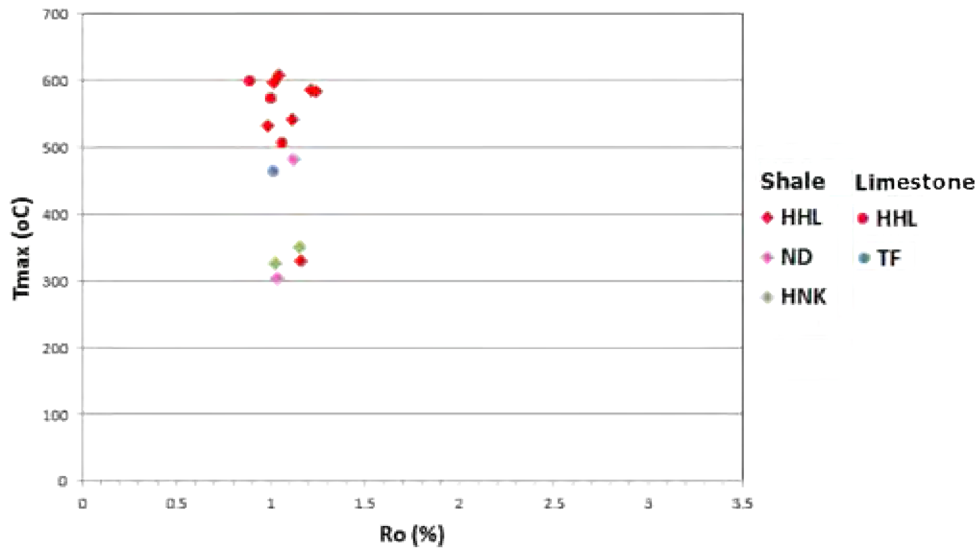

Figure 5.2 Bivariate plot between vitrinite reflectance (%Ro) and Tmax (^{o}C).

In this study, several indicators were used for identifying the level of thermal maturity such as CPI and Ts/(Ts+Tm) ratio, Tmax, PI and vitrinite reflectance. The result from PI, Ts/(Ts+Tm) ratio and vitrinite reflectance were positively correlated with one another and showed that sample from Huai Hin Lat Formation and Saraburi Group have the thermal maturity levels of late mature and from late mature to post mature, respectively. This interpretation is supported by Pr/Ph, Pr/nC$_{17}$ and Ph/nC$_{18}$ ratios (except samples HHL8, HNK2 and TF2). C$_{31}$ homohopane 22S/(22S+22R) ratio indicates that the maturity level of the studied samples are ranging from immature to mature level.

All geochemical data from samples of Huai Hin Lat Formation and Saraburi Group were used to interpret the source rock potential. Source rock potential was considered from three parameters including (1) quantity of organic matter by TOC value, (2) type of kerogen (quality) by visual kerogen typing and (3) thermal maturity level by Ro value and other indicators. Visual kerogen analysis suggest that all samples contain kerogen predominantly type III (i.e. gas-prone). Source rock potential classification based on TOC and Ro data (see Table 4.6) are as follows.

Location: Amphoe Pakchong, Changwat Nakhon Ratchasima (Figure 5.3)

HHL1 of Huai Hin Lat Formation, TOC = 1.01%wt, Ro = 1.063%, is possibly a good source rock. SB of Sap Bon Formation in Saraburi Group with corrected TOC and Ro values of 0.01%wt and 1.935%, respectively. This sample can be classified as possibly a poor source rock.

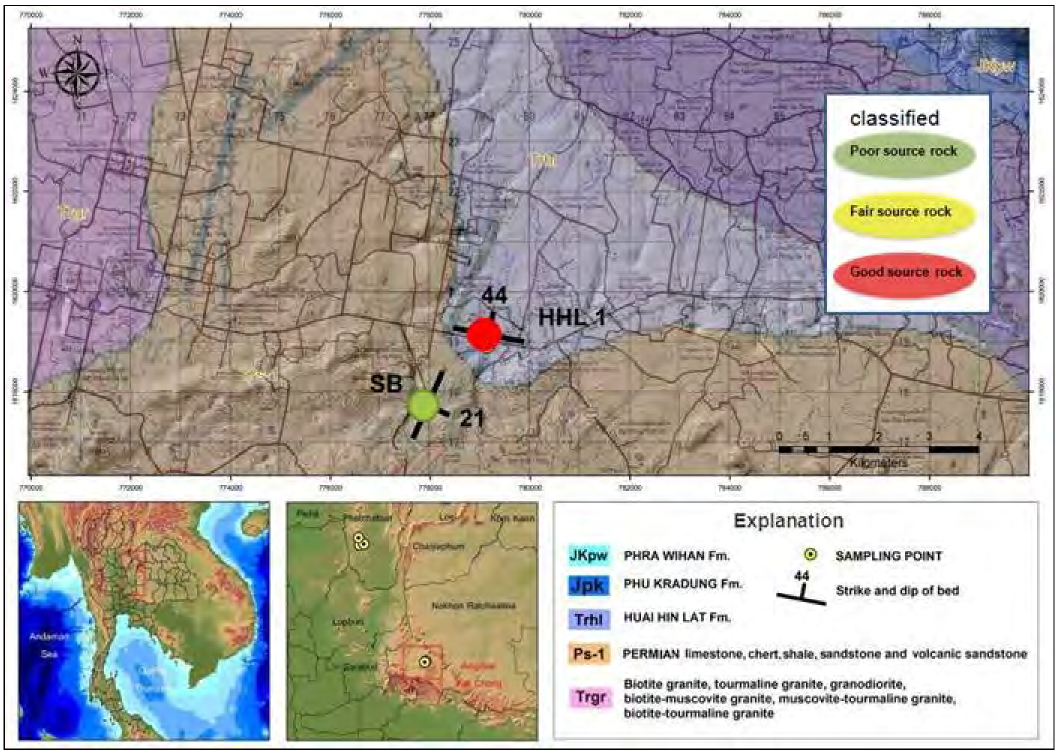

Figure 5.3 Source rock potential classification of samples HHL1 and SB collected from Amphoe Pakchong, Changwat Nakhon Ratchasima, plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2007).

Location: Amphoe Bueng Samphan, Changwat Phetchabun (Figure 5.4)

TF3 from Tak Fa Formation, TOC = 0.37%wt and Ro = 1.021%, can be classified as a good source rock. TF1 and TF2 are considered as poor source rocks since both of them have TOC value too low (lower than 0.001%wt) even though they have relatively high Ro values (1.490% and 1.578%, respectively).

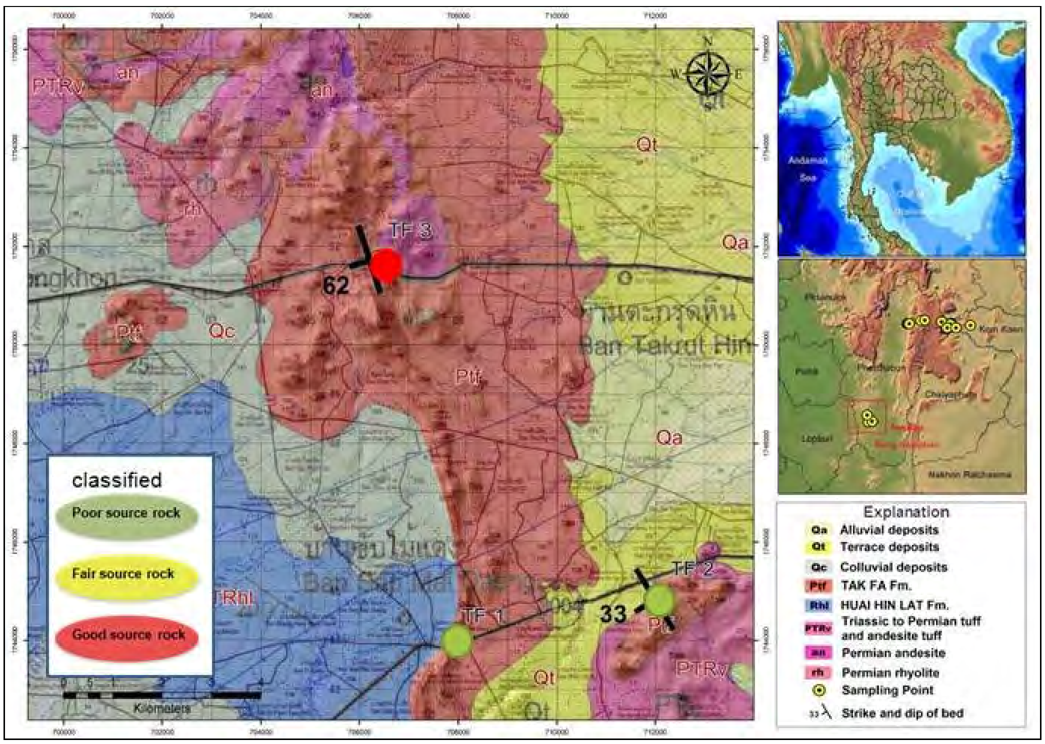

Figure 5.4 Source rock potential classification of samples TF1, TF2 and TF3 collected from Amphoe Bueng Samphan, Changwat Phetchabun, plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2009).

Location: Amphoe Lom Sak, Changwat Phetchabun (Figure 5.5)

HHL2, HNK1 and HNK2 contain high TOC contents (2.54%wt, 1.47%wt and 1.74%wt, respectively) with high Ro values (1.162, 1.023 and 1.159%, respetively). These point to a potential to be a good source rock. Both samples of Nam Duk Formation (ND1; 0.66%wt of TOC and 1.122% Ro and ND2; 0.75%wt of TOC and 1.041% Ro) can be classified as fair source rocks based on their relatively low TOC contents.

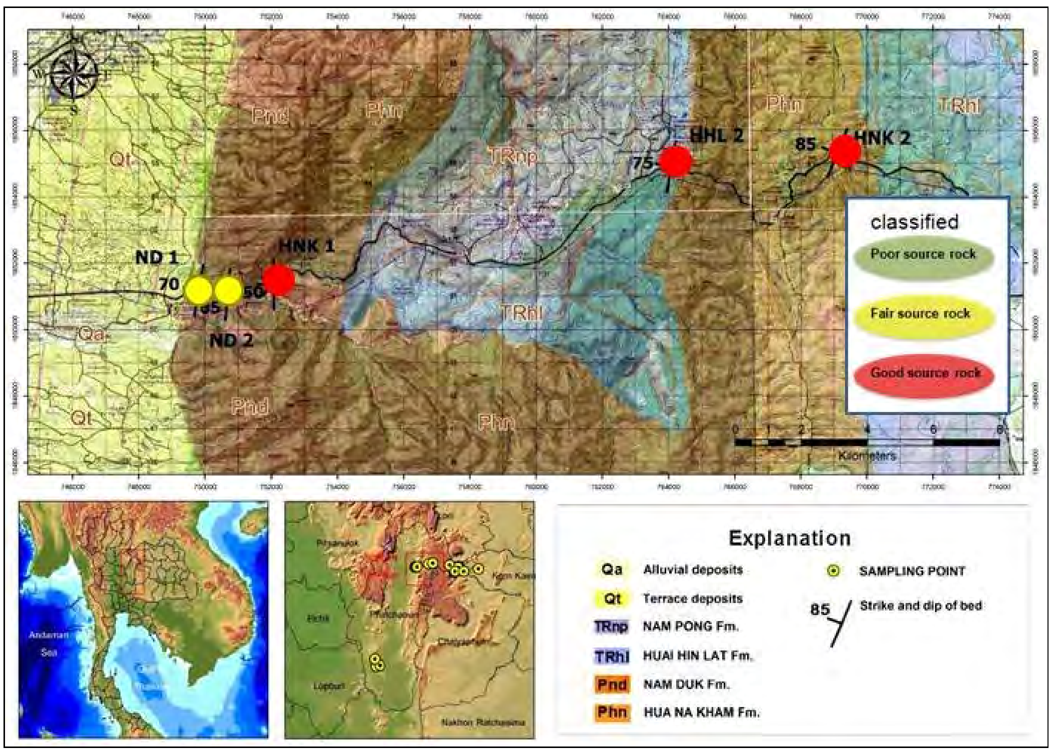

Figure 5.5 Source rock potential classification of HHL2, HNK1, HNK2, ND1 and ND2 collected from Amphoe Lom Sak, Changwat Phetchabun, plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2009).

Location: Amphoe Nam Nao, Changwat Phetchabun (Figure 5.6)

At this location, seven samples (HHL3, HHL4, HHL5, HHL6, HHL7, HHL8 and HHL10) of Huai Hin Lat Formation were analyzed and based on TOC and Ro values (0.79-13.80%wt and 0.898-1.216%), they could be considered as good source rocks.

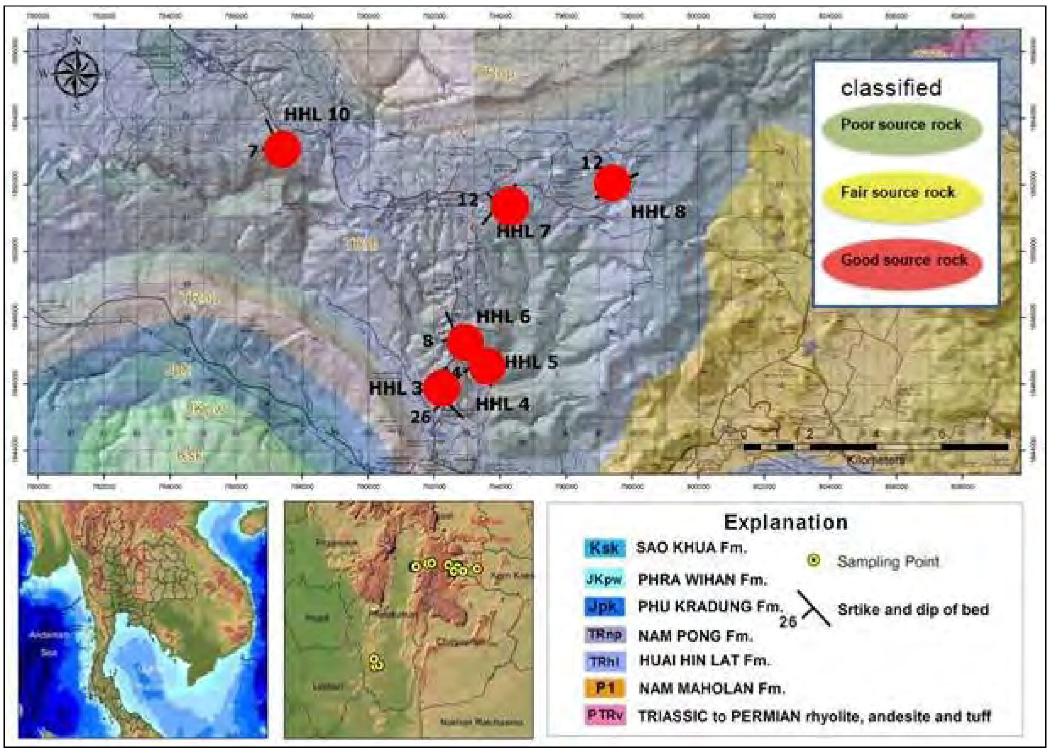

Figure 5.6 Source rock potential classification of HHL3-HHL8 and HHL10 collected from Amphoe Nam Nao, Changwat Phetchabun, plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2009).

Location: Amphoe Phu Pha Man, Changwat Khon Kaen (Figure 5.7)

Sample HHL9 of Huai Hin Lat Formation with TOC content of 3.76%wt and Ro of 1.018% is probably a good source rock (high TOC, high Ro). Limestone (NML) of Nam Maholan Formation could be considered a poor source rock (very low TOC value) though Ro value is high (1.265%).

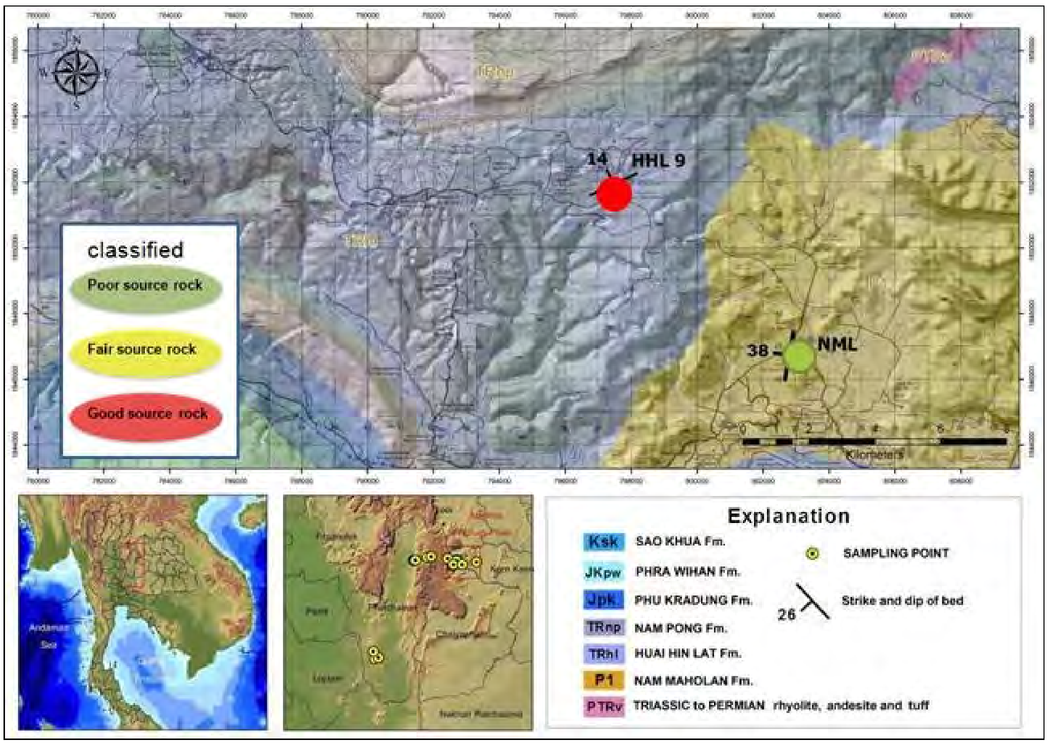

Figure 5.7 Source rock potential classification of HHL9 and NML collected from Amphoe Phu Pha Man, Changwat Khon Kaen, plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2009).

Location: Amphoe Chumpae, Changwat Khon Kaen (Figure 5.8)

Limestone (HHL11) from Huai Hin Lat Formation was collected from the location shown in Figure 5.8. It has the TOC content of <0.001%wt and Ro value of 1.176% suggesting a poor source rock.

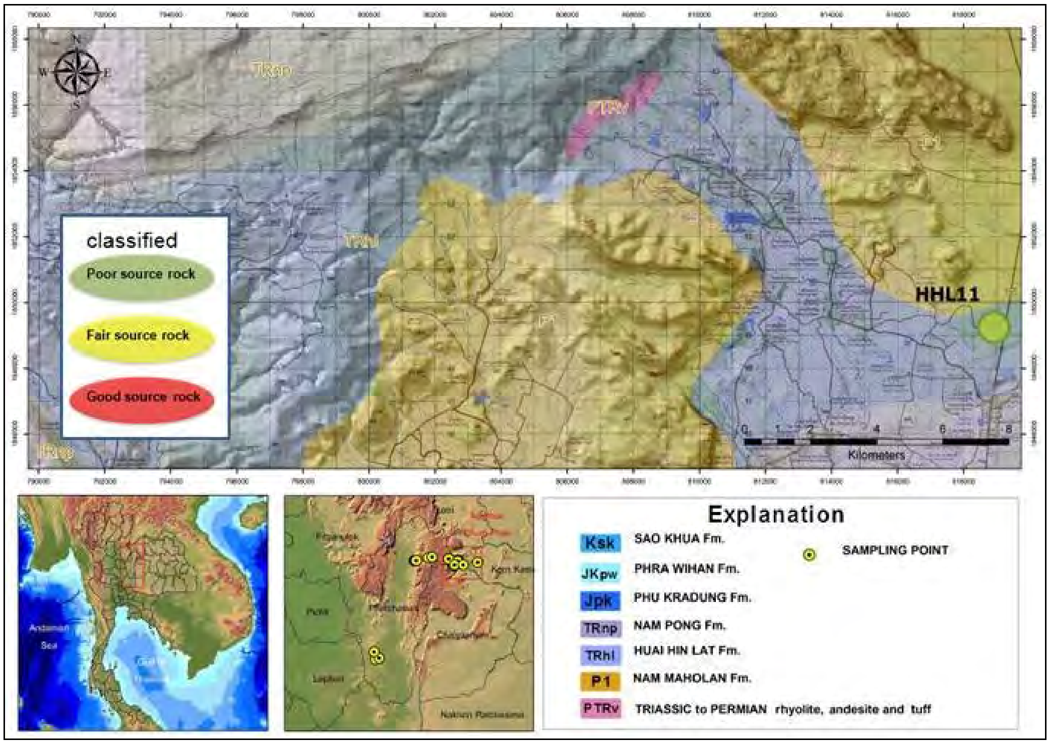

Figure 5.8 Source rock potential classification of HHL11 collected from Amphoe Chumpae, Changwat Khon Kaen, plotted on a topographic map overlaying a geologic map of the area by Department of Mineral Resources (2009).

C_{27}-C_{29} regular steranes ternary diagram showed that the depositional environment of studied samples were possibly estuarine environment while the presence of gammacerane support that possible depositional environment is lacustrine environment. These are supported by others indicator such as Pr/Ph, Pr/nC_{17} and Ph/nC_{18}.

5.2 Conclusion

Organic geochemical properties of Huai Hin Lat Formation from this study are as follows. TOC contents of all the samples are ranging 0.69-3.27% for shale samples, <0.001-1.56%wt for limestone and 12.00%wt for sample HHL3 which is thought to be coal. EOM values are 320-3,474 ppm. Samples of Huai Hin Lat Formation studied include limestone, muddy limestone, argillaceous limestone, calcareous shale which is supported by $\%CO_3$ content 5.05-99.32%wt, with average 47.6%wt. TOC and EOM values suggest that Huai Hin Lat Formation is a potential source rock.

Kerogen typing of Huai Hin Lat Formation shows that they contain 55-75% vitrinite maceral with average of 65% content of kerogen type III. Kerogen typing data of all studied samples support very low HI values from Rock-Eval pyrolysis (1.57-14.28) suggesting kerogen type III/IV, gas-prone or no petroleum generation potential, as shown in Figure 4.3. Thus, Huai Hin Lat Formation has a potential to generate gas.

Vitrinite reflectance of all samples studied ranges 0.898-1.245% indicating maturity level of most samples as late mature. This result is supported by Pr/nC_{17}, Ph/nC_{18} ratio, and Ts/(Ts+Tm) ratios and CPI values which suggest that samples from Huai Hin Lat Formation has maturity levels of mature to late mature. C_{31} homohopane 22S/(22S+22R) ratio also show good correlation with other indicators (except for HHL1 and HHL10 samples which indicate immature level).

Rock-Eval pyrolysis data show potential yield 0.02-2.01, HI 1.57-14.28, OI 2.03-56.44 and Tmax value 335-607^{o}C (Table 4.7). These results suggest that samples from Huai Hin Lat Formation is of poor source rock, contain kerogen type III/IV which is gas-prone or has no petroleum generating potential and of post mature level. This result was supported by Leythaeuser (1973) studying shale outcrop sample which found drastic changes in some organic geochemical parameters due to weathering. Sample studied are of high maturity level and possibly already generated and expelled petroleum as indicated by their very low HI values.

In conclusion, all organic geochemical data of outcrop samples suggest that Huai Hin Lat Formation is a potential gas-prone source rock with good thermal maturity level. However, core or cutting sample analysis is recommended for studying Huai Hin Lat Formation in order to minimize an effect of weathering.

Apart from Huai Hin Lat Formation, Saraburi Group samples were also studied and described as follows;

1. Quantity of organic matter

TOC of samples from Nam Duk, Hua Na Kham and Tak Fa Formations are 0.37-1.74 wt% which indicate good potential source rocks. EOM of samples are more than 200 ppm which is adequate to be considered as potential source rocks.

2. Quality of organic matter

Almost all formations contain predominantly kerogen type III (vitrinite) and therefore are gas-prone source rocks, except Tak Fa Formation which contain kerogen type III/IV of amorphinite (non fluorescent amorphous) with potential to generate gas and/or has no potential for petroleum generation. HI and OI values, from Rock-Eval pyrolysis, suggest that samples studied contain kerogen type III/IV, which is defined by HI values 1.52-81.08. This suggests that the samples have no or little potential to generate gas.

3. Thermal Maturity

Ro values, Pr/nC$_{17}$, Ph/nC$_{18}$ and CPI values suggest that samples from Saraburi Group are of late mature to post mature. This result is supported by Ts/(Ts+Tm) ratios. Tmax values suggest that most of sample from Saraburi Group are immature to post mature which is not correlated with other indicators and is discarded as a possible effect of weathering on the Tmax values of outcrop samples.

4. Depositional environment

Pr/Ph, Pr/nC_{17} and Ph/nC_{18} ratios and ternary diagram of relative abundance of C_{27}-C_{29} regular steranes suggest that samples contain mixed organic sources between terrigenous and marine organic matters deposited in a reducing environment. This is supported by a presence of gammacerane in all samples which further suggests lacustrine depositional environment of the samples.

Among 4 formations studied, Huai Hin Lat Formation has the best potential to be a good source rock (high TOC, high EOM and thermally mature - Ro = 0.898-1.245%). Within the Saraburi Group, Hau Na Kham Formation has better potential to be good source rock than Nam Duk and Tak Fa Formations. Based on available data and geochemical data obtained from this study, it can be primarily suggest that Huai Hin Lat and Hau Na Kham Formations are likely the source of petroleum found in the Khorat Plateau area.

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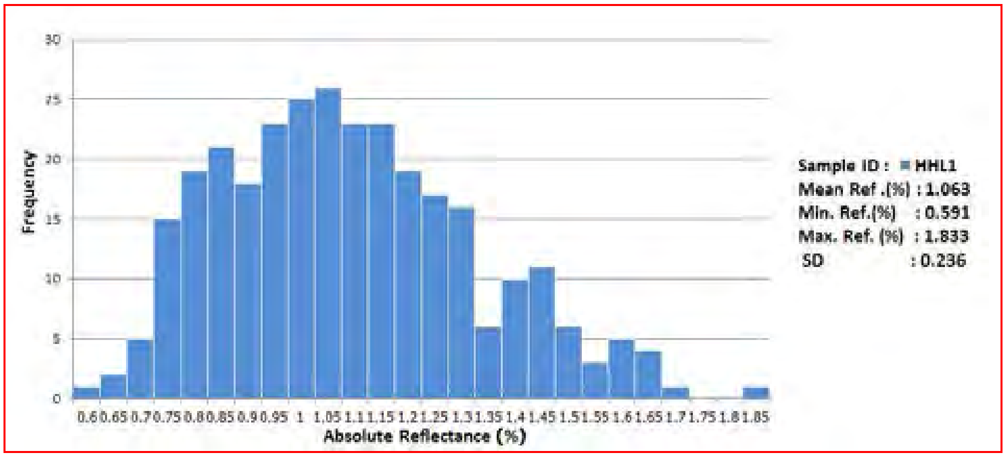
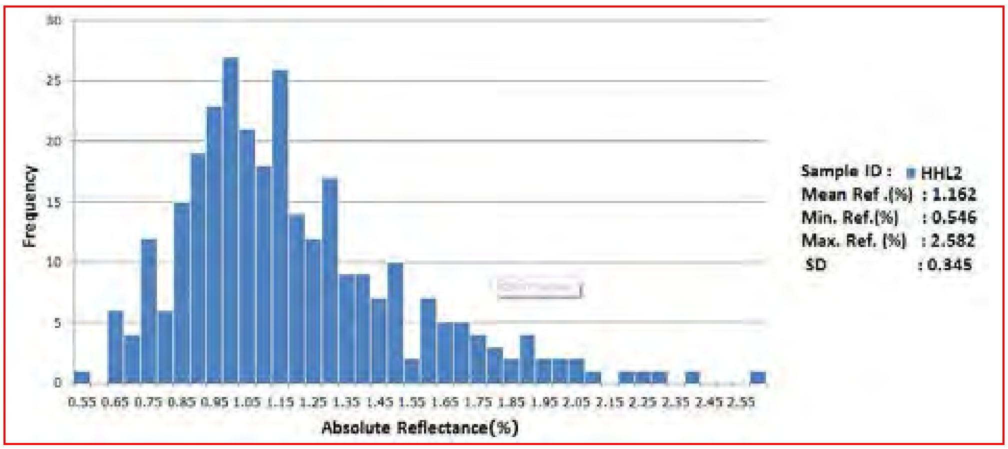
APPENDICES

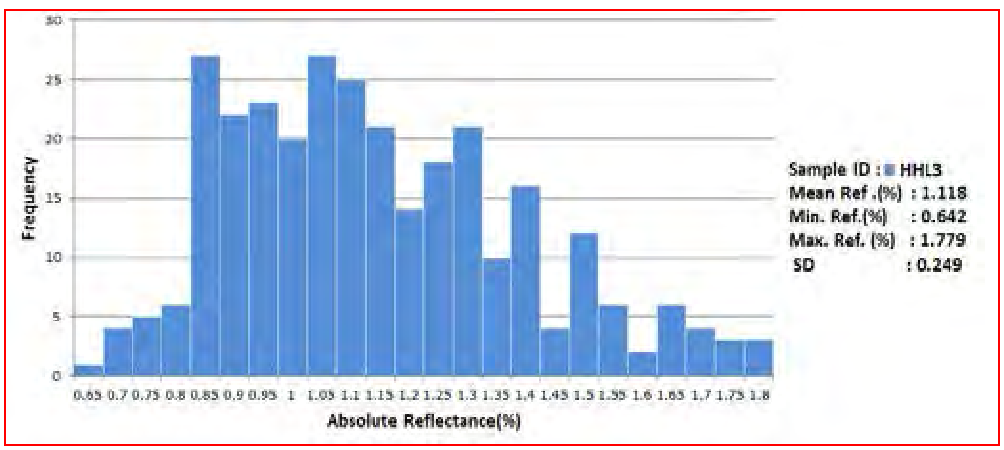
APPENDIX A

Vitrinite reflectance histogram

Analyzed at Chulalongkorn University.







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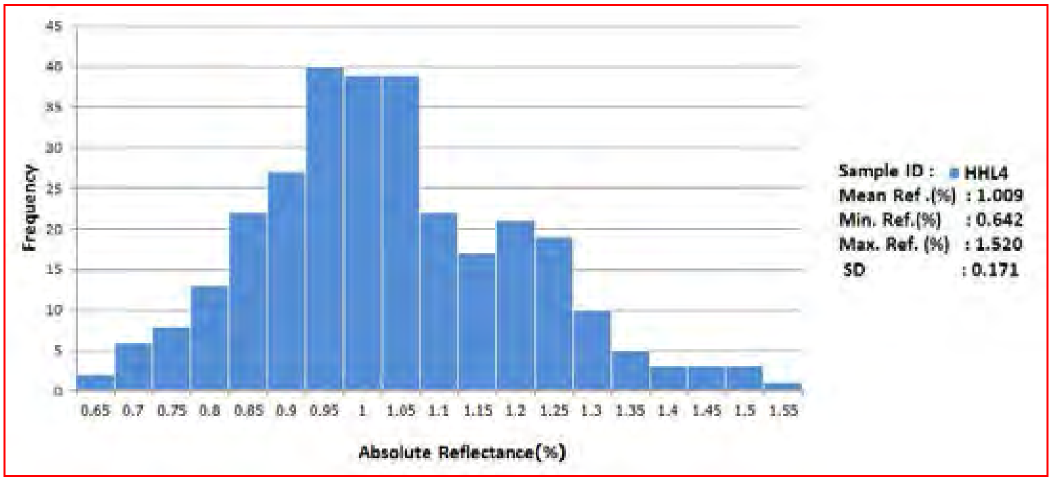

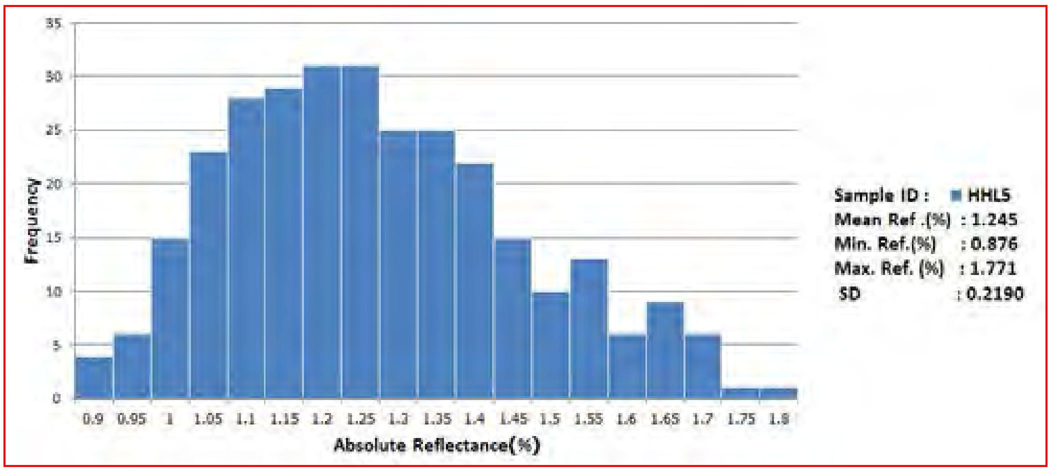

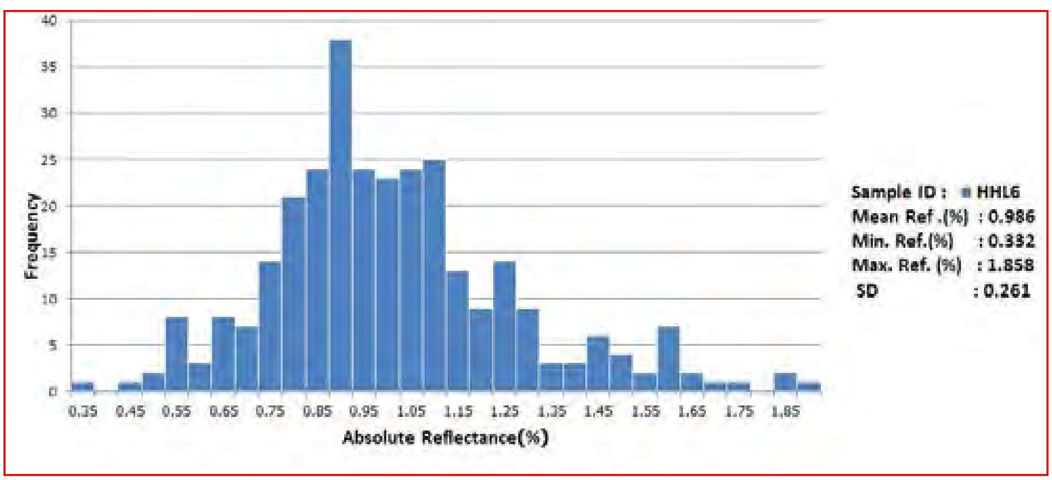

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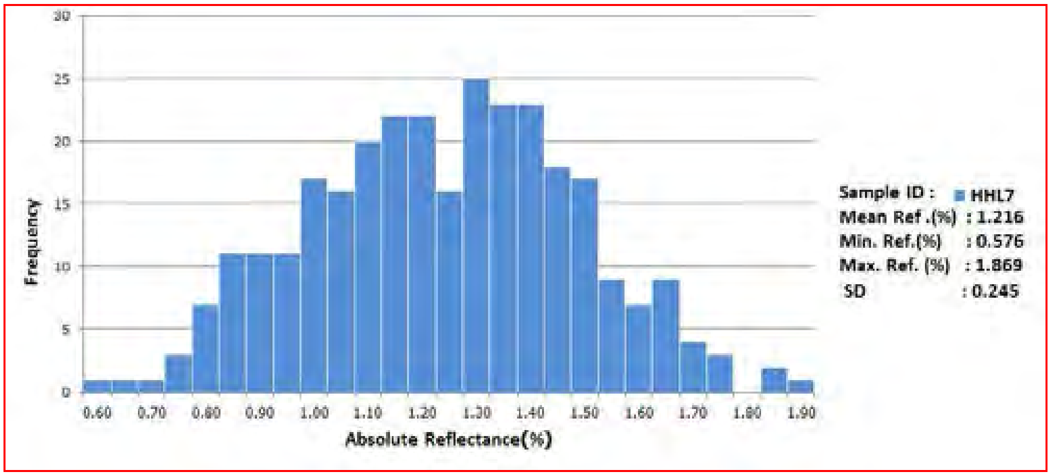

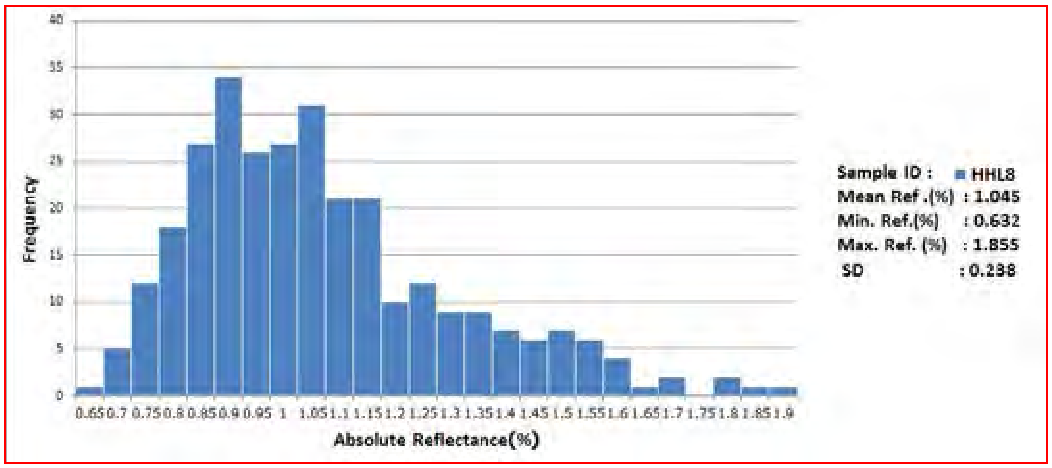

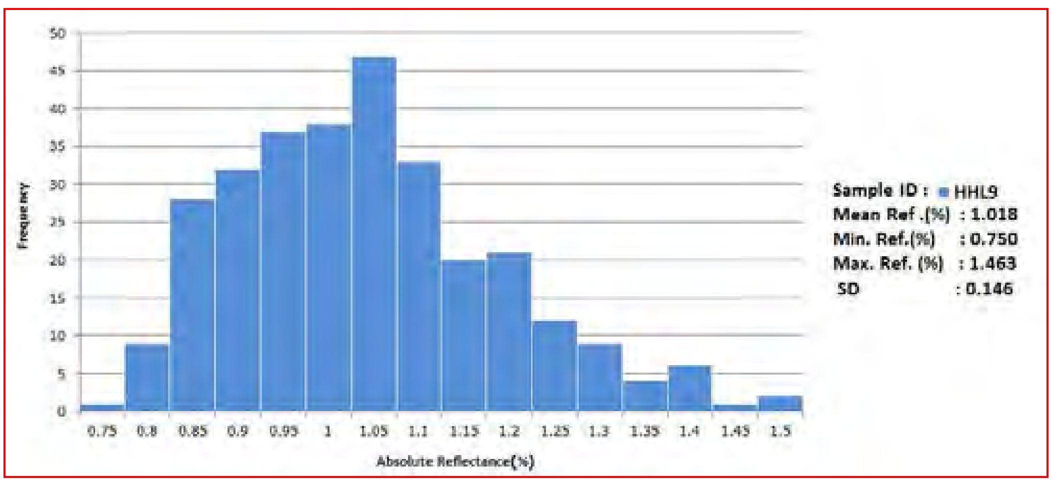

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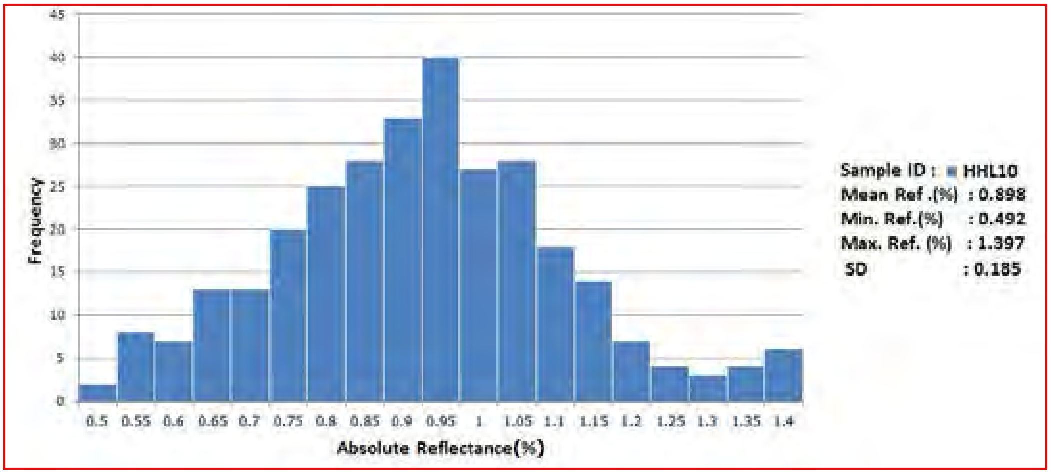

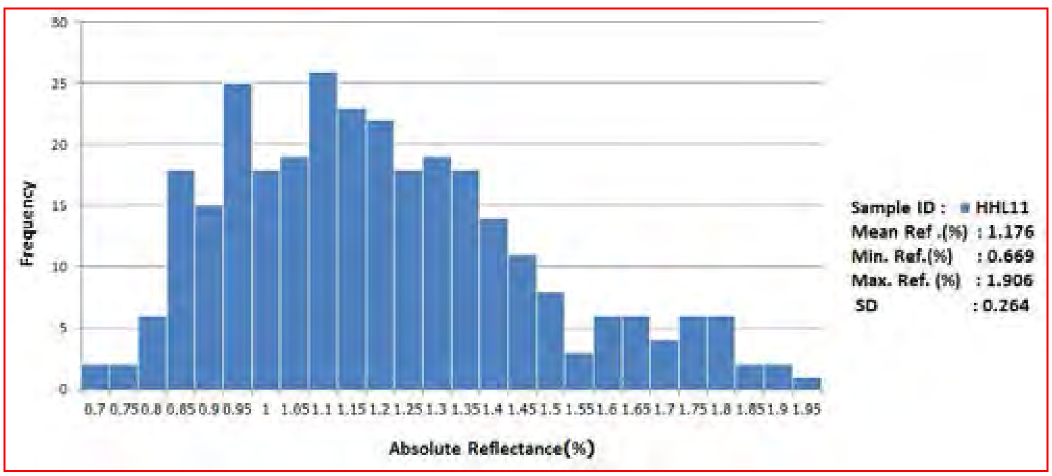

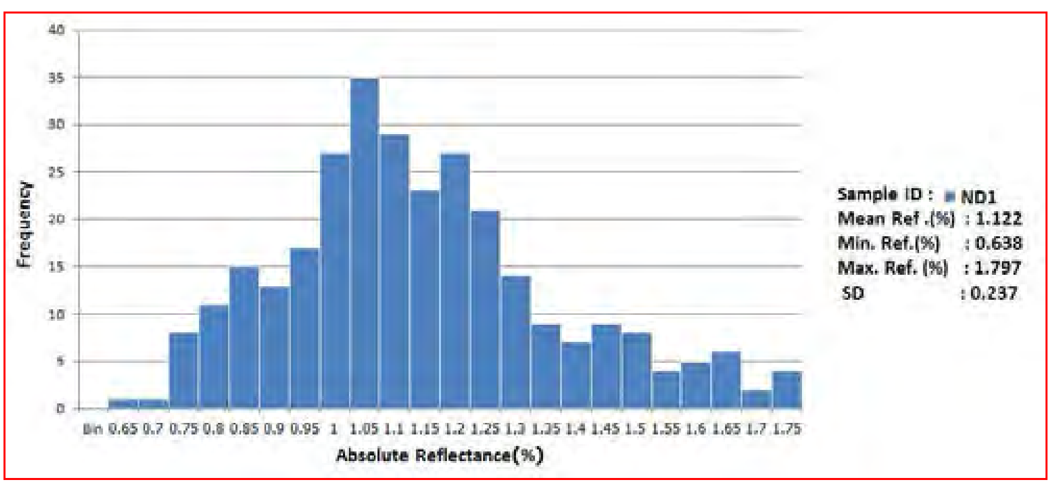

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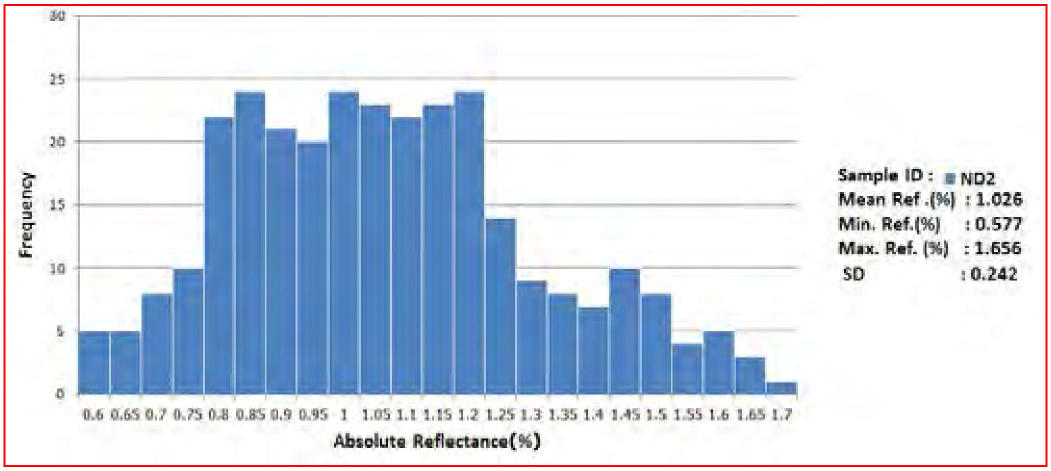
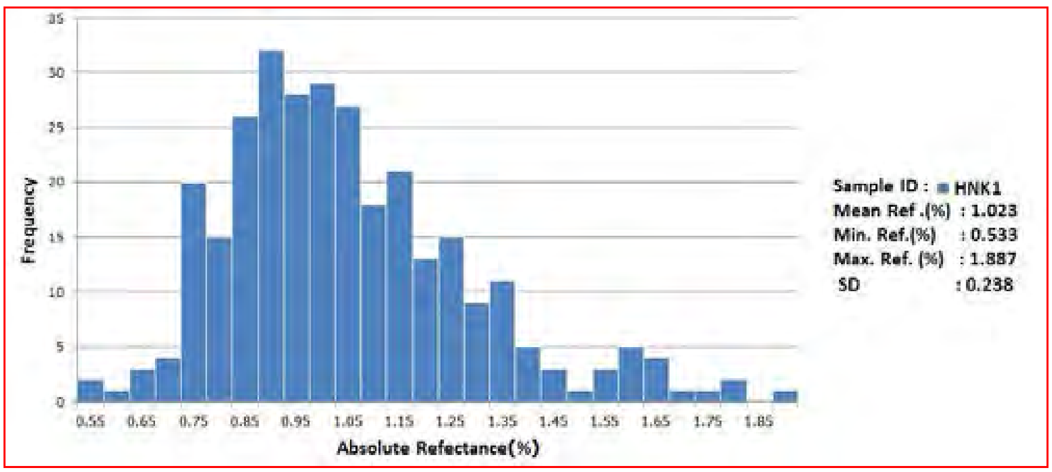
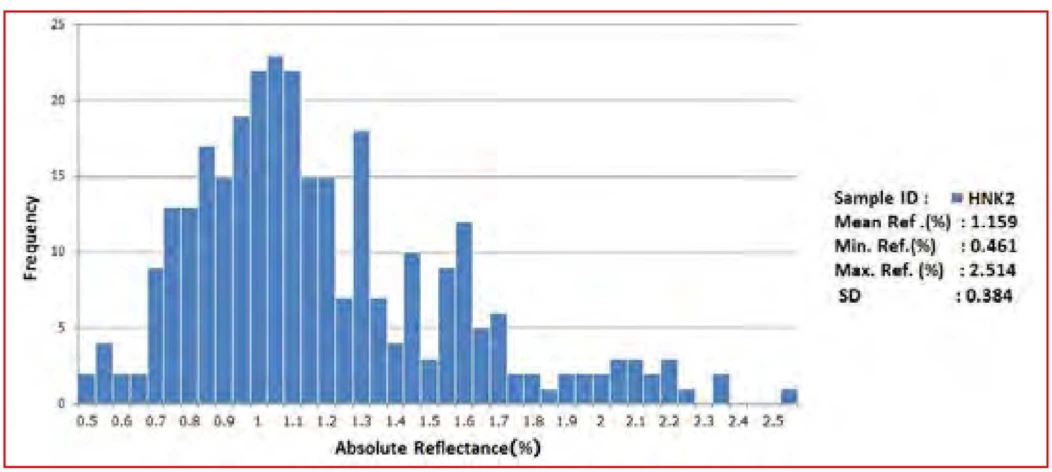
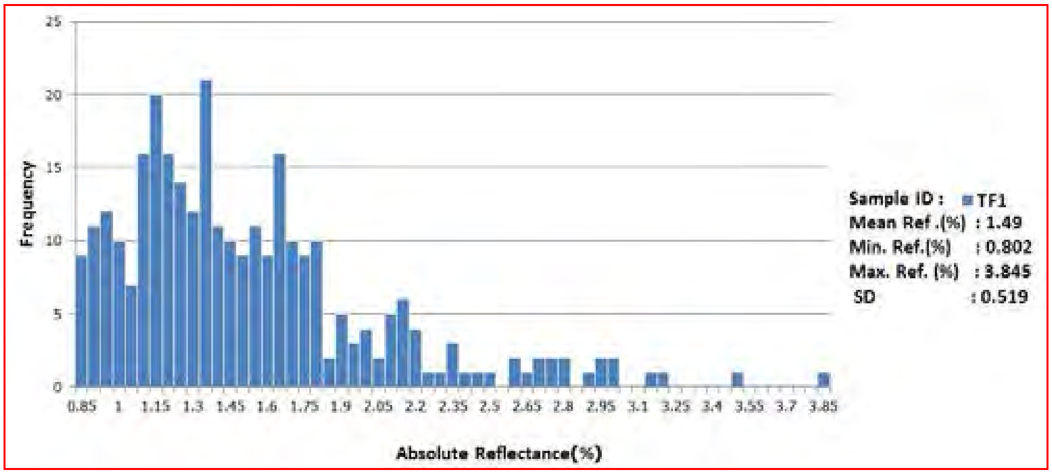
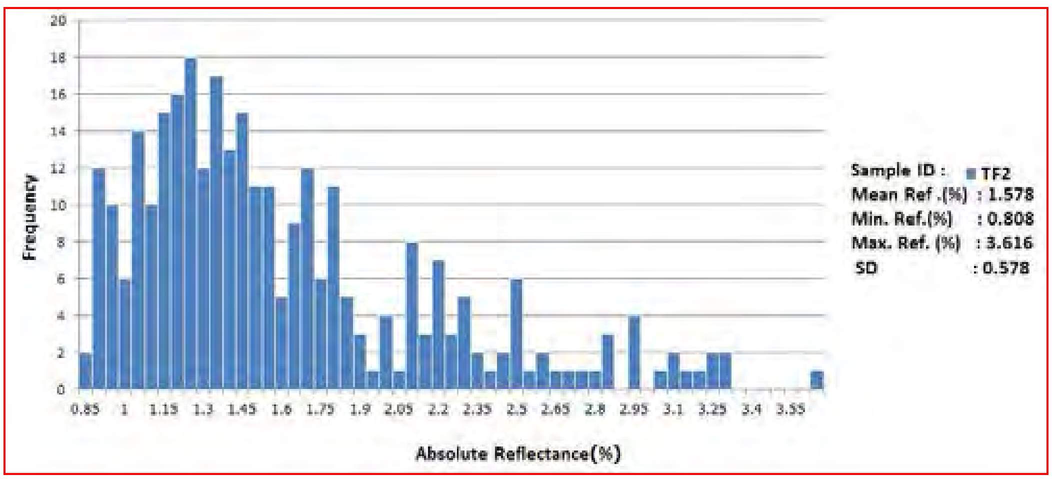


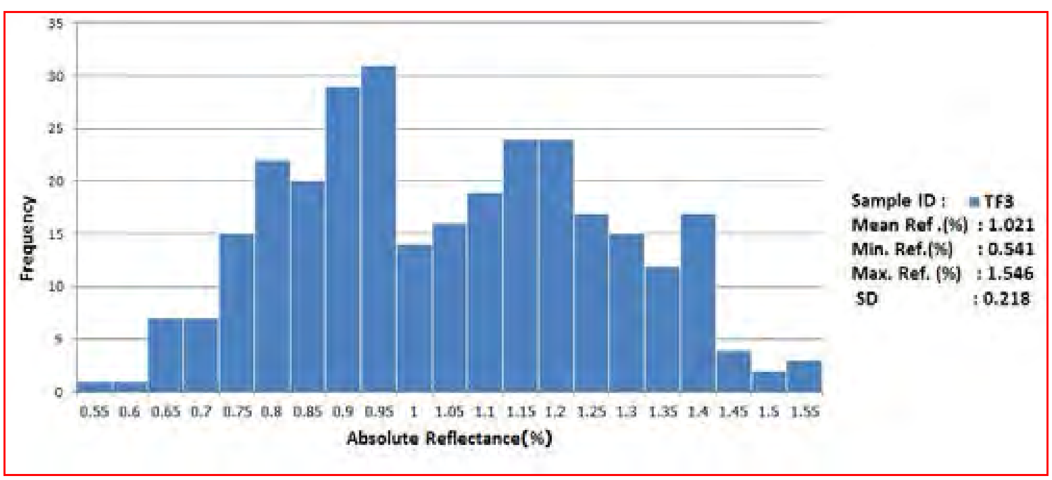




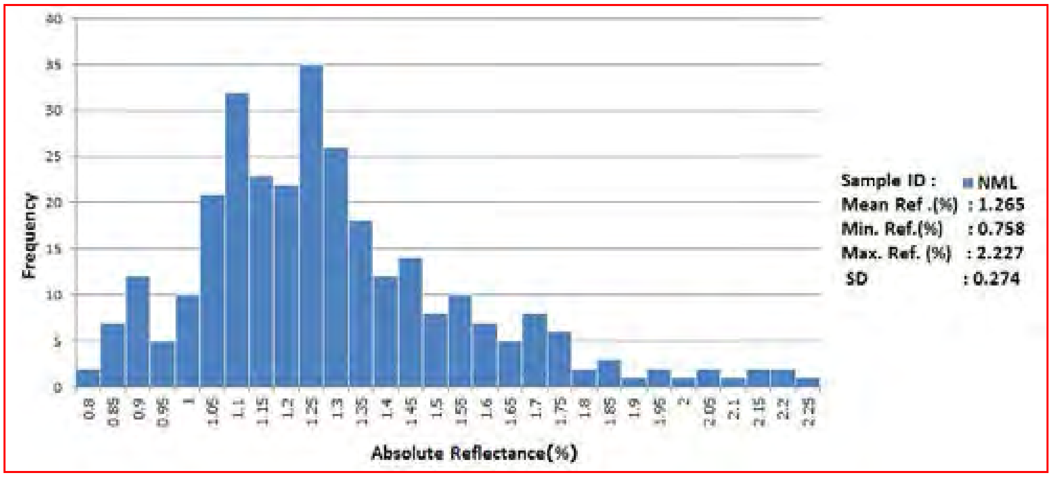
Analyzed at Chulalongkorn University.

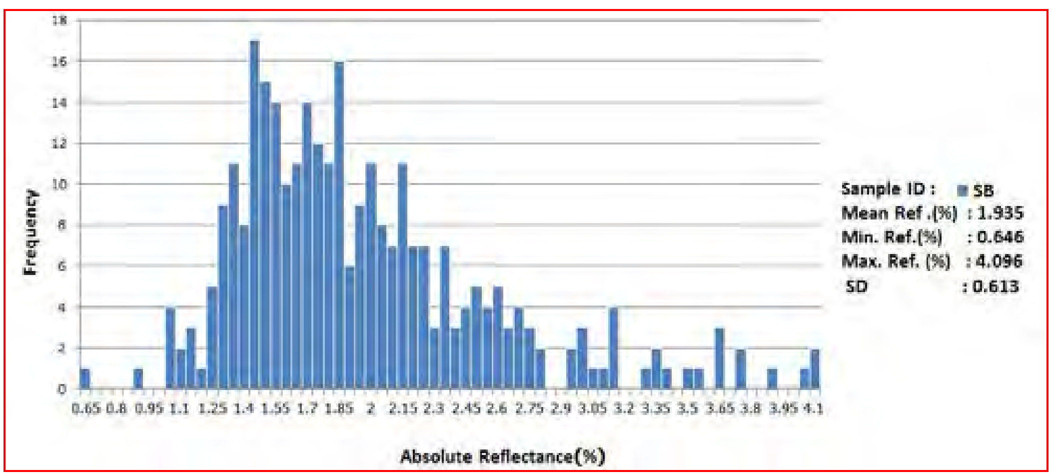




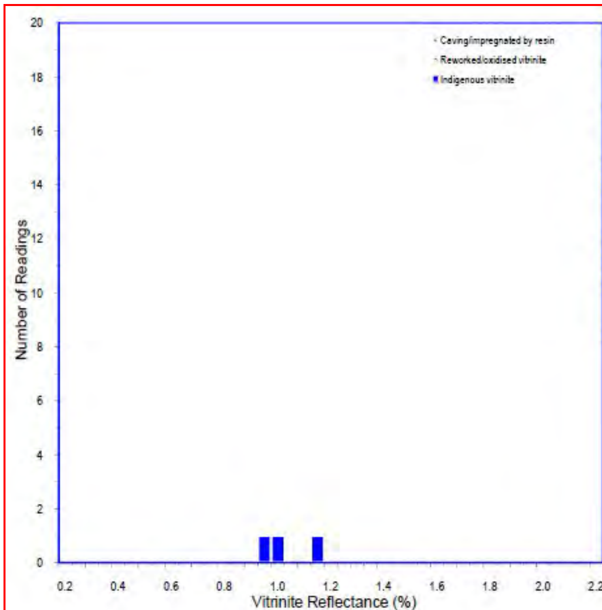


Analyzed at Chulalongkorn University.



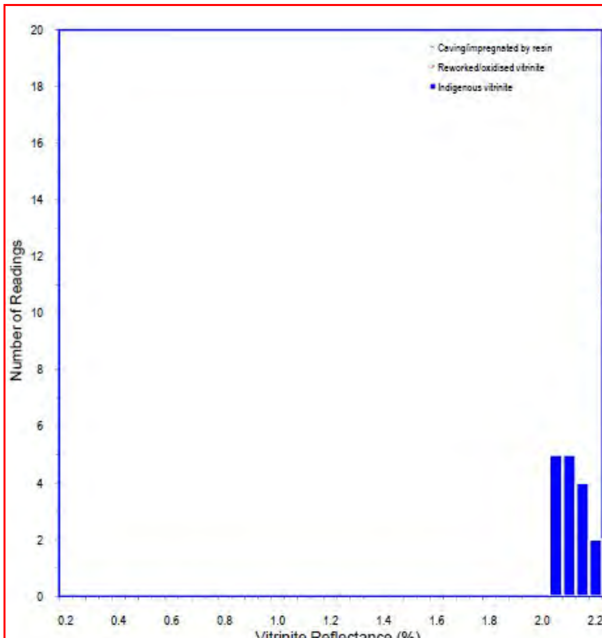


Analyzed at Core Laboratories (Core Lab) in Indonesia.



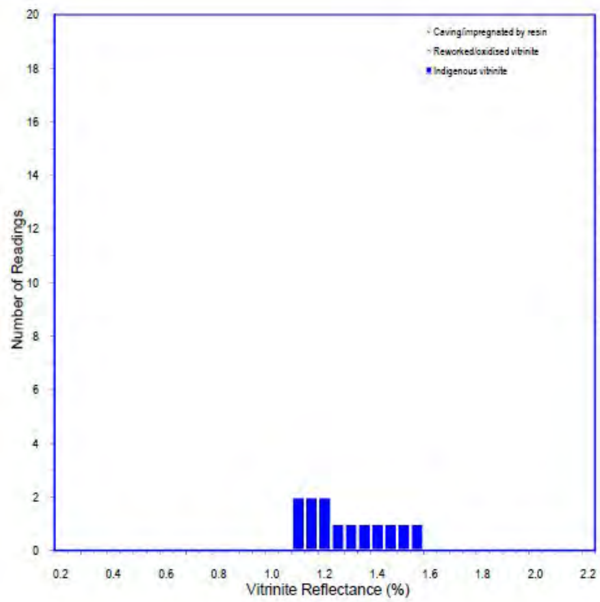
Company	: Chulalongkorn University
Well	: -
Sample ID	: HHL-1
Mean Ref.	: 1.05%
Readings	: 3
Min. Ref.	: 0.98%
Max. Ref.	: 1.16%
SD	: 0.079
Sample	: Core

Geochem-13033 (2)



Company	: Chulalongkorn University
Well	: -
Sample ID	: HHL-2
Mean Ref.	: 2.24%
Readings	: 28
Min. Ref.	: 2.06%
Max. Ref.	: 2.46%
SD	: 0.131
Sample Type	: Core

Analyzed at Core Laboratories (Core Lab) in Indonesia.



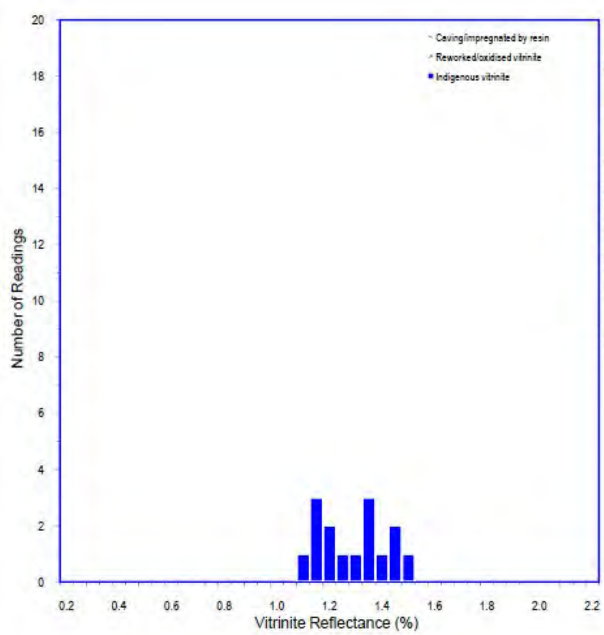
Company : Chulalongkorn University

Well : -

Sample ID : HHL-4
Mean Ref. : 1.31%
Readings : 13
Min. Ref. : 1.12%
Max. Ref. : 1.55%
SD : 0.144

Sample : Core

Geochem-13033 (3)



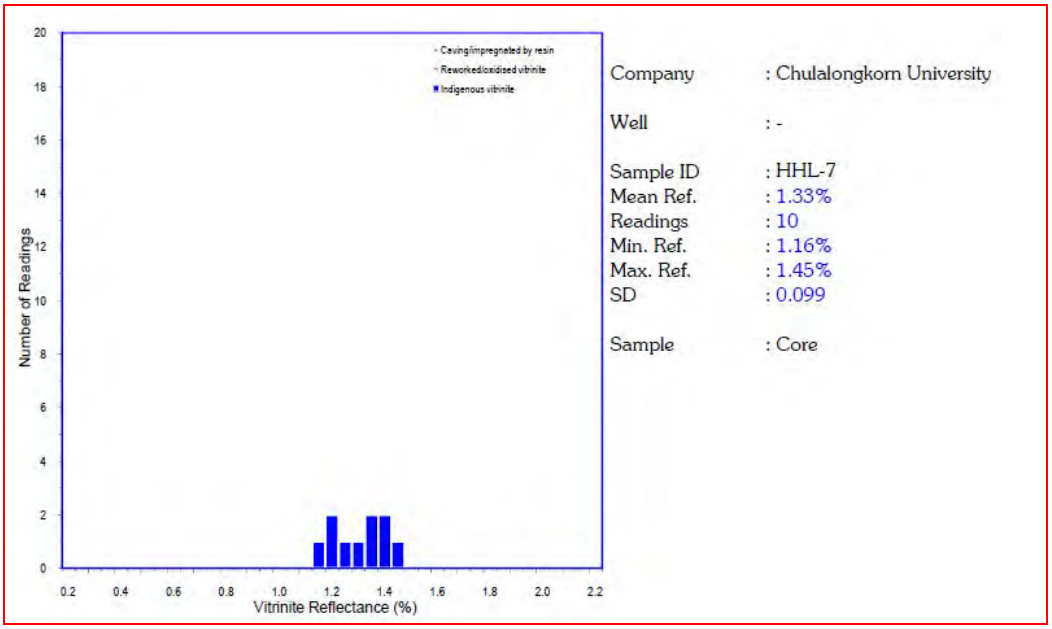
Company : Chulalongkorn University

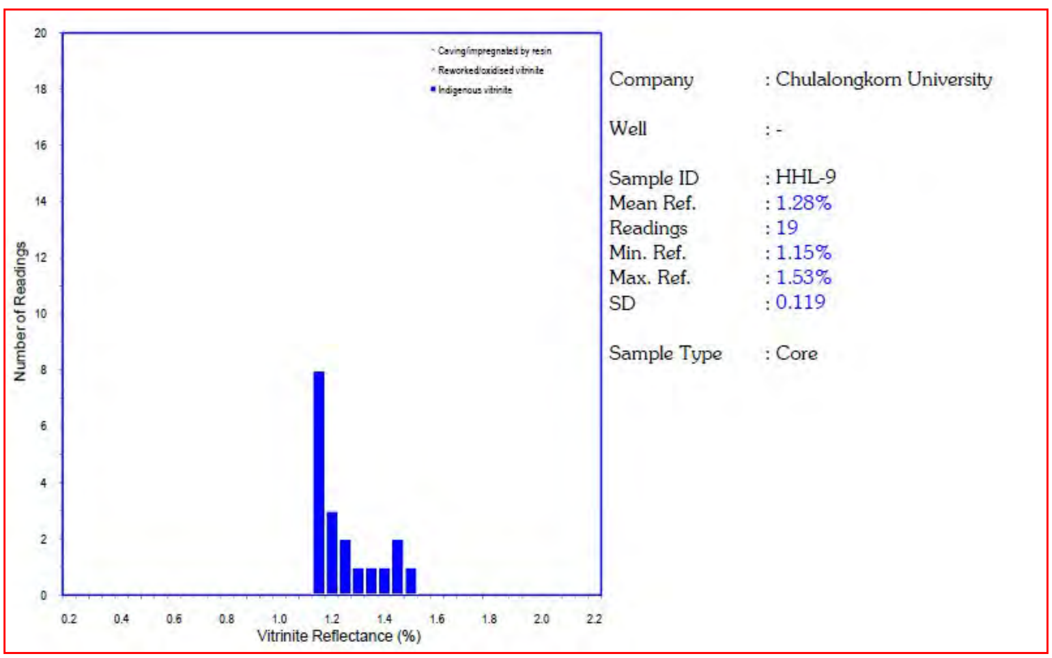
Well : -

Sample ID : HHL-6
Mean Ref. : 1.31%
Readings : 15
Min. Ref. : 1.13%
Max. Ref. : 1.51%
SD : 0.122

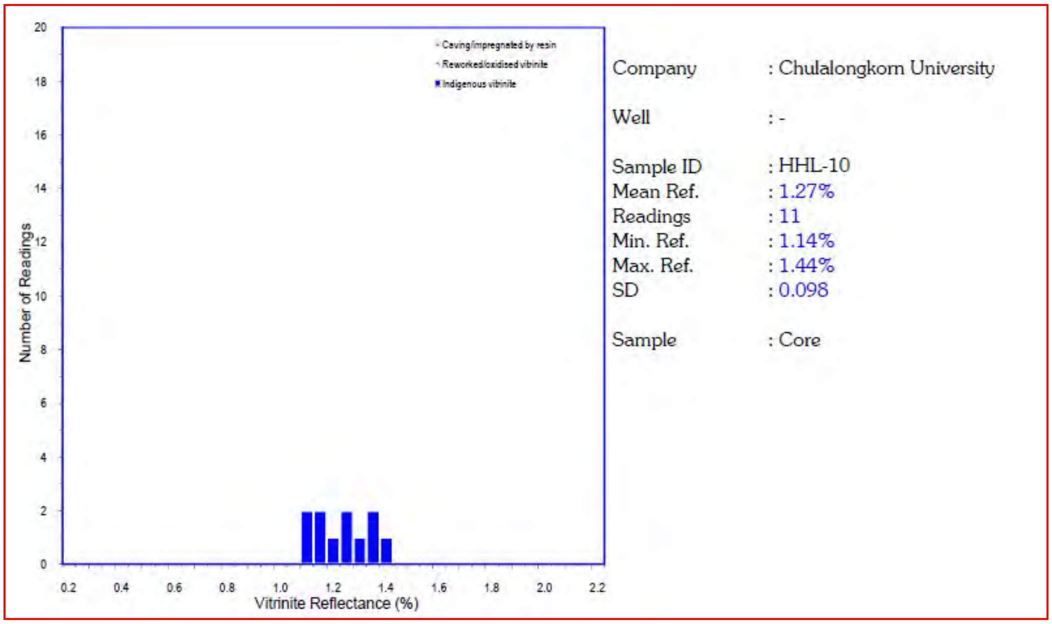
Sample Type : Core

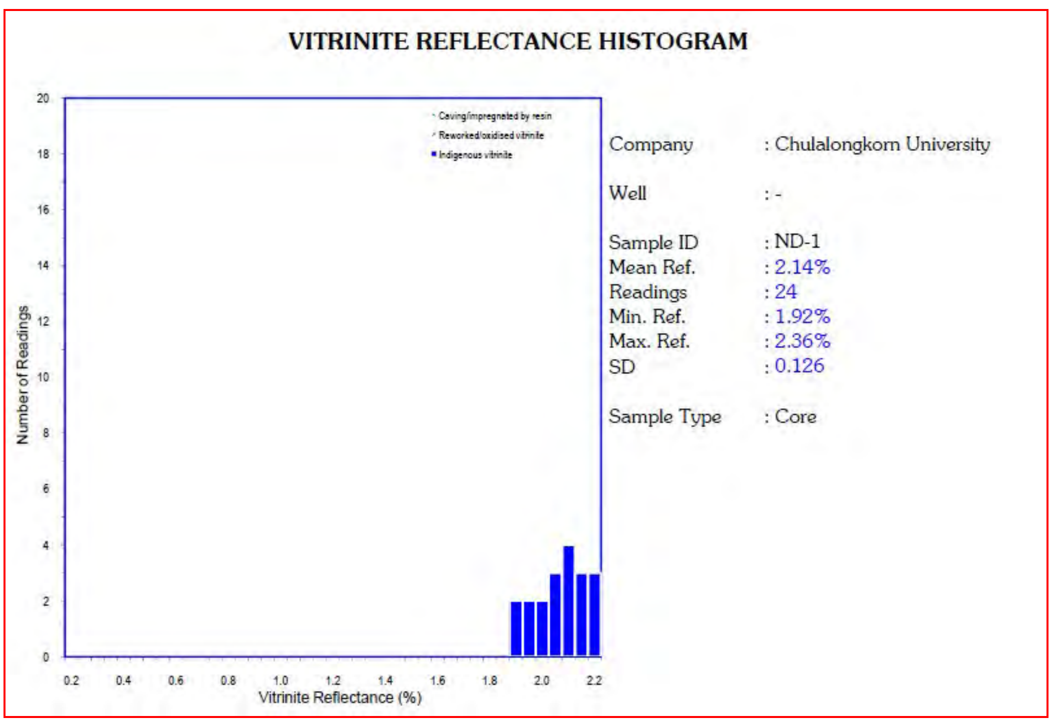
Analyzed at Core Laboratories (Core Lab) in Indonesia.



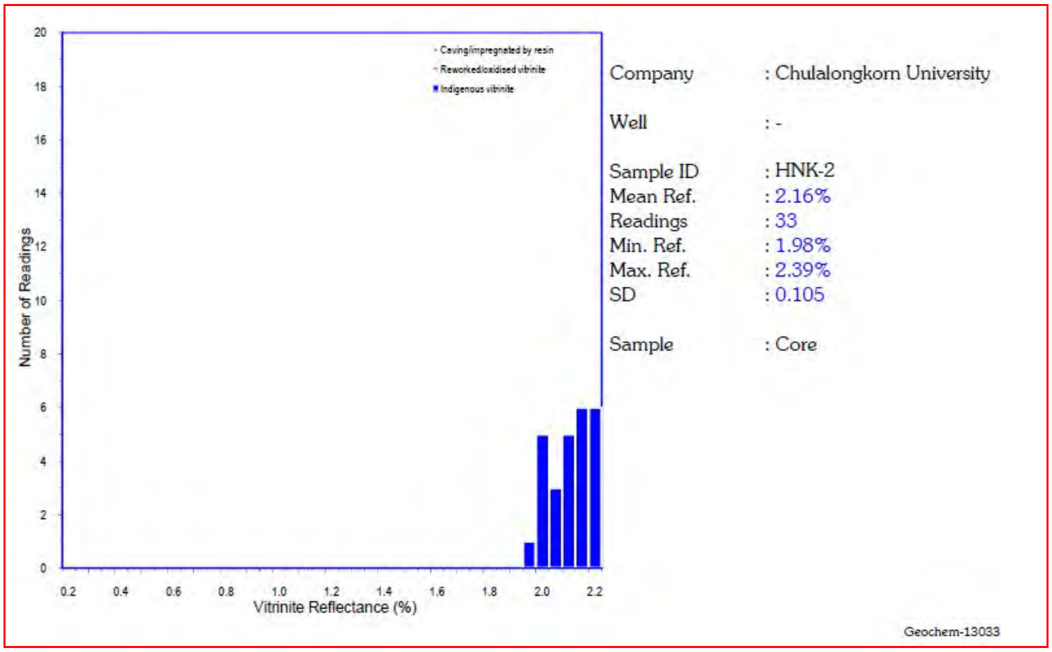


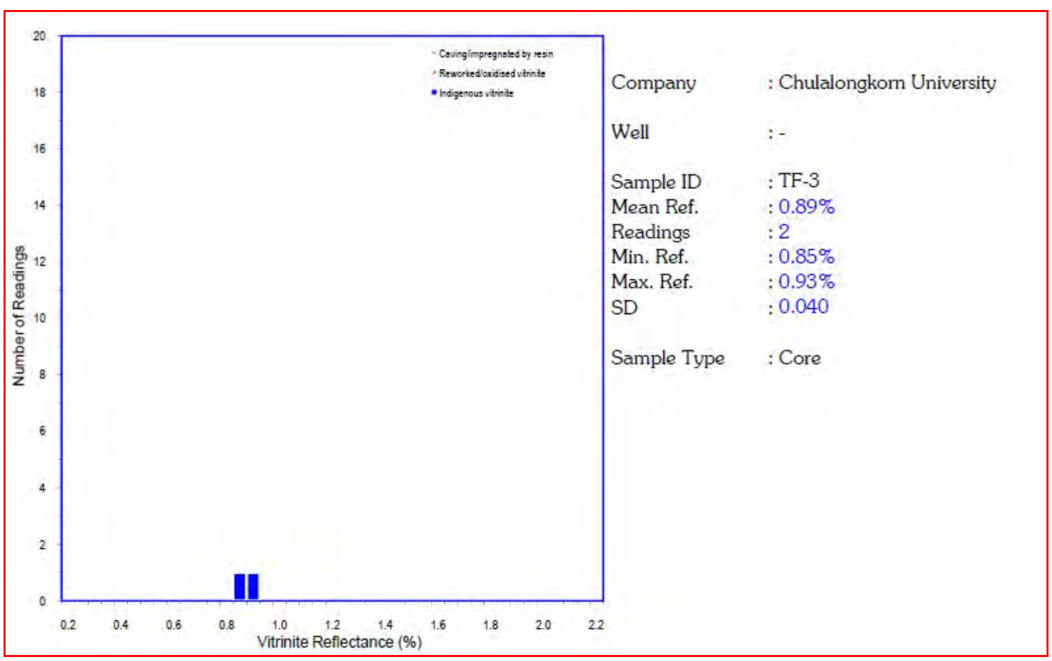
Analyzed at Core Laboratories (Core Lab) in Indonesia.





Analyzed at Core Laboratories (Core Lab) in Indonesia.



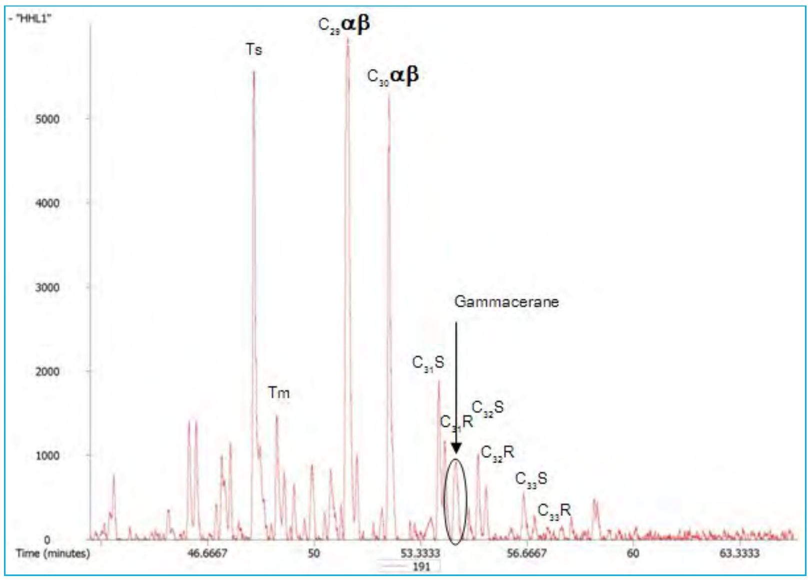


APPENDIX B

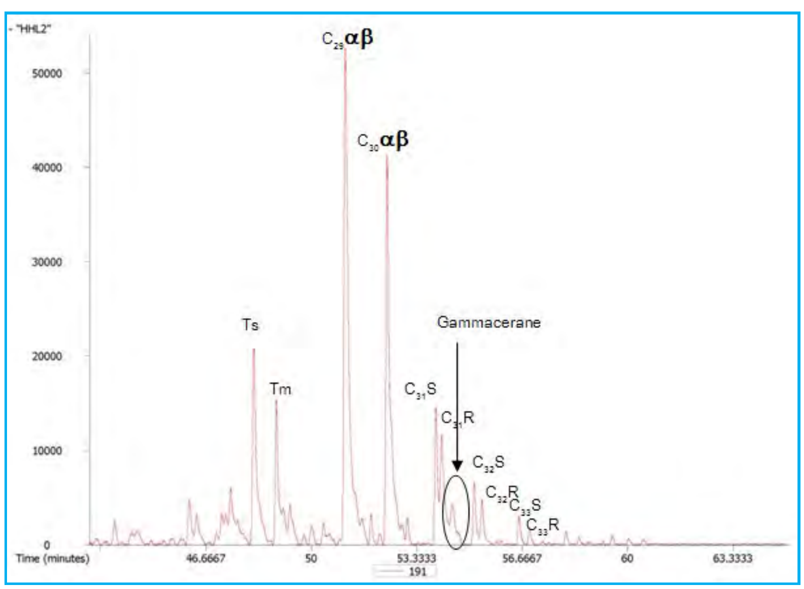
GC-MS fragmentograms

Mass fragmentograms (m/z 191) of Huai Hin Lat Formation and Saraburi Group showing relative distribution of Ts, Tm, C_{29} αβ norhopane, C_{30} αβ hopane, 22S and 22R C_{31}- C_{33}homohopanes and gammacerane.

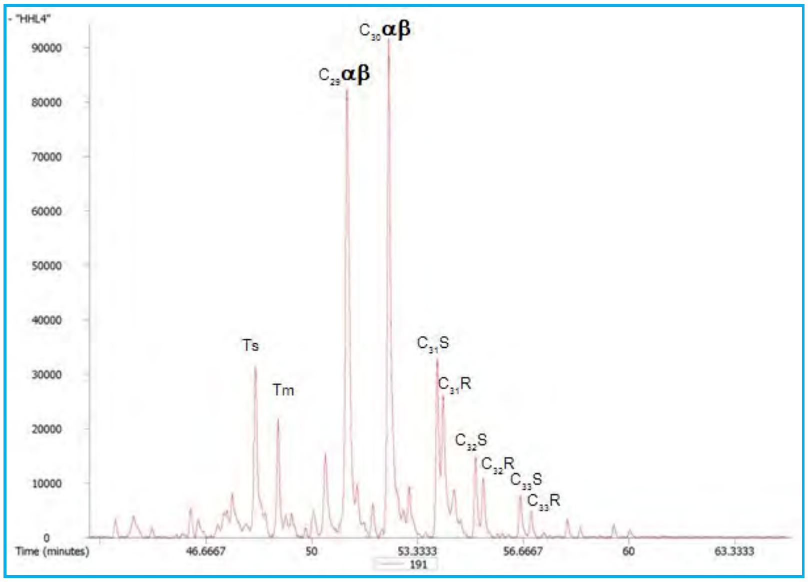
HHL 1: C_{31} [22S/(22S+22R)] = 0.11, Ts/(Ts+Tm) = 0.84



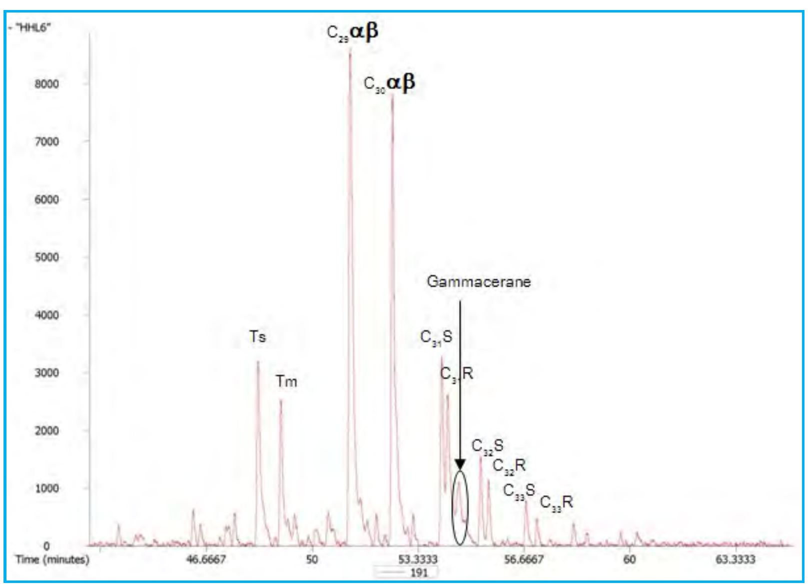
HHL2: C_{31} [22S/(22S+22R)] = 0.72, Ts/(Ts+Tm) = 0.66



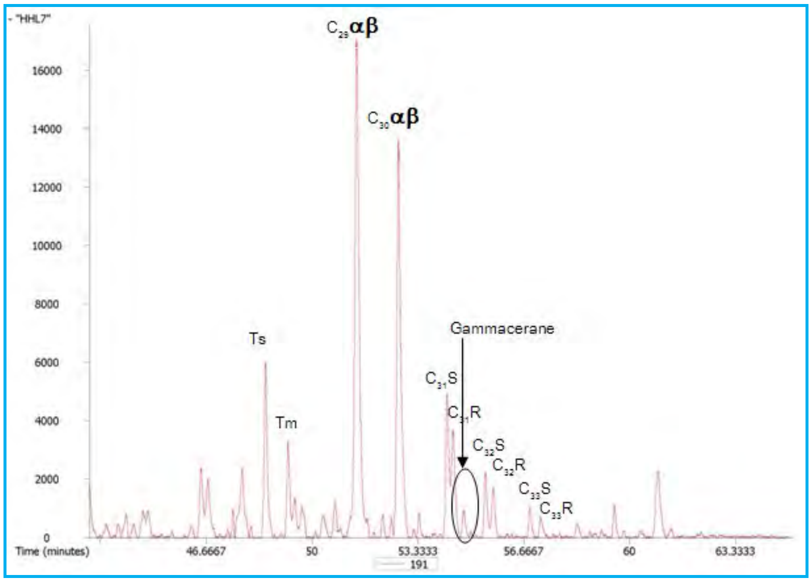
HHL 4: C_{31} [22S/(22S+22R)] = 0.56, Ts/(Ts+Tm) = 0.64



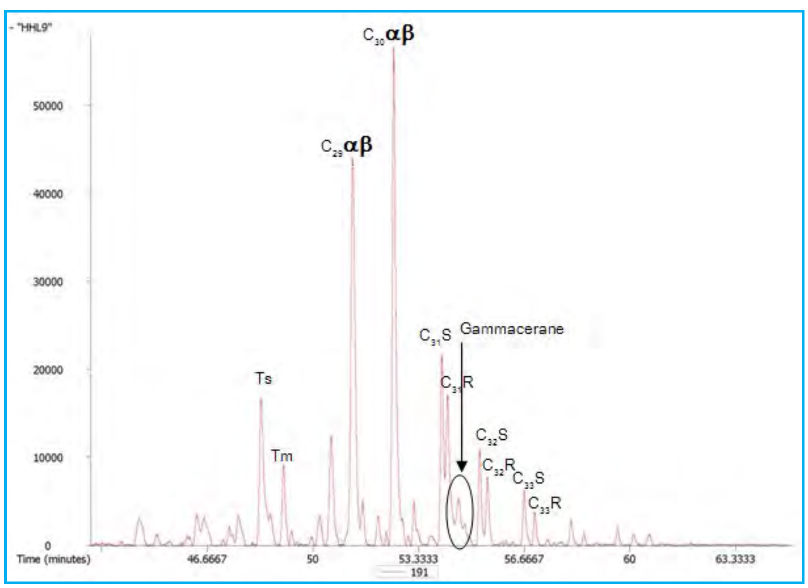
HHL 6: C_{31} [22S/(22S+22R)] = 0.51, Ts/(Ts+Tm) = 0.62



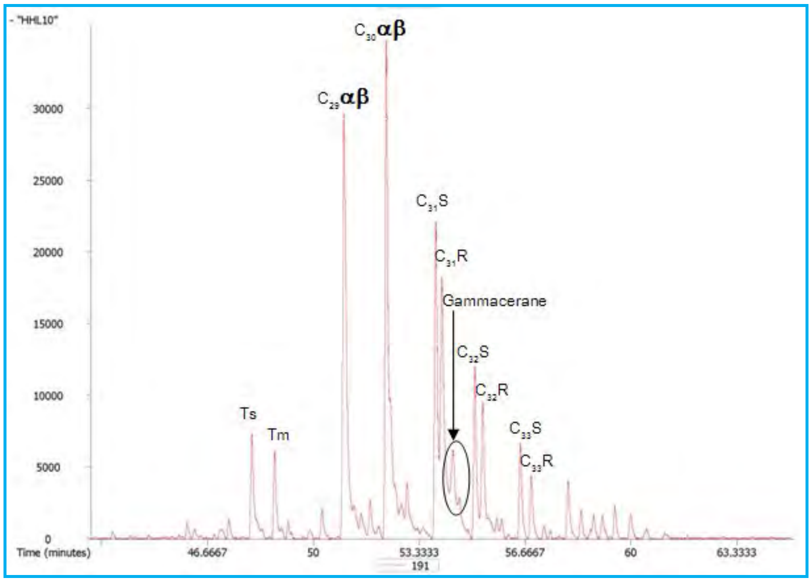
HHL 7: C_{31} [22S/(22S+22R)] = 0.52, Ts/(Ts+Tm) = 0.94



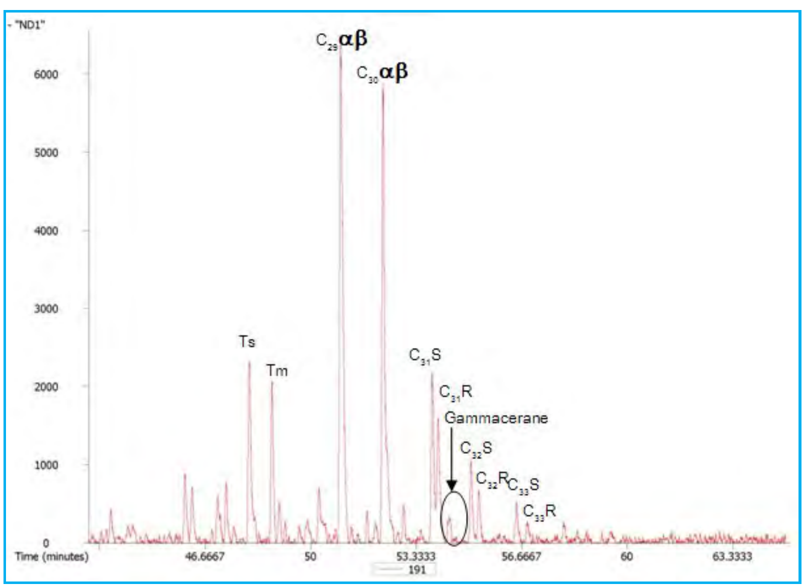
HHL 9: C_{31} [22S/(22S+22R)] = 0.55, Ts/(Ts+Tm) = 0.72



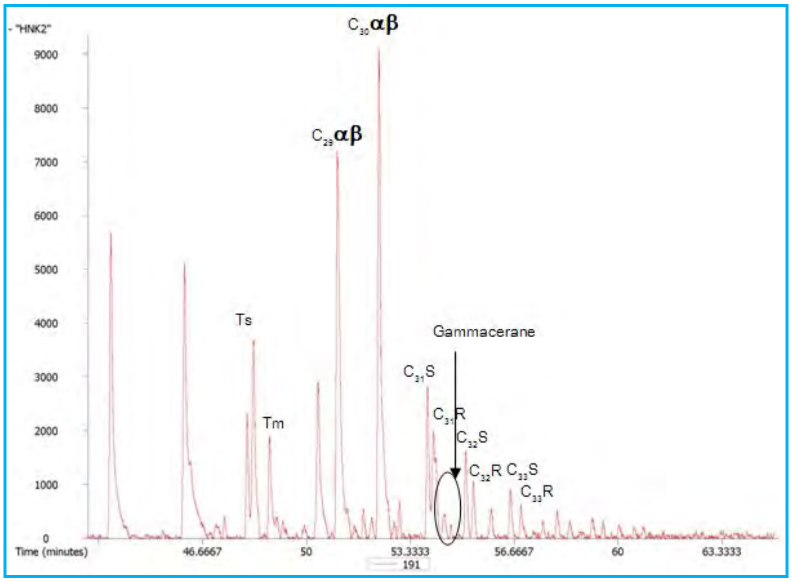
HHL 10: C_{31} [22S/(22S+22R)] = 0.39, Ts/(Ts+Tm) = 0.56



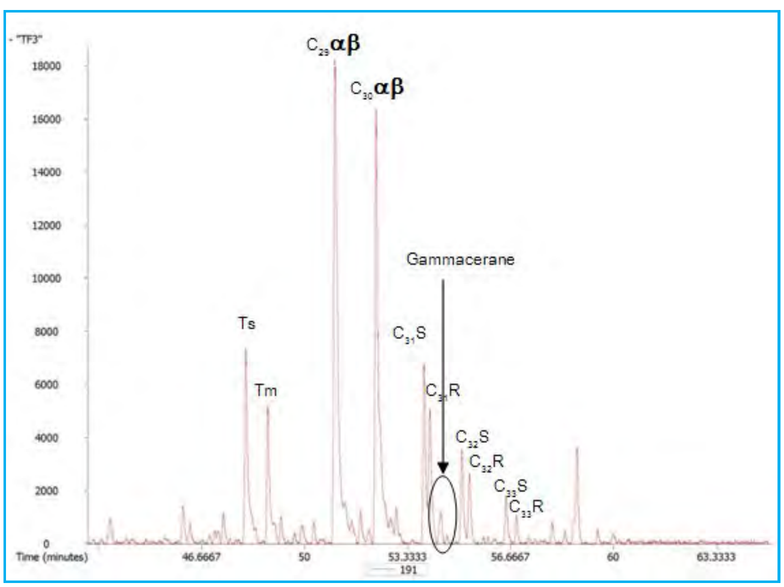
ND 1: C_{31} [22S/(22S+22R)] = 0.34, Ts/(Ts+Tm) = 0.58



HNK 2: C_{31} [22S/(22S+22R)] = 0.61, Ts/(Ts+Tm) = 0.83

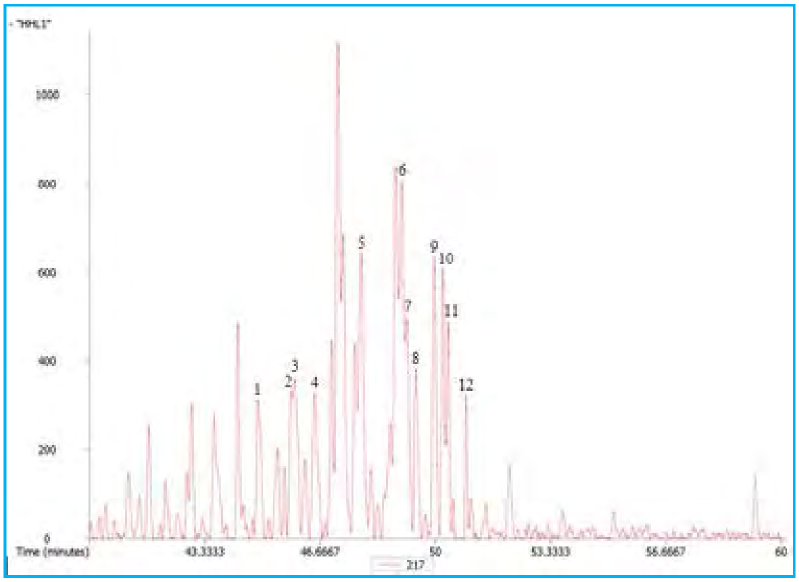


TF 3: C_{31} [22S/(22S+22R)] = 0.48, Ts/(Ts+Tm) = 0.72

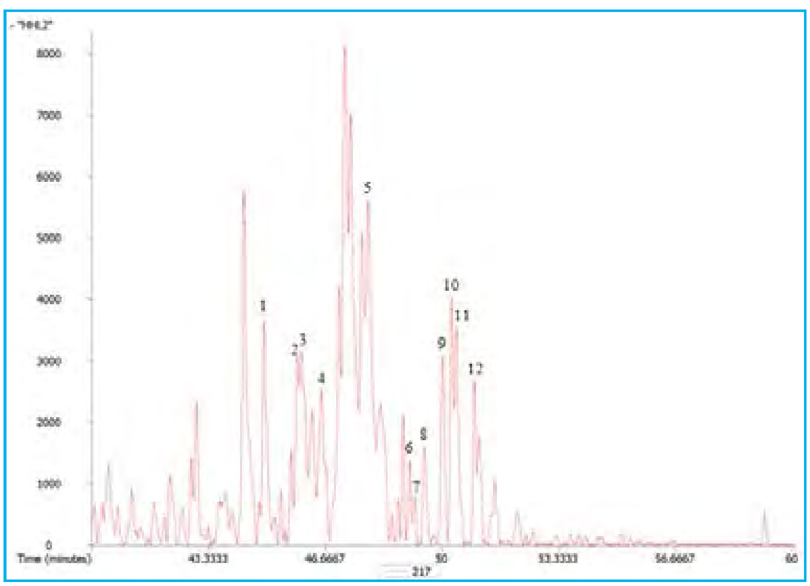


Mass fragmentograms (m/z 217) of Huai Hin Lat Formation and Saraburi Group showing relative distribution of C_{27}-C_{29} regular steranes.

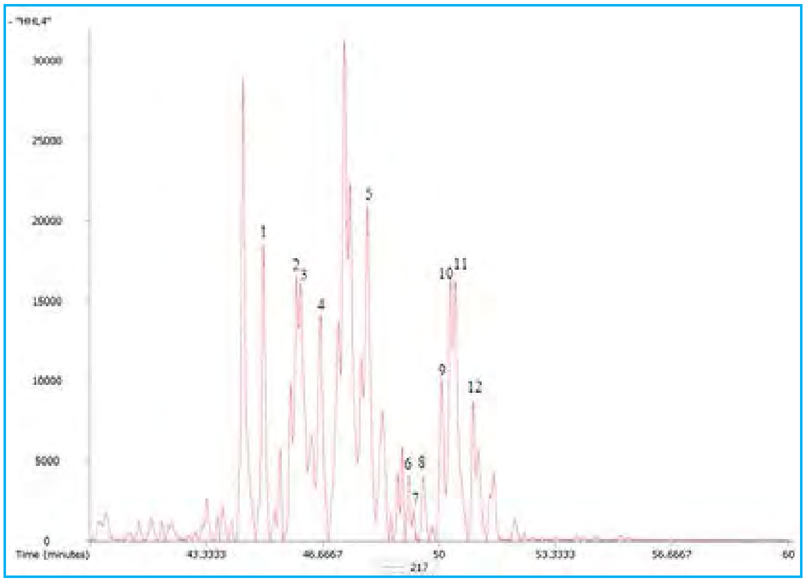
HHL 1: %$C_{27}\alpha\alpha\alpha R$ = 34.49%, %$C_{28}\alpha\alpha\alpha R$ = 21.08%, %$C_{29}\alpha\alpha\alpha R$ = 44.43%



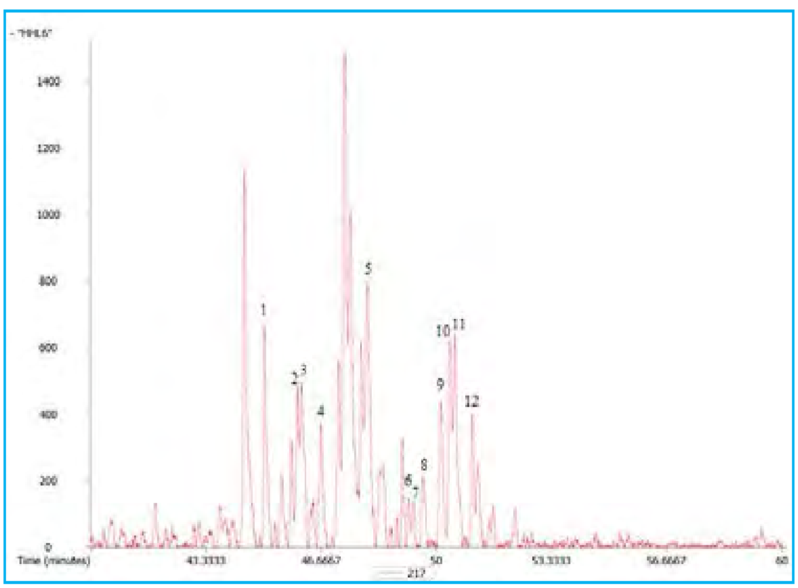
HHL2: %$C_{27}\alpha\alpha\alpha R$ = 26.92%, %$C_{28}\alpha\alpha\alpha R$ = 22.74%, %$C_{29}\alpha\alpha\alpha R$ = 50.33%



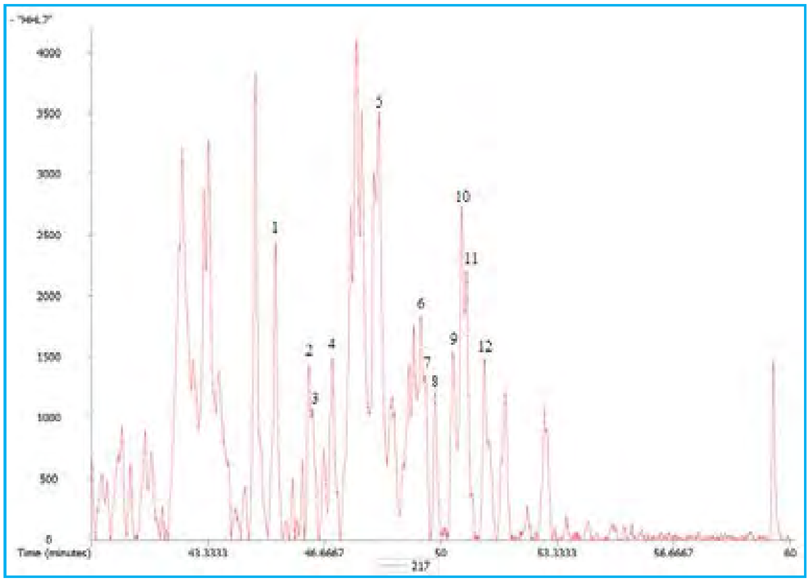
HHL 4: %$C_{27}\alpha\alpha\alpha R$ = 12.01%, %$C_{28}\alpha\alpha\alpha R$ = 30.14%, %$C_{29}\alpha\alpha\alpha R$ = 57.84%



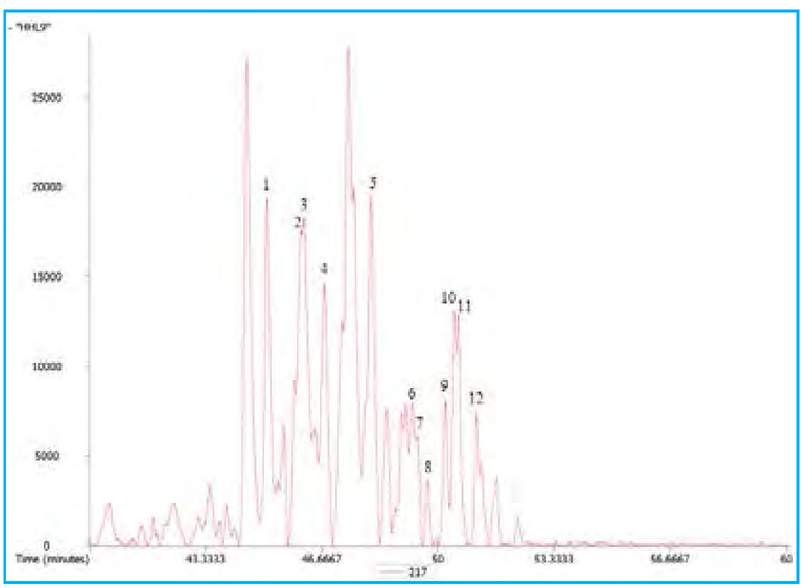
HHL 6: %$C_{27}\alpha\alpha\alpha R$ = 29.03%, %$C_{28}\alpha\alpha\alpha R$ = 47.56%, %$C_{29}\alpha\alpha\alpha R$ = 23.41%



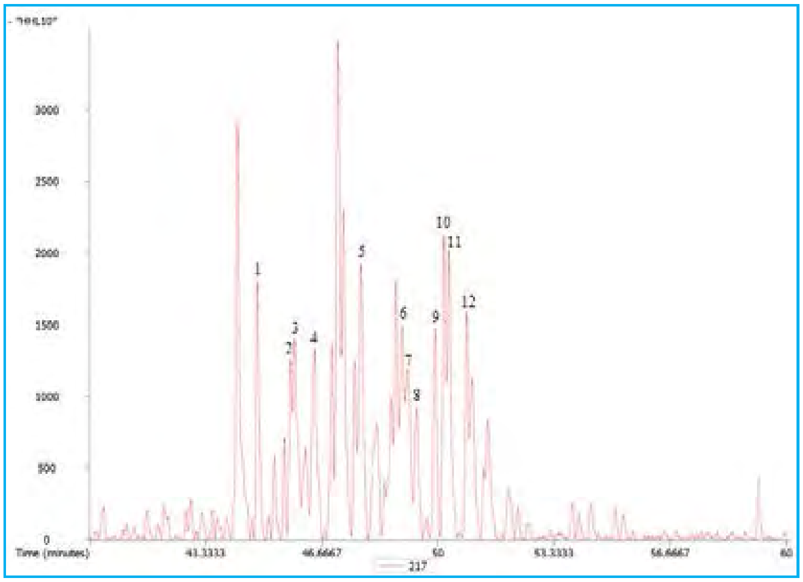
HHL 7: %$C_{27}\alpha\alpha\alpha R$ = 42.11%, %$C_{28}\alpha\alpha\alpha R$ = 34.98%, %$C_{29}\alpha\alpha\alpha R$ = 22.91%



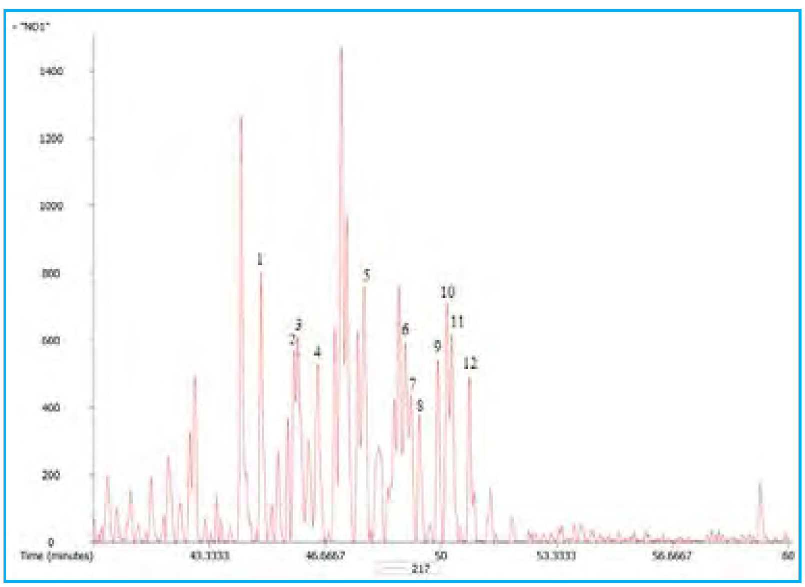
HHL 9: %$C_{27}\alpha\alpha\alpha R$ = 19.82%, %$C_{28}\alpha\alpha\alpha R$ = 20.99%, %$C_{29}\alpha\alpha\alpha R$ = 59.19%



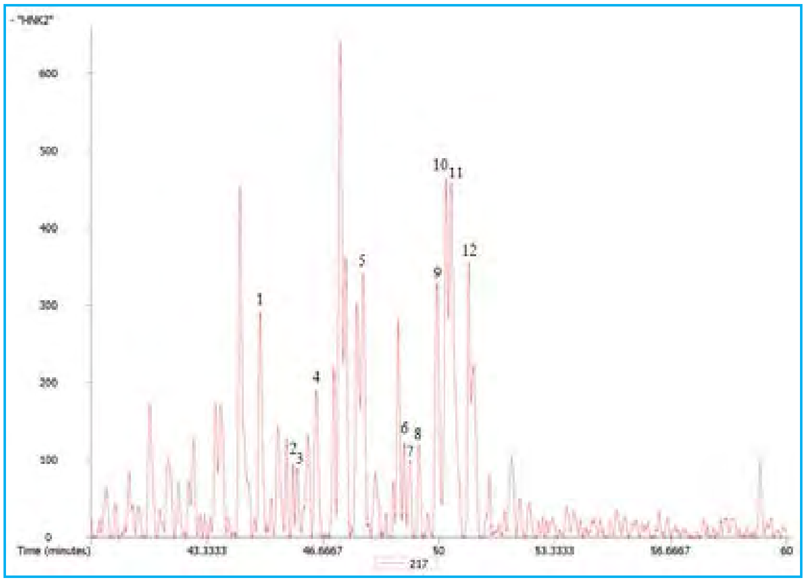
HHL 10: %$C_{27}\alpha\alpha\alpha R$ = 33.86%, %$C_{28}\alpha\alpha\alpha R$ = 23.76%, %$C_{29}\alpha\alpha\alpha R$ = 42.37%



ND 1: %$C_{27}\alpha\alpha\alpha R$ = 17.23%, %$C_{28}\alpha\alpha\alpha R$ = 55.02%, %$C_{29}\alpha\alpha\alpha R$ = 27.75%



HNK 2: %C_{27}αααR = 25.06%, %C_{28}αααR = 48.11%, %C_{29}αααR = 26.77%



TF 3: %C_{27}αααR = 34.66%, %C_{28}αααR = 38.84%, %C_{29}αααR = 26.50%

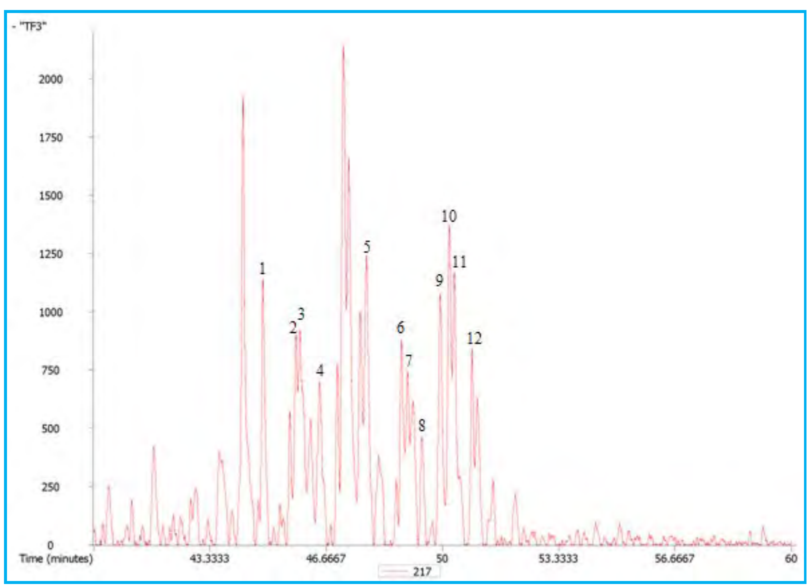


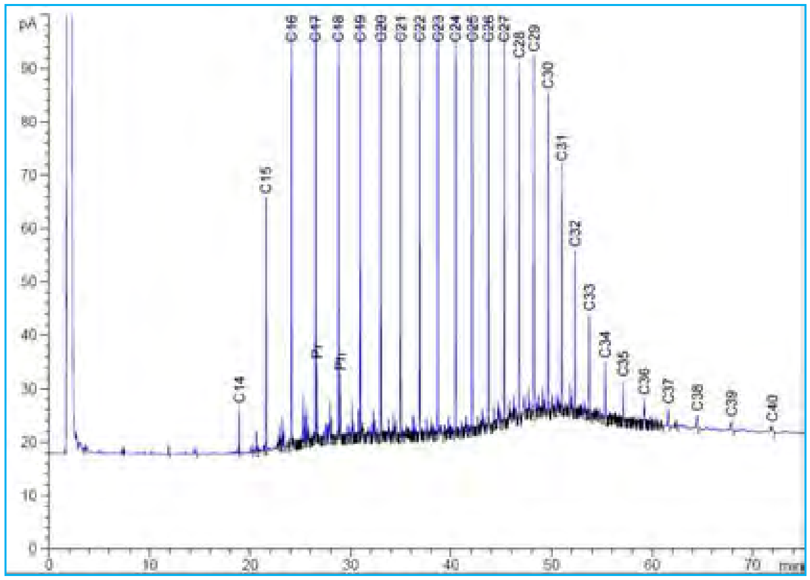
Table show identified peak in list of mass fragmentograms (m/z 217) of C_{27}-C_{29} regular steranes.

Peak	Identification	Carbon number
1	5α, 14α, 17α(H)-Cholestane 20S	27
2	5α, 14β, 17β(H)-Cholestane 20R	27
3	5α, 14β, 17β(H)-Cholestane 20S	27
4	5α, 14α, 17α(H)-Cholestane 20R	27
5	5α, 14α, 17α(H)-Ergostane 20S	28
6	5α, 14β, 17β(H)- Ergostane 20R	28
7	5α, 14β, 17β(H)- Ergostane 20S	28
8	5α, 14α, 17α(H)- Ergostane 20R	28
9	5α, 14α, 17α(H)-Stigmastane 20S	29
10	5α, 14β, 17β(H)- Stigmastane 20R	29
11	5α, 14β, 17β(H)- Stigmastane 20S	29
12	5α, 14α, 17α(H)- Stigmastane 20R	29

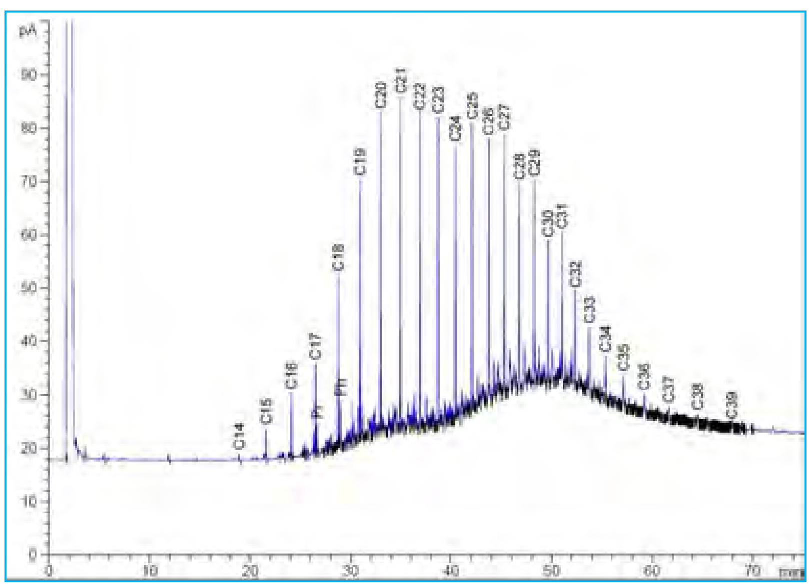
APPENDIX C

Total ion chromatograms (TIC) from GC

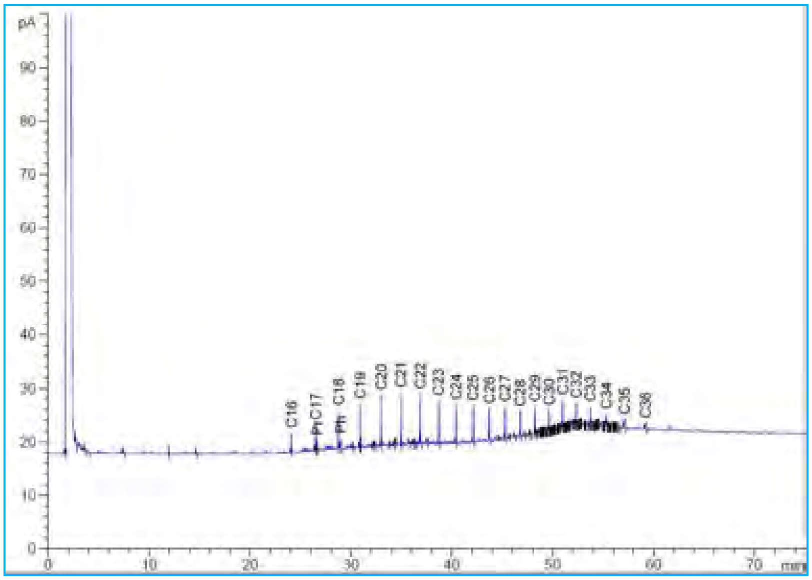
HHL 1: Pr/Ph = 0.96, Pr/nC_{17} = 0.24, Ph/nC_{18} = 0.23, CPI = 1.00



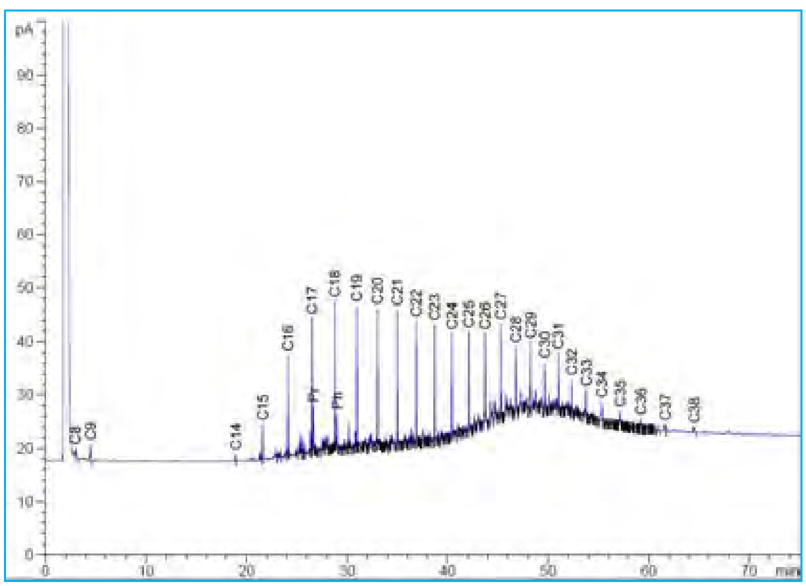
HHL 2: Pr/Ph = 0.50, Pr/nC_{17} = 0.50, Ph/nC_{18} = 0.51, CPI = 1.00



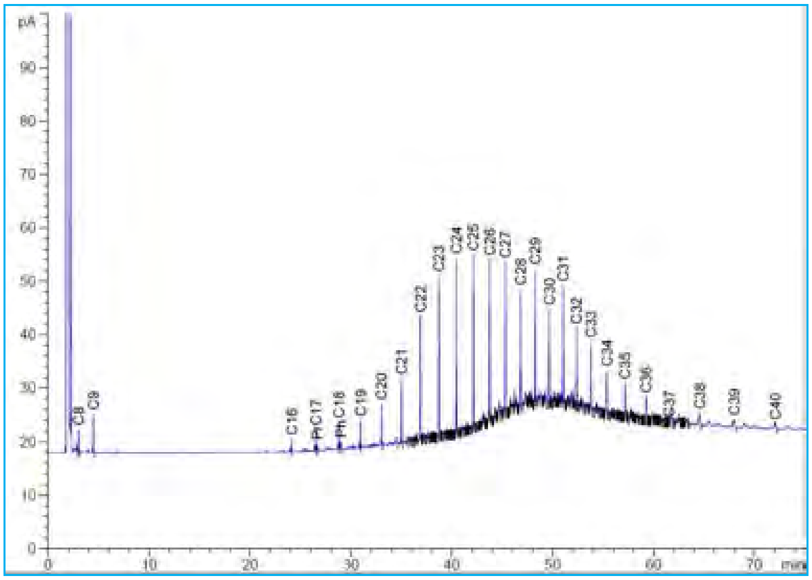
HHL 3: Pr/Ph = 0.80, Pr/nC_{17} = 0.60, Ph/nC_{18} = 0.52, CPI = 1.07



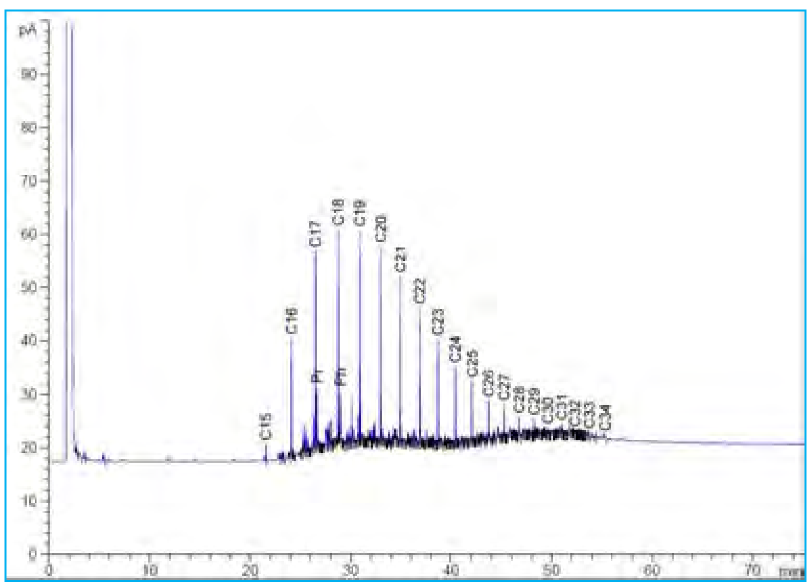
HHL 4: Pr/Ph = 1.02, Pr/nC_{17} = 0.53, Ph/nC_{18} = 0.46, CPI = 1.09



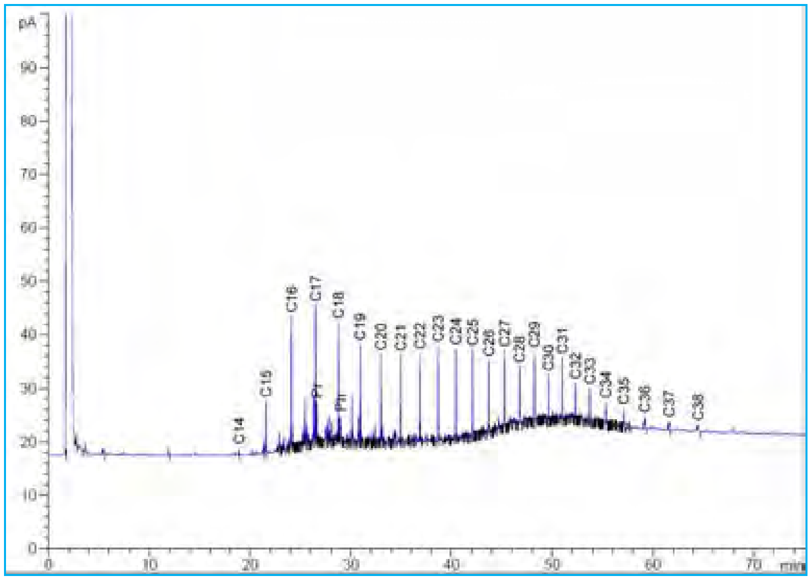
HHL 5: Pr/Ph = 0.77, Pr/nC$_{17}$ = 0.45, Ph/nC$_{18}$ = 0.43, CPI = 1.06



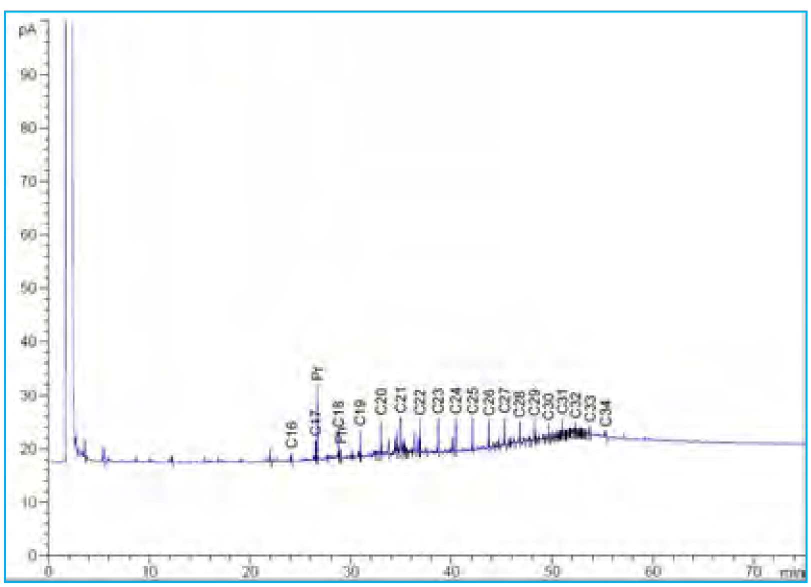
HHL 6: Pr/Ph = 0.90, Pr/nC$_{17}$ = 0.49, Ph/nC$_{18}$ = 0.48, CPI = 1.05



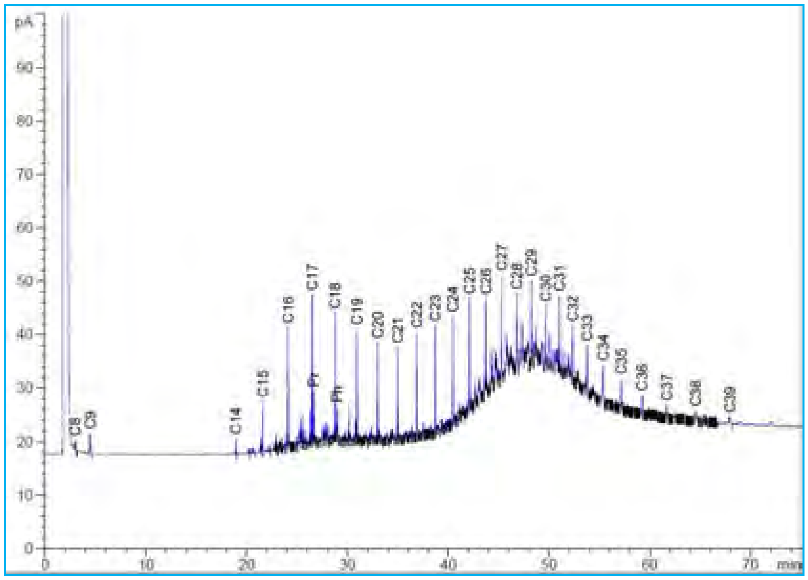
HHL 7: Pr/Ph = 1.23, Pr/nC_{17} = 0.49, Ph/nC_{18} = 0.45, CPI = 1.13



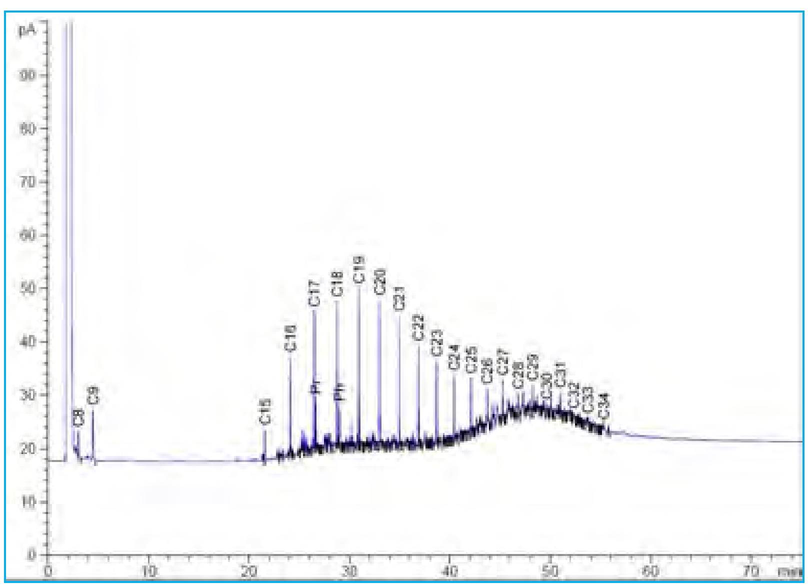
HHL 8: Pr/Ph = 5.07, Pr/nC_{17} = 4.18, Ph/nC_{18} = 0.58, CPI = 0.97



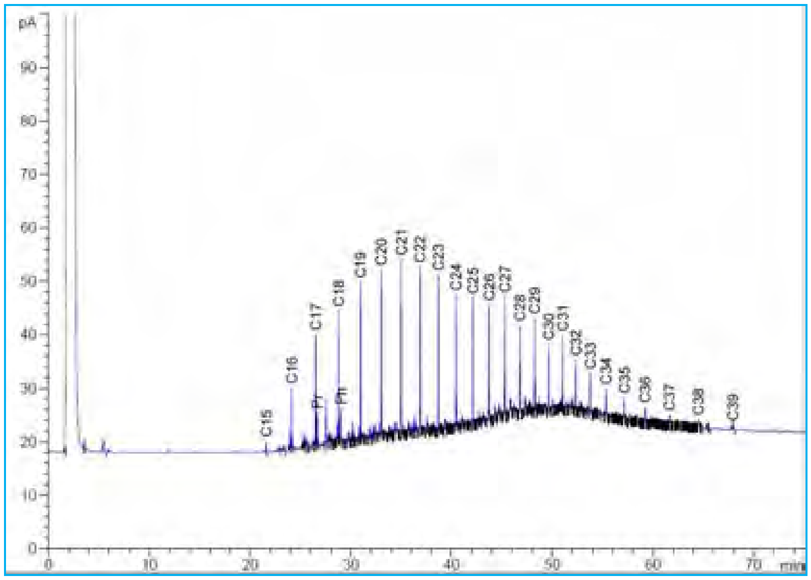
HHL 9: Pr/Ph = 1.18, Pr/nC_{17} = 0.55, Ph/nC_{18} = 0.50, CPI = 1.04



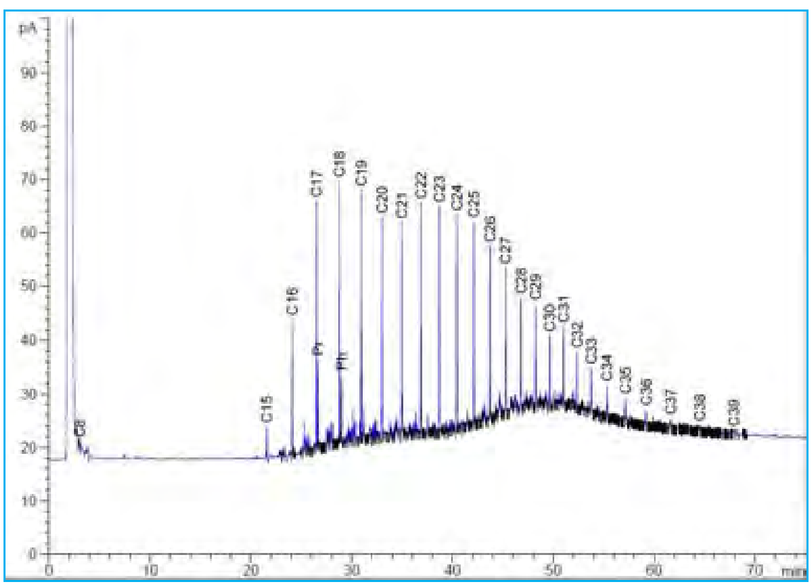
HHL 10: Pr/Ph = 1.04, Pr/nC_{17} = 0.57, Ph/nC_{18} = 0.49, CPI = 0.92



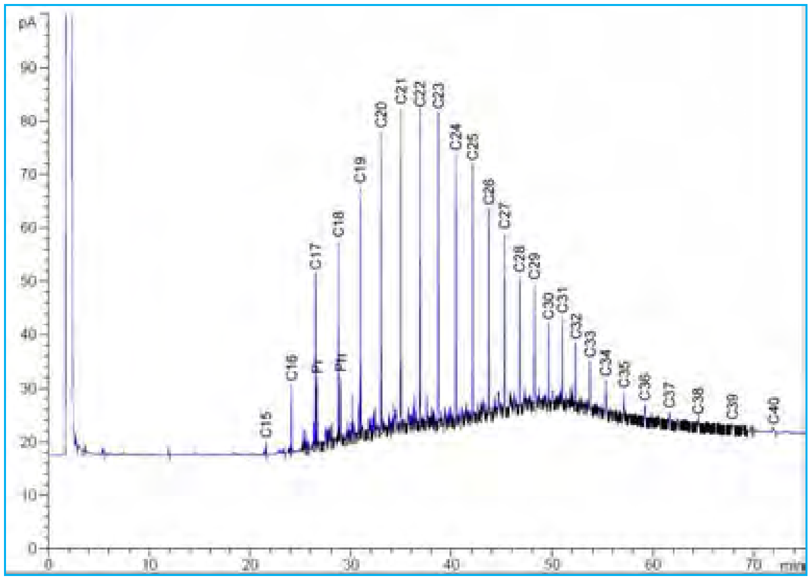
HHL 11: Pr/Ph = 0.78, Pr/nC$_{17}$ = 0.48, Ph/nC$_{18}$ = 0.48, CPI = 1.00



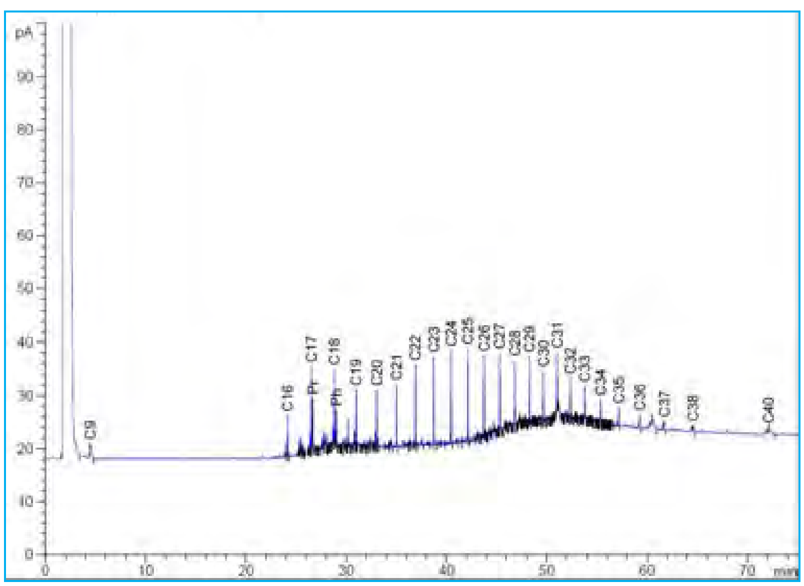
ND 1: Pr/Ph = 0.96, Pr/nC$_{17}$ = 0.55, Ph/nC$_{18}$ = 0.49, CPI = 1.13



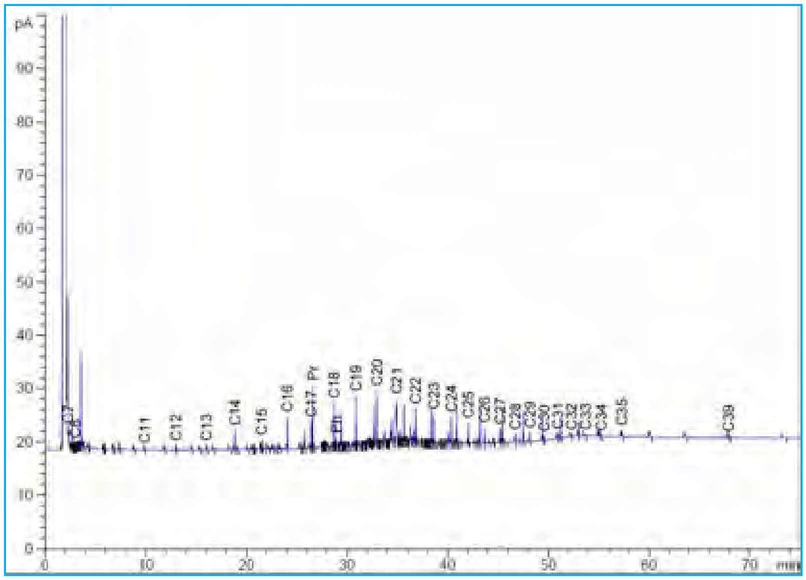
ND 2: Pr/Ph = 0.82, Pr/nC_{17} = 0.58, Ph/nC_{18} = 0.57, CPI = 1.15



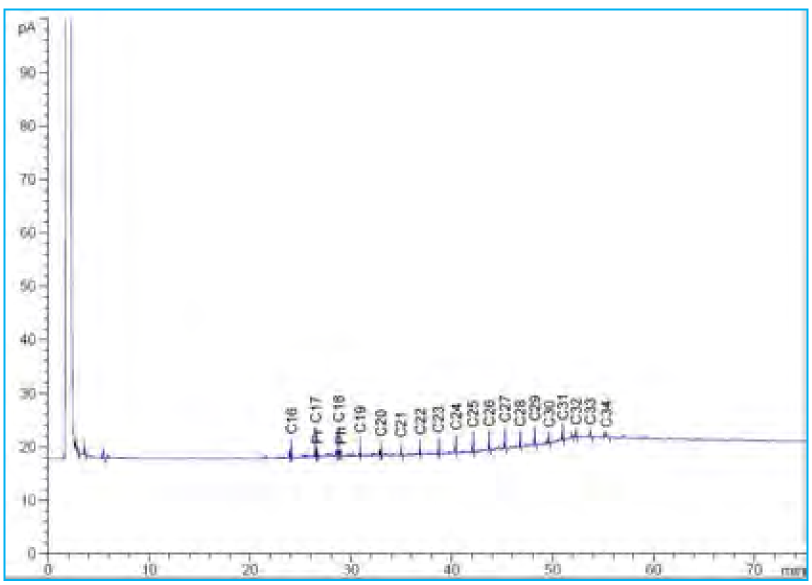
HNK 1: Pr/Ph = 1.05, Pr/nC_{17} = 0.85, Ph/nC_{18} = 0.81, CPI = 1.12



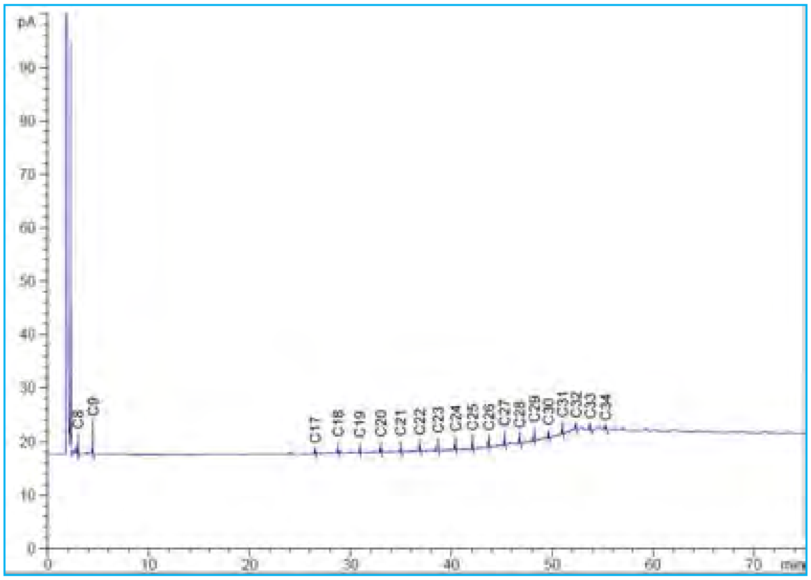
HNK 2: Pr/Ph = 4.54, Pr/nC_{17} = 2.64, Ph/nC_{18} = 0.33, CPI = 1.10



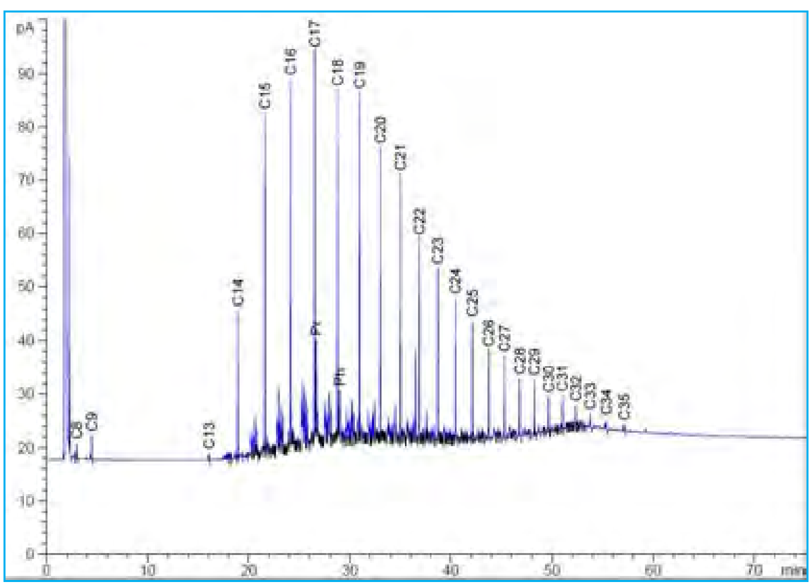
TF1: Pr/Ph = 1.21, Pr/nC_{17} = 0.46, Ph/nC_{18} = 0.39, CPI = 1.12



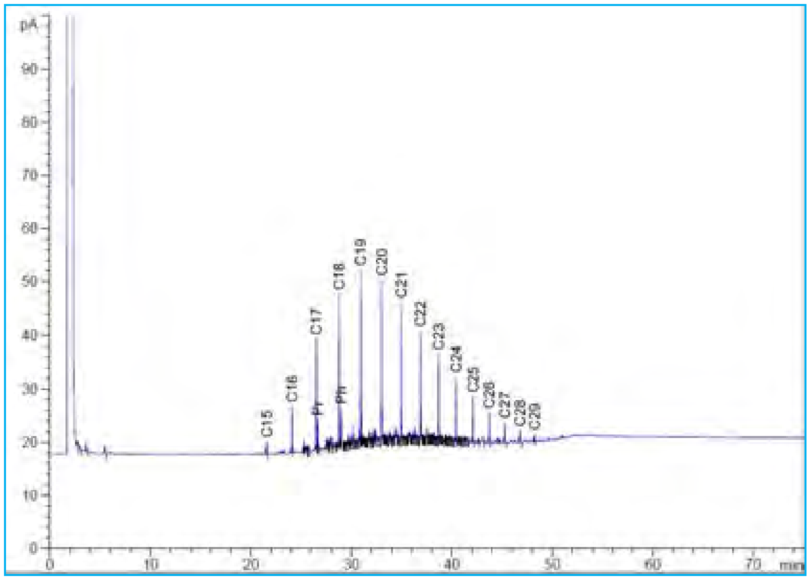
TF 2: Pr/Ph = 1.53, Pr/nC_{17} = 1.04, Ph/nC_{18} = 0.37, CPI = 1.15



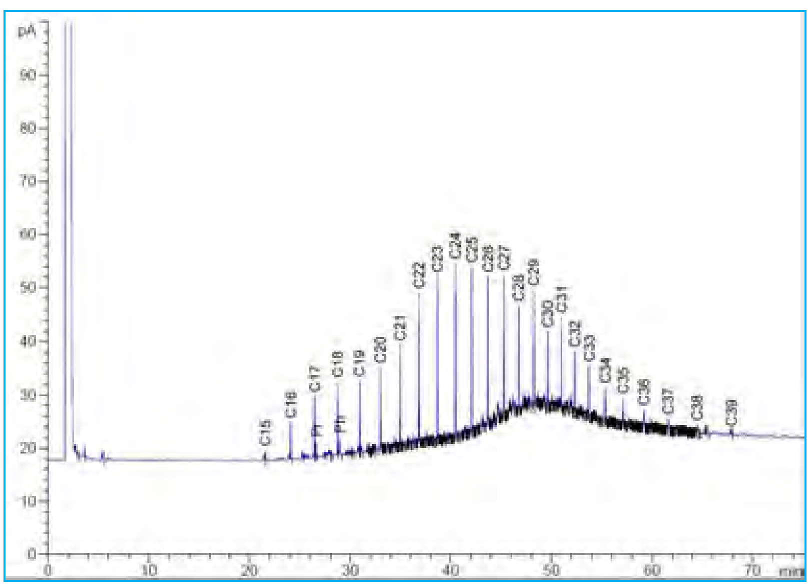
TF 3: Pr/Ph = 1.41, Pr/nC_{17} = 0.43, Ph/nC_{18} = 0.33, CPI = 1.06



NML: Pr/Ph = 0.58, Pr/nC_{17} = 0.42, Ph/nC_{18} = 0.48, CPI = 1.20



SB: Pr/Ph = 0.65, Pr/nC_{17} = 0.36, Ph/nC_{18} = 0.44, CPI = 1.02



BIOGRAPHY

Miss Wilairat Khositchaisri was born in Bangkok in 1982. She studied at Satri Si Suriyothai School in Bangkok from 1993-1999. She graduated in Bachelor Degree of Science of Chemistry from King Mongkut's University of Technology Thonburi in 2004. After graduation, she worked for Double A (1991) Plc. in 2005-2009. She has been studied in Master Degree of Science in Earth sciences at Chulalongkorn University since 2009.