ธรณีเคมีของหินที่มีศักยภาพเป็นต้นกำเนิดปิโตรเลียมในหมวดหินตากฟ้า จังหวัดเพชรบูรณ์

นายศุภวิชญ์ เฟื่องฟู

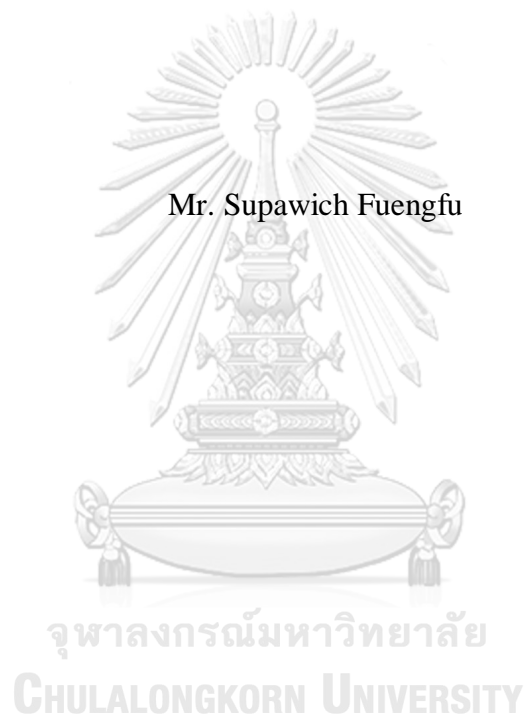วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาโลกศาสตร์ ภาควิชาธรณีวิทยา
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
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GEOCHEMISTRY OF PETROLEUM POTENTIAL SOURCE ROCK IN
TAK FA FORMATION, PHETCHABUN PROVINCE

Mr. Supawich Fuengfu

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

A Thesis Submitted in Partial Fulfillment of the Requirements
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By   Mr. Supawich Fuengfu

Field of Study   Earth Sciences

Thesis Advisor   Piyaphong Chenrai, Ph.D.

Thesis Co-Advisor   Assistant Professor Piyada Jittangprasert, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.... Dean of the Faculty of Science
(Professor Polkit Sangvanich, Ph.D.)

THESIS COMMITTEE

.... Chairman
(Associate Professor Srilert Chotpantarat, Ph.D.)

.... Thesis Advisor
(Piyaphong Chenrai, Ph.D.)

.... Thesis Co-Advisor
(Assistant Professor Piyada Jittangprasert, Ph.D.)

.... Examiner
(Akkaneewut Chabangborn, Ph.D.)

.... External Examiner
(Tawatchai Chualaowanich, Ph.D.)

ศุภวิชญ์ เฟื่องฟู : ธรณีเคมีของหินที่มีศักยภาพเป็นต้นกำเนิดปิโตรเลียมในหมวดหินตากฟ้า จังหวัด
เพชรบูรณ์ (GEOCHEMISTRY OF PETROLEUM POTENTIAL SOURCE ROCK IN TAK
FA FORMATION, PHETCHABUN PROVINCE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร. ปิยพงษ์ เชน
ร้าย, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร. ปิยะดา จิตรตั้งประเสริฐ, หน้า.

การสำรวจปิโตรเลียมบริเวณที่ราบสูงโคราชเริ่มมีมาตั้งแต่ปี พ.ศ.2505 จนกระทั่งถึงปัจจุบัน โดยพบ
ก๊าซธรรมชาติและก๊าซธรรมชาติเหลวสะสมตัวอยู่ในชั้นหินกักเก็บในหมวดหินผานกเค้า ซึ่งเป็นหินปูนยุคเพอร์
เมียน ตั้งอยู่บริเวณแหล่งน้ำพองและสินภูฮ่อมในปัจจุบัน คาดว่ากลุ่มหินสระบุรี ในช่วงปลายยุคคาร์บอนิเฟอรัส
ถึงยุคเพอร์เมียนเป็นหินต้นกำเนิดปิโตรเลียมของแหล่งเหล่านี้ในงานวิจัยนี้ได้ทำการวิเคราะห์ศักยภาพของหินต้น
กำเนิดปิโตรเลียมในหมวดหินตากฟ้า กลุ่มหินสระบุรี ในลานหินปูนเขาขวาง ซึ่งเป็นหินตะกอนช่วงกลางยุคเพอร์
เมียน ในจังหวัดเพชรบูรณ์ โดยทำการเก็บตัวอย่างหินโผล่ทั้งหมด 9 ตัวอย่าง จาก 3 จุดศึกษาได้แก่อำเภอบึงสาม
พัน อำเภอชนแดน และอำเภอหนองไผ่ และใช้วิธีทางธรณีเคมีปิโตรเลียม ในการประเมินศักยภาพของหินต้น
กำเนิด ได้แก่ 1) ประเมินปริมาณของสารอินทรีย์ในหินตะกอนหรือเคอโรเจน (Kerogen) ด้วยวิธีการวิเคราะห์
ปริมาณสารอินทรีย์ทั้งหมด (TOC) และการวิเคราะห์ปริมาณบิทูเมน (Bitumen หรือ EOM) 2) วิเคราะห์คุณภาพ
ของสารอินทรีย์ 3) ประเมินความพร้อมในการให้ปิโตรเลียม และ 4) บ่งบอกสภาพแวดล้อมการสะสมตัวของหิน
ต้นกำเนิดปิโตรเลียมโดยการใช้ข้อมูลตัวบ่งชี้ทางชีวภาพ (Biomarker) จากการวิจัยพบว่าหินตัวอย่างมีปริมาณ
ของเคอโรเจนค่อนข้างสูง คือมากกว่า 2.0 wt. % ในหินปูน และมากกว่า 1.0 wt. % ในหินดินดาน อย่างไรก็ตาม
ปริมาณบิทูเมนน้อยกว่า 500 ppm จึงถูกจัดว่าไม่มีศักยภาพในการเป็นหินต้นกำเนิดปิโตรเลียม จากค่าการเผาไหม้
สูงสุดของเคอโรเจน (Tmax) รวมถึงผลการทดสอบตัวบ่งชี้ชีวภาพ Moretane/(Hopane+Moretane)
Ts/(Ts+Tm) และอัตราส่วน C_{31} 22S/(22S+22R สนับสนุนว่าหินต้นกำเนิดมีการให้ปิโตรเลียมอยู่ในระดับตอน
ปลาย (late mature) ถึงระดับเกินกว่าจะให้ปิโตรเลียม (over mature) จากการวิเคราะห์ชนิดของเคอโรเจนโดย
การใช้ข้อมูล Pr/n-C_{17} และ Ph/n-C_{18} ซึ่งเป็นข้อมูลเชิงคุณภาพ บ่งชี้ว่าสารอินทรีย์เป็นเคอโรเจนชนิดที่ II และ
III โดยมีแหล่งที่มาจากทั้งบนบกและในทะเล ส่วนข้อมูลของลิพิดกลุ่มสเตียเรนทั่วไป (regular steranes) ที่ C_{27},
C_{28}, C_{29} บ่งชี้ว่าสารอินทรีย์สะสมตัวในสภาพแวดล้อมแบบชวากทะเล (estuarine) และสะสมตัวภายใต้สภาวะ
ไร้ออกซิเจน จนถึงมีออกซิเจนปานกลาง ซึ่งโดยรวมสามารถอธิบายได้ว่าหมวดหินตากฟ้าจากพื้นที่ศึกษามีการ
สะสมตัวของตะกอนในสภาพแวดล้อมแบบหลังแนวปะการัง และจากการศึกษาหินโผล่สรุปว่าสารอินทรีย์ภายใน
ไม่มีศักยภาพในการให้กำเนิดปิโตรเลียม ทั้งนี้ปัจจัยจากการกระทำจากสภาพแวดล้อมทั้งการกัดกร่อนทาง
กายภาพและเคมีที่กระทำกับหินโผล่ ส่งผลให้ปริมาณของไฮโดรเจน (Hydrogen index หรือ HI) และออกซิเจน
(Oxygen index หรือ OI) ในเคอโรเจนมีค่าต่ำอย่างเห็นได้ชัด

ภาควิชา	ธรณีวิทยา	ลายมือชื่อนิสิต	
สาขาวิชา	โลกศาสตร์	ลายมือชื่อ อ.ที่ปรึกษาหลัก	
ปีการศึกษา	2560	ลายมือชื่อ อ.ที่ปรึกษาร่วม	

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KEYWORDS: TAK FA FORMATION / PETROLEUM SOURCE ROCK / PETROLEUM GEOCHEMISTRY / SARABURI GROUP

SUPAWICH FUENGFU: GEOCHEMISTRY OF PETROLEUM POTENTIAL SOURCE ROCK IN TAK FA FORMATION, PHETCHABUN PROVINCE. ADVISOR: PIYAPHONG CHENRAI, Ph.D., CO-ADVISOR: ASST. PROF. PIYADA JITTANGPRASERT, Ph.D., pp.

Since 1962, petroleum exploration was begun in Khorat Plateau until now (2018). Nam Phong and Sin Phu Horm are two onshore petroleum commercial fields. Gas and condensate have been accumulated in Permian carbonate Pha Nok Khao Formation. Upper Carboniferous – Upper Permian in Saraburi Group was predicted to a petroleum source rock beneath the Khorat Plateau. This study analyses potential source rock in Khao Khwang Platform of Tak Fa Formation as Middle Permian sedimentary rock by nine outcrop samples from Bueng Sam Phan, Chon Daen and Nong Phai areas, Phetchabun province. Petroleum geochemistry methods are used to determine petroleum potential by 1) quantity of organic matter by total organic carbon (TOC) or amount of kerogen and extractable organic matter (EOM) or bitumen content, 2) quality of organic matter, 3) maturity level, and 4) depositional environment by biomarkers. As a result, limestone is appeared with TOC higher than 2.0 wt.% as excellent potential while shale having TOC higher than 1.0 wt.%. However, EOM is showed less than 500 ppm indicating a non-potential hydrocarbon source rock. Tmax data from pyrolysis and biomarker data, Moretane/(Hopane+Moretane), Ts/(Ts+Tm), and C_{31} 22S/(22S+22R), suggest the study area is in late to over mature level at the present day. Kerogen type can be defined by non-biomarker within Pr/n-C_{17} and Ph/n-C_{18} suggested, samples from this study is kerogen type II and III from marine and terrestrial source. The results from biomarker of C_{27}, C_{28}, C_{29} regular steranes (m/z 217) plot, Ph/Pr ratio and diterpenoid/n-alkane plot reveal that organic matters have been preserved under estuarine environment with under anoxic to suboxic condition. In conclusion, the depositional environment of Tak Fa Formation in this study is interpreted to be back reef depositional environment. Organic matters in sedimentary rock of this study are non-potential source rock by outcrop analysis, possibly due to physical and chemical weathering of the rocks leading to low hydrogen index and low oxygen index.

Department:	Geology	Student's Signature	
Field of Study:	Earth Sciences	Advisor's Signature	
Academic Year:	2017	Co-Advisor's Signature	

ACKNOWLEDGEMENTS

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CHULALONGKORN UNIVERSITY

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Chapter I

Introduction

Nowadays, while Thailand's fossil fuel consumption or demand has been increasing every year, but domestic petroleum production has been insufficient. Thus, import of petroleum products includes liquid gas, oil and crude oil make up a significant portion for adequate demand to commercial and household petroleum consumption. These imported petroleum products resulted in a huge loss of budget for petroleum imports that affect decreasing domestic productive of crude oil, natural gas including lignite 4.6% since 2018 from Energy Situation Congress, Department of Mineral Fuels (DMF) in January 2018. For decreasing imports of petroleum, DMF has a strategic plan to establish and maintain the security of mineral fuel supply. In the 2013 annual report, DMF has made efforts to continuously promote the development of continental petroleum fields in the country especially the northeastern region (the Khorat Plateau) (Chamchoy, 2014).

The Khorat Plateau is defined by the regional area about 200,000 square kilometers of Mesozoic (mainly Cretaceous) continental sedimentary rocks of Khorat Group (Chantong, 2007). Since 1962, petroleum exploration has been continued in the Khorat Plateau until now (2018). The 55 drilled exploration wells were drilled in this Plateau, but only 13 wells can be produced natural gas and condensate. They are located on two onshore petroleum commercial fields, Nam Phong and Sin Phu Horm. Furthermore, natural gas and condensate accumulation are found in Dong Mun and Si That fields, but Dong Mun field will be developed and manufactured in the future. As a result, from petroleum exploration in the Khorat Plateau, it can be proved this plateau have high potential for commercial production and development. Petroleum in this plateau have been found within Permian carbonate strata of Pha Nok Khao Formation of Saraburi Group. A potential source rock can be predicted from three potential source rocks including 1) Lower Cretaceous Khorat Group containing few centimeter of woody organic material in its lateral red bed sequence producing minimal gas by locally mature stage 2) Triassic Huai Hin Lat organic-rich shale (Kuchinarai Group), and 3) Upper Carboniferous – Upper Permian in Saraburi Group, which was proved to be petroleum source rock by total organic carbon (TOC) 0.3-1.6 wt. % with kerogen type

II and III ,comprising both micritic limestone and marine shale (Si That Formation) Upper Carboniferous beneath Pha Nok Khao Platform (Racey, 2011).

Besides, Permian carbonate platform have been distributed in the western of Pha Nok Khao Platform named Khao Khwang Platform, in accordance with petroleum potential source rock occurrence underlain Pha Nok Khao Platform, the fact that maybe similar in Khao Khwang Platform. Chonglakmani and Sattayarak (1979) suggested these two platforms have ever been identical platform before the collision event during end of Permian to Early Triassic. Thus, organic richness is probably distributed in both shale and carbonate rocks in Khao Khwang Platform as well as Pha Nok Khao Platform. Previous study by Khositchaisri (2012) suggested to petroleum source rock distribution in Khao Khwang Platform within argillaceous limestone from Tak Fa Formation in Bueng Sam Phan area, Phetchabun Province. Thus, petroleum geochemistry data from Tak Fa argillaceous limestone is a possible petroleum potential rock but insufficient data to locate potential source rock zone. In addition, geochemical data are also used to identify depositional environment in the study area. The expectation of this study is to describe petroleum source rock of condensate and gas for the Khorat Plateau as one of an important petroleum basin in Thailand.

1.1 Study Area

The study area is located the central north of Thailand. Samples of Tak Fa Formation were collected from four outcrop exposures within Khao Khwang Platform covering 3 areas of Phetchabun Province; Bueng Sam Phan area, Chon Dean area and Nong Phai area as shown in Figure 1.1.
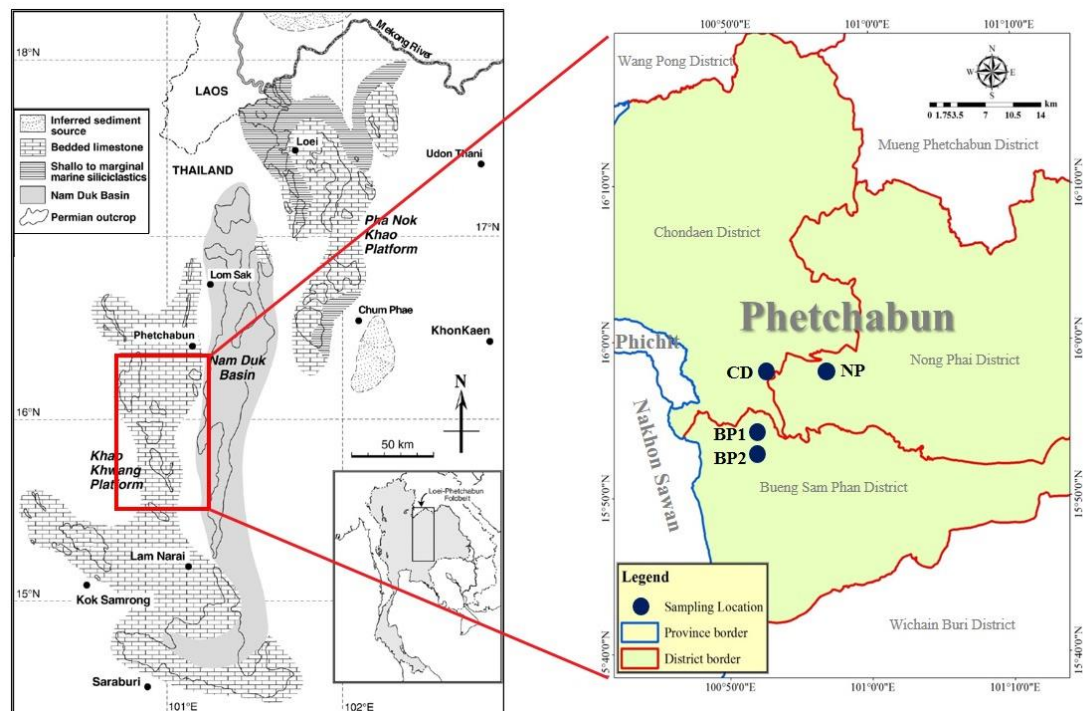
Figure 1.1 The study area and outcrop samples collected from four outcrop exposures within Khao Khwang Platform.

1.2 Objective

The aims of thesis are (1) to prove petroleum potential source rock from Permian Saraburi Group including shale, limestone and argillaceous limestone in Khao Khwang Platform that would be related to with migrated petroleum beneath several Khorat oil fields by geochemical analysis and (2) to reveal paleo-depositional environment of the study area.

1.3 Theory

The petroleum source rock is a significant element of petroleum system elements (PSE) and preserves massive ancient organic matters within organic-rich sedimentary rocks. It can generate hydrocarbon products under appropriate condition, temperature and pressure. Moreover, organic matters in a sedimentary rock can be divided in two phases, bitumen and kerogen as shown in figure 1.2. An insoluble organic matter phase called kerogen, due to composite kerogen is humin, is originated from fluvic acid and humic acid. Kerogen can be undergone insolubilization during diagenesis. These rocks

are enhanced by pressure and temperature for polycondensation of two organic acids. In contrast, the bitumen, that can be solute in organic solvent, is produced from two path ways; occurring in diagenesis and decompose from kerogen by heat and pressure.

Source rock can be evaluated by four major parameters of geochemical analysis for screening petroleum potential, including 1) quantity of organic matter, 2) quality of organic matter, 3) maturation of organic matter and 4) depositional environment.
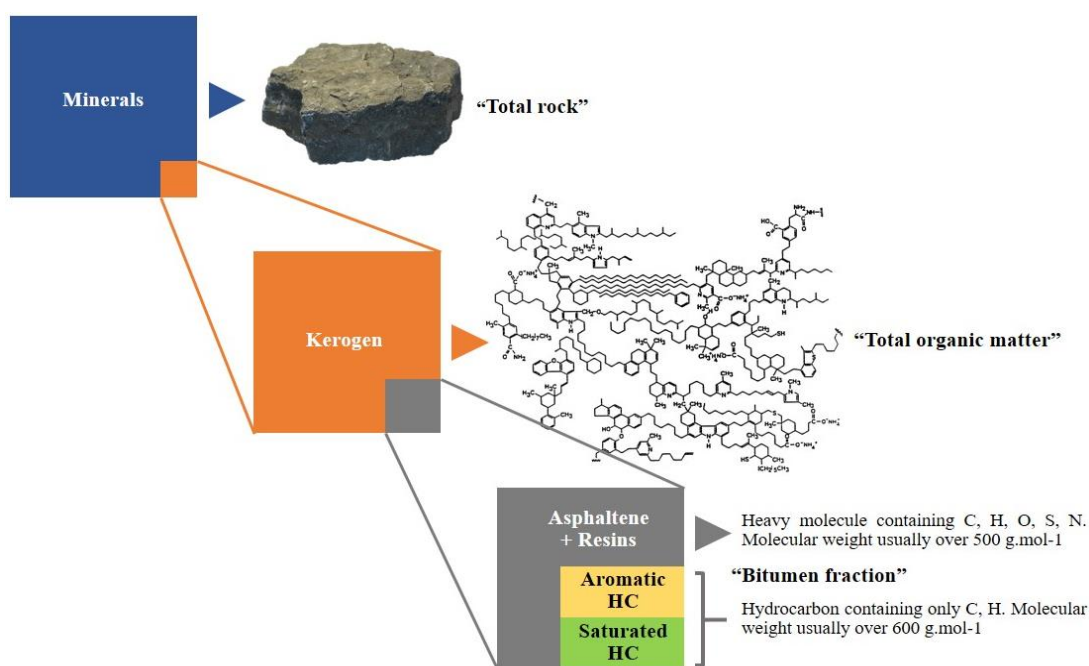
Figure 1.2 Composition of disseminated organic matter in deposited sedimentary rocks.

1.3.1 Quantity of organic matter

The general term to define organic hydrocarbon quantity has two path ways consisting total organic carbon (TOC) referring to amount of kerogen and extractable organic matter (EOM) referring to bitumen (Peters and Cassa, 1994).

TOC reveals the result in percent weight (wt. %) of organic matter in microgram per rock in gram. The combustion technique and weight loss calculation from material are the technique for hydrocarbon potential qualification. TOC criteria are produced for organic matter qualification in shale and carbonate rock because difference in porosity and permeability within rocks. These properties are effect on intense petroleum grade in each rock type (Peters and Cassa, 1994).

Table 1.1 Total organic hydrocarbon contents in two rocks type (Peters and Cassa, 1994).

Status	TOC (wt. %)	
	Carbonate	Shale
Poor	0.0-0.2	0.0-0.5
Fair	0.2-0.5	0.5-1.0
Good	0.5-1.0	1.0-2.0
Very good	1.0-2.0	2.0-5.0
Excellent	>2.0	>5.0

The criteria for screening richness of organic matter in petroleum source rock have different conditions. From table 1.1, carbonate rock has less organic matter scale than shale in same criteria (Jones, 1987). The major factor is grained size of two sedimentary rocks due to organic matter capacity and porosity for preserving organic matter in sediment materials. In addition, carbonate rocks are in early stage of sediment deposits before diagenetic process as low water column such as reefs, thus highly oxygenated of oxic condition. Organic matter of carbonate rocks is oxidized by humidity and air contact, causing low TOC contents since immature. On the other hand, shale is deposits under low kinetic of low oxygenated water (anoxic condition) thus TOC content is high or than the carbonate rock since immature levels.

The dissolved or dispersed organic matter in organic solvent called bitumen can be used as an alternative tool for identification quantity of organic matter in petroleum source rock. The quantification scales of EOM are defined into five levels, that are poor, fair, good, very good, and excellent as shown in table 1.2. Bitumen content is one of important factors to use for considering a potential in source rocks. The bitumen fractions consist saturated hydrocarbon, aromatic hydrocarbon and hetero-aromatic compound; saturated hydrocarbon referring to only single bond structure of organic compound including aliphatic hydrocarbon (paraffinic), acyclic compound (i.e. isoprenoid) and cycloalkane (i.e. tricyclic terpane, hopane, gammacerane); aromatic compound referring to conjugated pi system of organic compound for electron delocalization (resonance) (i.e. naphthalene, benzene); similar in hetero-aromatic

compound (resin), but allowed nitrogen, oxygen, phosphorous and sulphur to substitute in its molecular structure (i.e. chlorpyrifos, methyl ester) (Rabbani and Kamali, 2005; Sachse et al., 2011; Tissot and Welte, 1984). EOM or bitumen is combine saturate hydrocarbon as n-alkane, aromatic hydrocarbon and hetero-aromatic hydrocarbon that has properties to give a petroleum potential in commercial production. In other words, this parameter called productive index (PI) use for maturity indicator depending on maturity level, total organic carbon as well as kerogen type (Tissot and Welte, 1984).

Table 1.2 EOM richness scale for petroleum potential assessment of an immature source rock(Peters and Cassa, 1994).

Status	Hydrocarbon: HC (ppm)
Poor	<500
Fair	500-1000
Good	1000-2000
Rich	2000-4000
Excellent	>4000

1.3.2 Organic matter quality

The controlled parameter of petroleum products within oil and gas field is kerogen type. The kerogen is inherited living organism. Especially, microorganism like algae, phytoplankton and zooplankton, these are the bloom living organism and spread over the lake or ocean. When they died within under low energy or gentle kinetic wave or current in their place, these dead organisms can be deposited under the bottom of basin and burial by sediment supply. Furthermore, higher plant also transforms to kerogen and give different type of them. In fact, the kerogen defines as insoluble organic matter in the usual organic solvent of rocks also called total organic matter is not strictly equivalent, except in ancient sediments, once the early diagenesis is complete (Durand, 1980). Some authors seem to use the term kerogen for degradable of biomass including protein, carbohydrate and lipid into fluvic acid, humic acid and humin (figure 1.3). In final stage, degraded biomass transforms into kerogen which pressure and temperature are under burial zone (Tissot and Welte, 1984). A kerogen

has abundant organic matter 1000 times than summarize coal and petroleum in reservoir and is 50 times more than bitumen and other dispersed petroleum in non-reservoir rocks (Tissot and Welte, 1984). Thus, the kerogen is an important factor for petroleum resource. Kerogen is often range from 80 to 99 % of total residual organic matter within sedimentary rocks including limestone, shale and other fine grain sediments, the rest is bitumen.
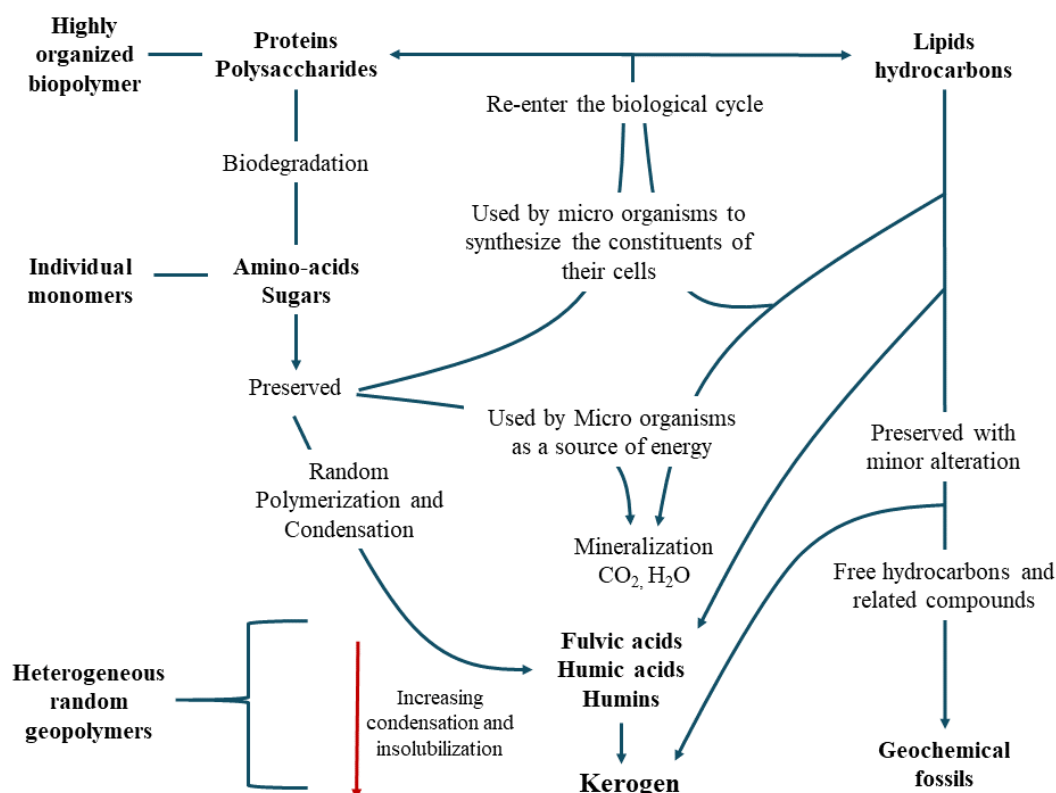
Figure 1.3 Schematic of organic material during sedimentation and diagenesis forming kerogen (Tissot and Welte, 1984).

Originally, kerogen type can be classified by using Van-Krevelen diagram as shown in figure 1.4a, created in 1961. This diagram expresses the relationship between atomic hydrogen (H/C) and atomic oxygen (O/C), used for characterizing coals and their evolution path at various depth in same formation. Nowadays, the Van-Krevelen plot is modified with TOC values. This modified plot is call "Pseudo Van-Krevelen" diagram presented in Figure 1.4b. The kerogen can be recognized by 4 types as follow in section below.

Kerogen type I, constituent rich aliphatic chain hydrocarbon with minimum aromatic nuclei, has a high hydrogen index (HI) or H/C. The petroleum product from type I is mainly oil due to enrich aliphatic hydrocarbon in composition. The fresh water algal lipid is the source of type I within lacustrine environment.

Kerogen type II, aromatic hydrocarbon and naphthene compound is predominant in this type, with moderate hydrogen index or H/C. The occurrence of aromatic hydrocarbon causes reducing hydrogen atom. The origin of type II is marine phytoplankton and enriches in marine shale and micrites within reducing environment.

Kerogen type III, aromatic and O-functional group is the major element with minor element as aliphatic chain, hence hydrogen index or H/C is too low. The higher plants are the source of type III, and most of this type deposits in marine source rocks with terrigenous sediments. The major product of type three is gas.

Kerogen type IV, the extremely oxidizing organic matter or over mature type I, II, III of kerogen into charcoal. This type is not a petroleum potential property, or is not able to generate oil or gas due to high oxygen index (OI) or O/C and lack H/C in molecular structure (Peters and Cassa, 1994).
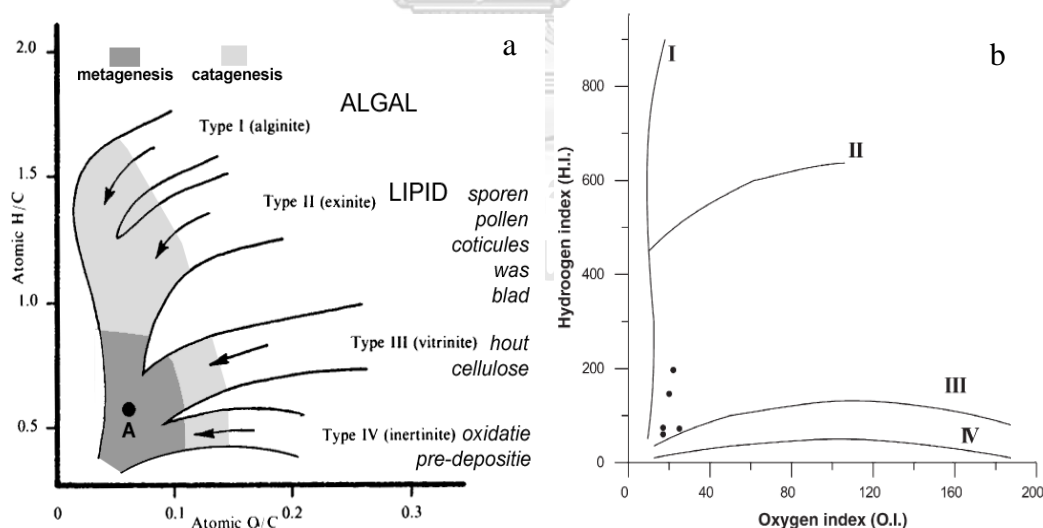
Figure 1.4 (a) The modified Van-Krevelen diagram adapt the maturity state in diagram (after Tissot and Welte, 1984); (b) Pseudo Van-Krevelen diagram (Alkhafaji et al., 2015).

The hydrogen index and oxygen index values can obtain from consequent of rock-eval pyrolysis parameter in S2 and S3 data (figure 1.5) and TOC value by equation follow in equation 1 and equation 2. The eq. 1.1 is the S2 pyrogram abundant as numerator calculated with TOC as denominator, the consequence of this point is HI, depended on enrich hydrogen in molecular of organic matter per total mass of organic matter in the sample. The eq. 1.2 is the S3 pyrogram that reveal amount of carbon dioxide in the sample.

$$\frac{S2}{TOC} \; x \; 100 \qquad \text{(Eq. 1.1)}$$

$$\frac{S3}{TOC} \; x \; 100 \qquad \text{(Eq. 1.2)}$$
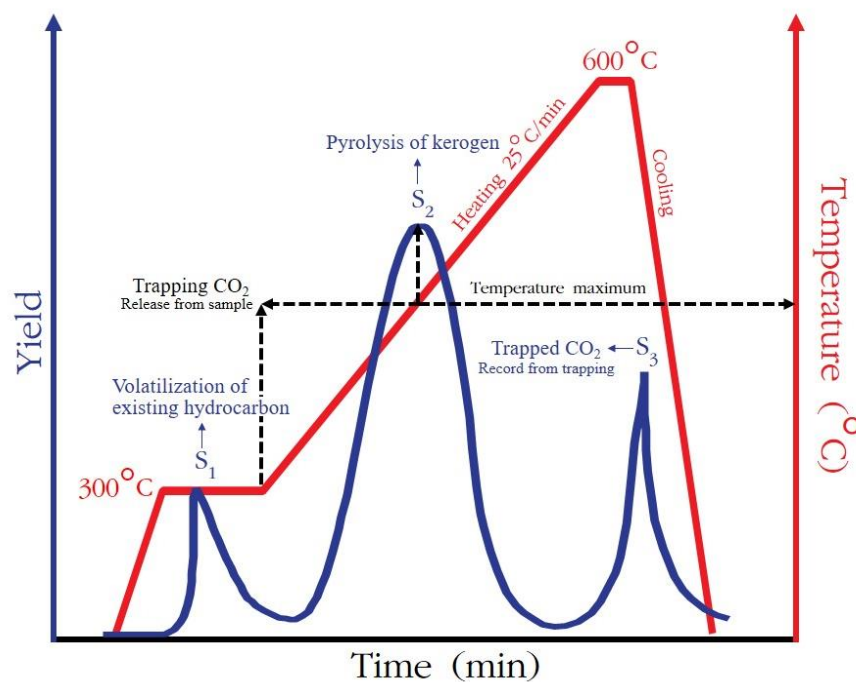
Figure 1.5 The pyrogram from rock-eval pyrolysis technique (Hart and Steen, 2015)

1.3.3 Maturation of organic matter

Maturation of organic matter, also known thermal maturation of petroleum, is the temperature level for converting kerogen or bitumen within sedimentary rock into oil and gas. The maturation is depended on heating level in burial depth of organic-rich sedimentary rock. Figure 1.6 represents the concordance of hydrocarbon generation, while increasing temperature and pressure from sediment loading over a source rock.
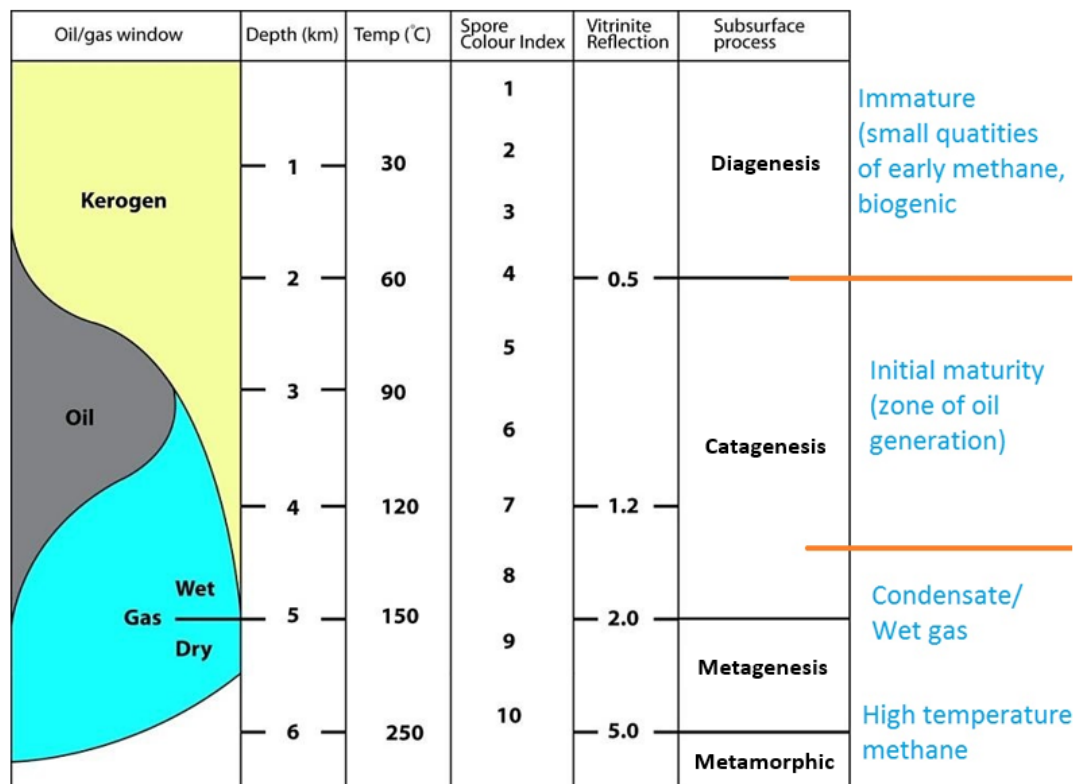
Figure 1.6 Maturity level of petroleum when burial depth increasing also burial temperature and pressure [after Tissot and Welte (1984)]

According to hydrocarbon generation diagram, there are three subsurface states of source rock; diagenesis, catagenesis and metagenesis, same as maturation levels that are immature, mature and over mature, respectively (Tissot and Welte, 1984). Immature or early mature source rocks are the first metamorphism in diagenesis, in which physical, chemical and biological processes are transformed from organic matter into minimal of gas during sediments deposit with burial temperatures between 60 and 80 °C. When burial depth is increased by deposition of sediments, temperature also

increase ranging of between 60 and 150 °C into catagenesis, this temperature levels cause source rock to generate oil. The last thermal range for generating petroleum from source rock is over mature that about 150-225 °C or is the gas window, wet and dry gas are occurred at this depth range. Source rock maturity can be evaluated using several methods such as vitrinite reflectance (Ro), fluorescence, thermal alternative index (TAI), thermal alternative scale (TAS) and maximum temperature (Tmax) from Rock-Eval pyrolysis (Chamchoy, 2014). However, only Tmax method is used to estimate source rock maturation in this research due to budget control.

1.3.4 Depositional environment

Living organisms can be transformed into petroleum, when they are buried and heated. In addition, chemical structure of these organisms can be regarded as biomarkers. The biomarker study is used to identify organic compounds that are composed of carbon, hydrogen and other elements. They can be used to classify source of organic matter for revealing biota of elements. Biomarkers can provide specific chemical data for defining their parent organic matter of living organisms by biomarker fingerprint (Peters et al., 2004).

Biomarker fingerprints can be analyzed from consideration of gas chromatogram by gas chromatography-mass spectrometer (GC-MS), which ionized parent organic compounds that are deformed into micro chemical structure. Previous studies of organic compounds were revealed in several petroleum research by geochemist (Didyk et al., 1978; Peters and Moldowan, 1993). Some examples of biomarker fingerprints for petroleum origin study are presented as follows;

1) The pristane/phytane ratio (Pr/Ph) is used to determine the oxicity of the depositional environment. Pr/Ph ratio less than 1.0 indicates anoxic conditions, and more than 3.0 indicates oxic conditions. The ratio values between 1.0 and 3.0 were interpreted as sub-oxic conditions as presented in figure 1.7 (Didyk et al., 1978).
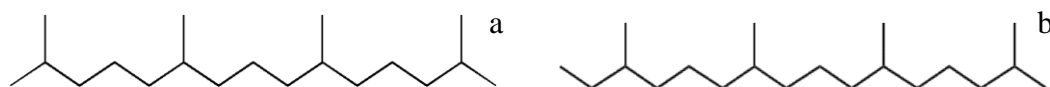
Figure 1.7 a) Pristane ($C_{19}H_{40}$) and b) Phytane ($C_{20}H_{42}$)

2) The isoprenoids/n-alkanes ratio (Pr/n-C17 and Ph/n-C18) provides valuable information on biodegradation, maturation and diagenetic conditions. The early effect of microbial degradation can be monitored by the ratios of biodegradable to the less degradable compounds. Isoprenoid hydrocarbons are generally more resistant to biodegradation than normal alkanes as presented in figure 1.8 (Hunt, 1996).
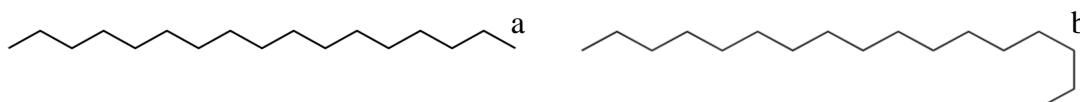
Figure 1.8 a) Heptadecane (n-C17; $C_{17}H_{36}$ and b) Octadecane (n-C18; $C_{20}H_{42}$)

3) The tricyclic terpanes (m/z 191) can be used to correlate crude oils and source rock extracts, to interpret organic matter input and to evaluate the extent of thermal maturity and biodegradation (Peters and Moldowan, 1993). Predominant C19 tricyclic terpanes reflects terrigenous organic matter, while higher C23 tricyclic terpanes indicate marine organic matter as presented in figure 1.9 (Moldowan et al., 1985).
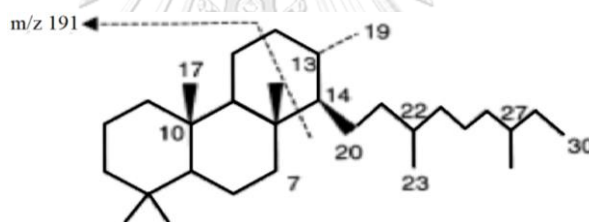
Figure 1.9 Tricyclic terpanes (m/z 191)(Peters, 2000).

4) Gammacerane (m/z 191) has been found in sediments from the Late Proterozoic (Summons et al., 1988), which is used as an indicator for water stratification during source deposition with both marine and lacustrine environments as presented in figure 1.10 (Damsté et al., 1995)
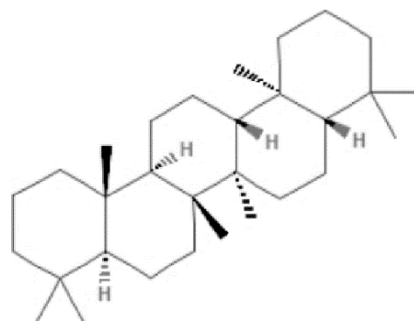
Figure 1.10 Gammacerane ($C_{30}H_{52}$)

5) The Trisnorneohopanes (Ts) and Trisnorhopane (Tm) ratio is used as a maturity indicator. Ts is more stable than Tm, at higher in maturity as represented in figure 1.11(Mackenzie et al., 1981).
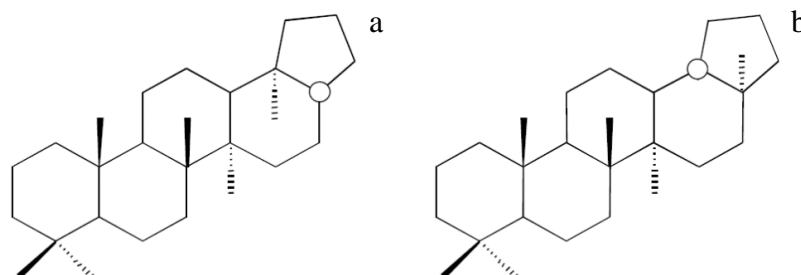
Figure 1.11 a) 18α-22,29,30-trisnorneohopane (Ts) and b) 17α-22,29,30-trisnorhopane (Tm)

6) The 17β(H),21α(H)-moretanes and 17α(H),21β(H)-hopanes ratio are used as maturity indicators. Moretanes are thermally less stable than hopanes, and the abundance of moretanes decreases relatively to the corresponding hopanes with thermal maturity as presented in figure 1.12 (Peters et al., 2004)
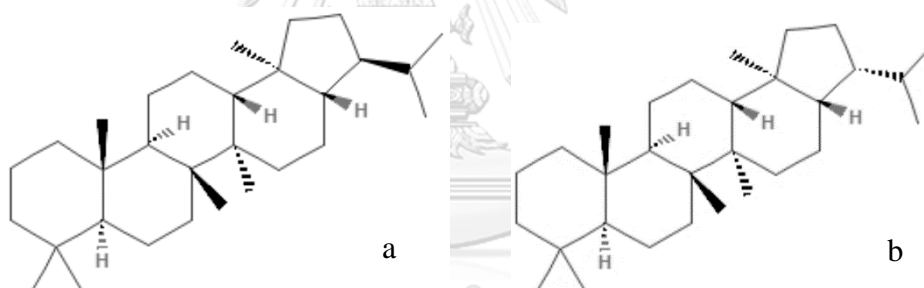
Figure 1.12 a) Moretanes, b) hopanes

7) The homohopanes distribution (m/z 191) is derived from bacteriopolyhopanol of prokaryotic cell membrane. Homohopane index can be used as an indicator of the associated organic matter type, and it can also be used to evaluate the oxic/anoxic conditions of organic matter during and immediately after deposition of the source sediments as presented in figure 1.13 (Yalçın et al., 2006).
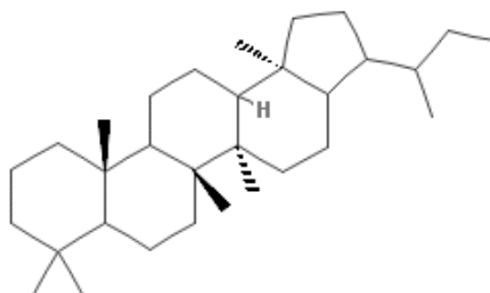
Figure 1.13 Homohopanes (m/z 191)

8) The Homohopane isomerization ratio, 22S/(22S+22R), can be used to assess the maturity of geological samples. This ratio reflects the more thermally stable 22S isomer compared to the biologically derived 22R stereochemistry (Peters and Cassa, 1994)

9) The distribution of steranes (m/z 217) is a characteristic fragment in the sterane series. Steranes are derived from sterols, where they are widely distributed in microorganisms and plants. The relative amounts of C27-C28-C29 steranes can be used to indicate characteristic source inputs and sedimentary facies. The predominance of C27 steranes show a marine influenced system and source input of plankton (algae), while C29 sterane predominance shows a terrestrial higher plant input and a swamp shallow water environment. C28 sterane is a unique biomarker signature of organic matter deposited in lacustrine facies as presented in figure 1.14 (Peters and Moldowan, 1993).
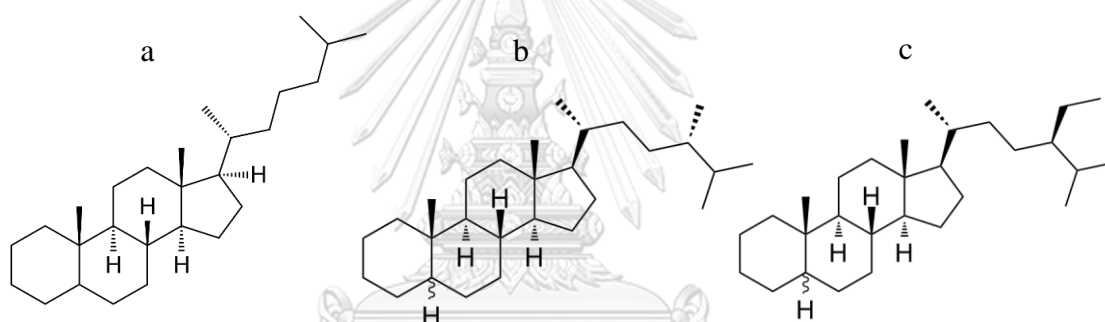
Figure 1.14 Structural of C27, C28, and C29 regular steranes; a) Cholestane (C27), b) Ergostane (C28), and c) Stigmastane (C29)

10) The regular steranes/17α(H)-hopanes ratio reflects input of eukaryotic (mainly algae and higher plants) versus prokaryotic (bacteria) organisms to the source rock as presented in figure 1.15 (Peters and Moldowan, 1993).
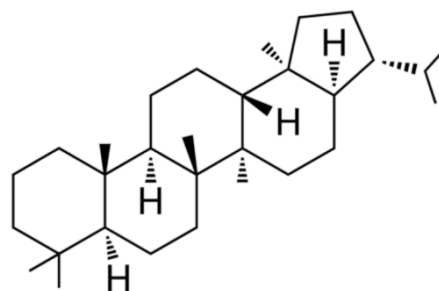
Figure 1.15 17α(H), 21(β)-hopanes

Chapter II

Literature Review

2.1 Rationale

The geology of Khorat Plateau consists of stacked Permo-Carboniferous, Triassic, Mesozoic and Tertiary rocks. Hydrocarbon exploration of these rocks was begun since 1971, when Union Oil drilled Kuchinarai-1, with minor gas shows. In 1997, PhuWiang-1 (Amerada Hess), a re-drilled well of Chonnabot-1, encountered significant overpressure and gas shows at massive levels. However, the Permian reservoir target was proved to be mixed marine clastics and carbonates rather than the prognosed fractured platform carbonate. The Permian and late Triassic sections failed to flow significant amounts of gas. Cairn's Si That-2, drilled up dip of Esso's 1983 well, was abandoned after testing a non-commercial volume of gas (Booth, 1998). To date the platform carbonates of the Permian Pha Nok Khao Formation have been proved to be the only productive reservoir, three main gas commercial field including Phu Horm, Dong Mun and Nam Phong gas fields. They were proved to be of reservoir quality, with dolomitization and fracture enhancement being the key elements in petroleum productivity.
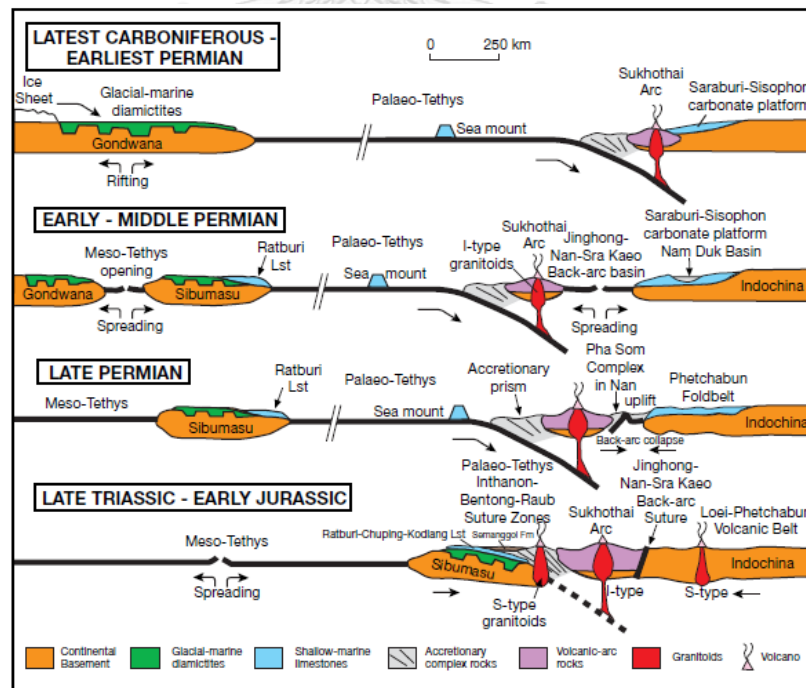
Figure 2.1 Schematic of tectonic evolution of Thailand during Late Carboniferous to Early Jurassic (Metcalfe, 2011).

Proved petroleum reservoir of Pha Nok Khao Formation as place in Pha Nok Khao Platform occurred. As a result, tectonic evolution of Shan-Thai and Indochina plate that involves two carbonate platforms on the north-east of Thailand including Khao Khwang Platform and Pha Nok Khao Platform. Since the collision event had been developed during Paleo-Tethys and closed by the end of Permian to early Triassic as shown in figure 2.1. Tectonism has controlled the sedimentation of platform and supplies of carbonate and clastic sediments into the basin area. Both Pha Nok Khao and Khao Khwang Platforms developed on an extensive distally steepened ramp-like margin which carbonates and siliciclastics accumulated (El Tabakh and Utha-Aroon, 1998). Between these two platforms, the Nam Duk Basin received coeval hemipelagics, siliciclastics and minor amounts of carbonates as shown on figure 2.2.
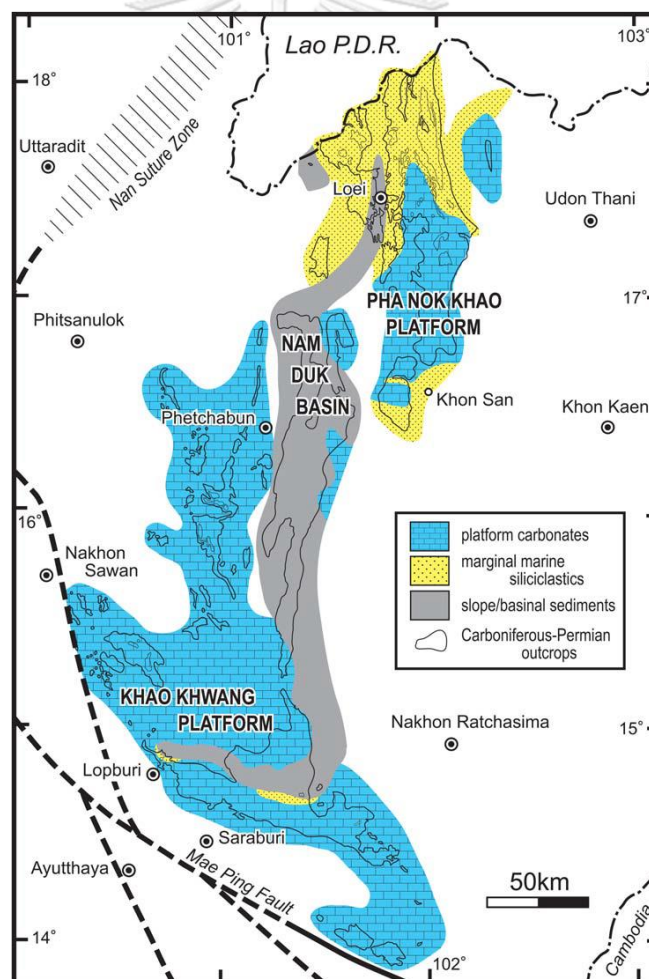
Figure 2.2 Both carbonate platforms and basin occurrence by extensive distally steepened ramp-like margin (Ueno and Charoentitirat, 2011).

2.2 Source rock problems

According to petroleum geochemical data of rock samples from both borehole and outcrop, the source rock in Khorat Basin is classified into three groups, 1) the fluvial sediment of Lower Cretaceous Khorat Group, 2) Triassic Huai Hin Lat Formation as organic rich shale, and 3) Upper Carboniferous to Upper Permian of Saraburi Group, summary as show in Table 2.1 (Sattayarak, 2005; Thongboonruang in Khositchaisri, 2012)

2.2.1 Permian Group (Upper Carboniferous to Upper Permian of Saraburi Group)

The shallow marine shale and limestone of the Permian Group overlain unconformity and can be divided into three parts. Firstly, the lower part, Lower clastics or upper part of the Wang Saphung Formation, consists of shales interbedded with limestone and occasional lignite beds. Secondly, the middle part, the Middle carbonates, comprises limestone and dolomite. The upper part, Upper clastics or the Hua Na Kham Formation is shales interbedded with sandstones and occasional limestone. Permian outcrop samples contain TOC contents about 0.29-1.59 wt.% (poor to fair organic richness) and are maturity level falling in over mature within dry gas. Moreover, petroleum geochemical data from 4 exploration wells including Phu Lop-1, Phu Wiang-1, Dao Ruang-1 and Kham Palai-1, reveal the sedimentary rocks of the Upper Saraburi Group have poor to excellent potential source rocks with kerogen type III/IV at late mature to over mature (Thongboonruang, 2008).

2.2.2 Triassic Huai Hin Lat Formation

Permian unconformity is overlain by Huai Hin Lat Formation and underlies the Khorat Group with a local unconformity. This sequence is represented as the Huai Hin Lat Formation that comprises shale, sandstone, limestone, conglomerate and volcanic rocks, which were deposited under lacustrine environment. The Huai Hin Lat can be divided into two facies including the dark gray sediments and the brownish red sediments by lake sedimentary rocks. The rock samples contain TOC contents around 0.2-5.76 wt.% as poor to very good organic richness, with vitrinite reflectance value of 0.9-4.57%Ro (Racey, 2011).

2.2.3 Lower Cretaceous Khorat Group

        The Khorat Group is the Mesozoic non-marine sequence including mainly of brownish red sediments which were deposited in streams and lakes under arid climate. Generally, this sequence contains poor organic matter (low TOC) with kerogen type II at mature source rock. Furthermore, it appeared rich woody organic matter beds or thin coal beds at some places, which can be a potential source rock as gas-prone source rocks (Racey, 2011).

Table 2.1 Source rock exploration of Khorat Basin by three main source rocks by Sattayarak (2005) and Thongboonruang (2008).

Group/Formation	Organic richness	Kerogen type	Thermal maturation
Saraburi Group			
Upper clastic and grey shale	Poor to very good	III/IV	Late to over mature
Triassic Pre-Khorat Group			
Huai Hin Lat Formation	Fair to very good	I/III	Late to over mature
Khorat Group			
Phu Phan Formation	Good	N/A	Mature
Sao Khua Formation	Poor	N/A	N/A
Phra Wihan Formation.	Poor	III	Late mature
Phu Kradung Formation	Poor	N/A	Late mature
Nam Phong Formation	Poor	N/A	Mature

        However, petroleum source rock problem of dolomitic reservoir of Pha Nok Khao Platform is probably from others source rock from above. For example, Department of Mineral Fuels annual reported in 2007 used 2D seismic exploration over Pha Nok Khao Platform area. They found high organic matter within Si That Formation of Pha Nok Khao Platform. Thus, it can be considered as a petroleum potential source rock contributed to reservoirs in the Khorat plateau area. This study is focused to find a petroleum potential source rock in Khao Kwang Platform. It is located south-west of

Pha Nok Khao Platform, which is considered as the same Permian Group. Therefore, there is a possibility of finding a possible source rock maybe occur on this carbonate platform, resemble to Si That Formation of Pha Nok Khao Platform. Permian Saraburi Group of Khao Khwang Platform is classified as Tak Fa Formation, that distributed in western to center of Phetchabun Province as shown in figure 2.3.
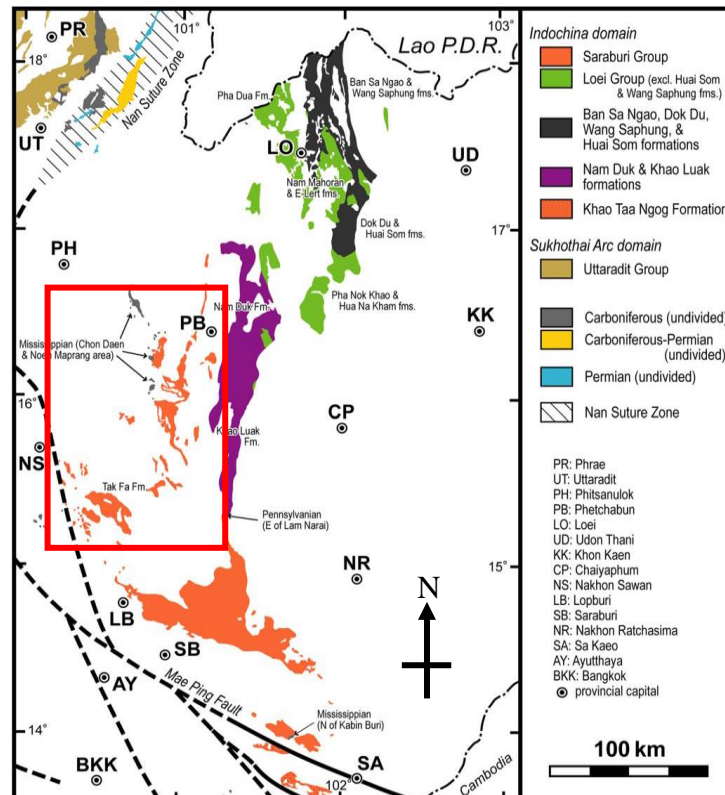
Figure 2.3 Tak Fa Formation of Permian Khao Khwang Platform distribution in Phetchabun Province (Ueno and Charoentitirat, 2011).

2.3 Stratigraphic of Carboniferous to Permian in Phetchabun Province

2.3.1 Carboniferous (286-360 Ma.)

Wang Sa Phung Formation consists grey slately-shale, brown shale, brownish-grey shale, grey chert, sandstone, and sandstone. This formation is occurred as minor craton intermittent distributed in the western part of Phetchabun Province

2.3.2 Carboniferous to Permian (245-360 Ma.)

Upper carboniferous rocks consist siltstone, slightly bedded greenish-gray to black shale and claystone. Moreover, bedded slaty-shale and bedded conglomerate are intermittent distribution in the west of Phetchabun Province.

2.3.3 Permian (245-286 Ma)

Permian rock in Phetchabun area consists four rock formation as follow (older to younger ascending)

1) Tak Fa Formation

The rock type of this formation consists bedded massive to slightly gray to black limestone with barely black chert nodule and slightly gray shale interbedded with limestone. This formation is distributed in center to south-west of Phetchabun Province.

2) Pha Nok Khao Formation

This formation consists bedded gray limestone overlies gray and yellowish-brown shale including gray chert. They are distributed south-east direction from Chon Daen District to Nong Phai District in Phetchabun Province.

3) Hua Na Kham Formation

This rock formation consists argillaceous limestone, limestone lens interbedded with gray shale, sandstone, siltstone including pyroclastic rock as andesite tuff and agglomerate. They are distributed from north to south at eastern of Nam Ngao District along to Sri Thep District in Phetchabun Province. Moreover, they are distributed over center of Punhetchab along to Nong Phai District at southern of Phetchabun.

4) Nam Duk Formation

This formation consists minor to middle crossbedding of grayish-black and reddish-brown shales, yellowish-brown and reddish-brown including fold with siliceous cements, barely interbedded with limestone lens. They are distributed from north to south direction of Phetchabun Province.
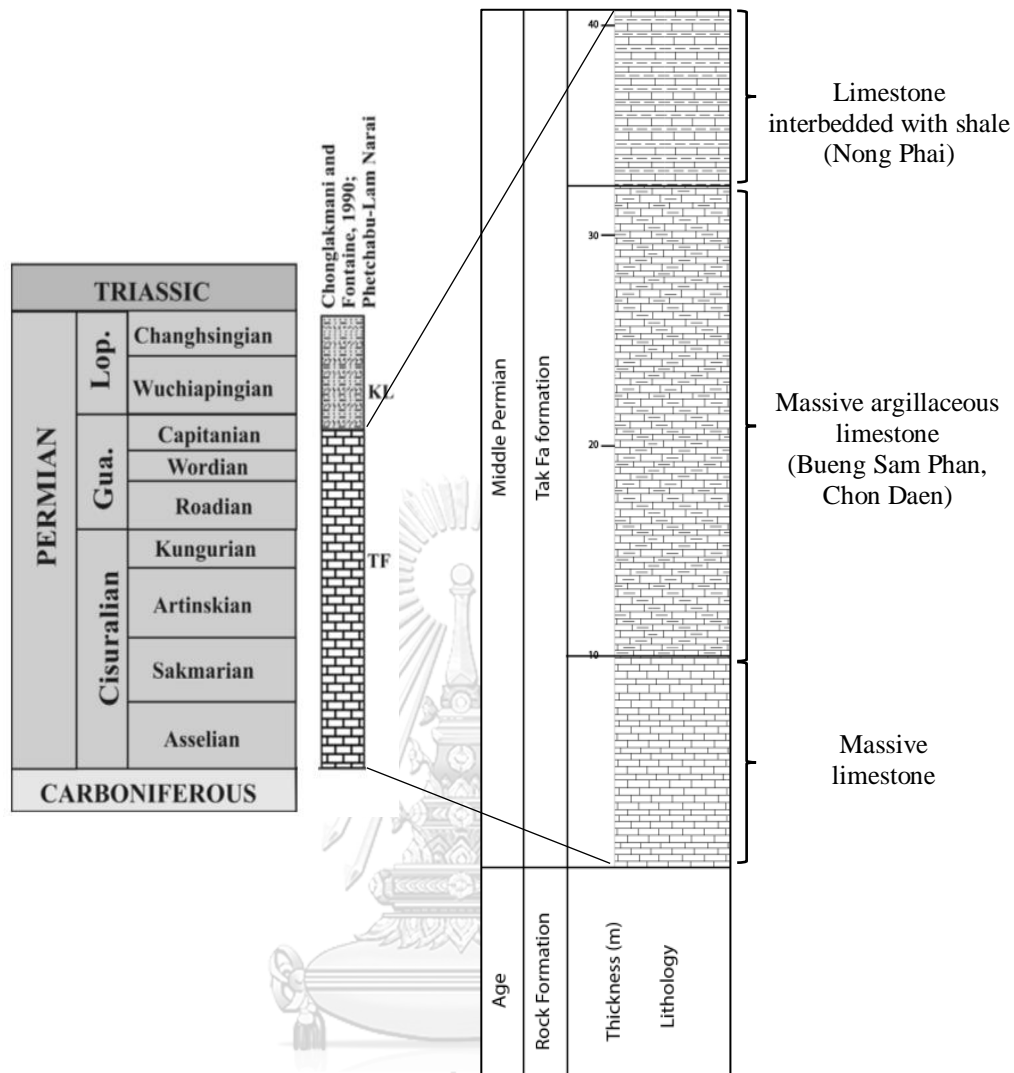
Figure 2.4 Stratigraphic column of Tak Fa Formation (Chonglakmani and Fontaine, 2000; Ketwetsuriya and Kanjanapayont, 2016; Udchachon et al., 2014).

Lithostratigraphy of Tak Fa Formation in the study area and vicinity is divided into three sections by Ketwetsuriya and Kanjanapayont (2016) including massive limestone at the lower section, massive argillaceous limestone at the middle section and limestone interbedded with argillaceous at upper section (figure 2.4). The massive argillaceous limestone distributes in Bueng Sam Phan and Chon Daen districts. The limestone interbedded with shale distribute in Nong Phai district on Phetchabun province.

This study is emphasized Tak Fa Formation for petroleum source rock assessment which underlies Pha Nok Khao Formation. Thus, it is considered that Tak

Fa Formation might be a possible potential source rock by using depositional environment study to confirm source of organic matter as kerogen.

2.4 Previous study

2.4.1 Petroleum source rock

Khositchaisri (2012) collected three argillaceous rocks of Permian Tak Fa Formation from Bueng Sam Phan in Phetchabun Province. Tak Fa Formation suggests to poor source rock that reveals by total organic carbon contents (TOC) at less than 0.001 to 0.37 wt. %. The organic matter is classified to kerogen type III by pseudo Van-Krevelen diagram with HI 81.08 and OI 57.76. Thermal maturation of Tak Fa Formation indicated late to over mature by vitrinite reflectance (%Ro) more than 1.0 %Ro, and all of biomarker methods confirmed sample reached in mature stage. Table 2.2 summarized the petroleum source rock assessment of Saraburi Group [in Khositchaisri (2012)] for Tak Fa Formation as shown poor to excellent organic richness with mature to over mature stages.

Table 2.2 Summarized of petroleum source rock assessment of Saraburi Group

Publication	Organic richness	Thermal maturation
Khositchaisri (2012)	Fair to good	Late mature to over mature
Chantong (2007)	Poor to good	N/A
Thongboonruang (2008)	Fair to excellent	Mature to over mature

2.2.2 Depositional environment

Most depositional environment study of Tak Fa Formation and adjacent carbonate platform is using fossil classification, due to predominance of their structural appeared in carbonate rock. According to fossil classification, Khao Khwang Platform represented by shallow marine carbonates, which are rich of fusulinaceans and local corals and brachiopods (Chitnarin et al., 2008). Ostracod species can be defined carbonate platform in Bueng Sam Phan reveals general composition points out a shallow marine, euryhaline, nearshore environment during the time of deposition. In addition, geochemical data as biomarker and non-biomarker are usually to confirm depositional environment by remain chemical skeleton from organic matter in

sedimentary rocks, both shale and carbonate rocks. According to Khositchaisri (2012), argillaceous limestone of Tak Fa Formation is deposited under estuarine environment by C_{27}, C_{28}, C_{29} regular steranes ratio on ternary diagram. Because of type of regular steranes is depended on lipid membrane of living organism, and gammacerane (m/z191) that was found in Tak Fa Formation samples and can be used to confirm organic matter accumulating during hypersaline condition. Non-biomarker results show organic matter from marine organic matter under reducing environment by bivariate plot of diterpenoid (pristane and phytane) and normal alkane (heptadecane and octadecane) ratios (Shanmugam, 1985).

Chapter III
Methodology

According to the rationale section of general geology in chapter II, Khao Khwang Platform is considered as petroleum potential source rock and can be investigated by geochemical analysis. From chapter 1, the petroleum potential can be evaluated by two main issues including quantity of organic matter for indicating organic richness in rock samples, and quality of organic matter in rocks for defining a kerogen type and maturity level. The source rock quantification is the prior consideration issue, then investigates quality of source rock as follow. In addition, one important factor to confirm the source rock type and specific the origin of organic matter is depositional environment study of organism in ancient sediments. A diagnostic depositional environment is using for defining source of organic material by biomarker identification. Due to the organic matter type provides both oil or gas prones, which important variant to define petroleum products. Up to next paragraph would be described the procedure and figure 3.1 show flow charts of procedure for petroleum geochemical analysis of this work.

Sampling

Treatment

Lithologic Description

Rough grinding
(Jaw Crusher)

Treatment

Pulverization
(Disc Mill)

| 20 grams | 100 grams | 50 grams |

Total Organic Carbon
(HSM Chulalongkorn University)

Rock-Eval Pyrolysis
(Core Laboratory Malaysia)

Soxhlet Extraction
(Geochemistry Laboratory)

Column Chromatography

Saturated HC   Aromatic HC   NSO compound

Gas Chromatography – Mass spectroscopy
(Biomarker and Non biomarker)
(STREC Chulalongkorn University)

Figure 3.1 Research flow chart.

3.1 Sampling

The field exploration was done in 10th-12th February 2017. Before the field work, the exploration plan was located, based on geological map series ND-47-4 also known Ban Mi (Nakornsri, 1977). In which, comprehensive Saraburi Group at Phetchabun area expected Tak Fa Formation. The sampling is selected by dark color outcrop exposure that suggests brown, grey and black colors. They are recognized to rich organic matter in a rock. The samples from Nong Phai District is considered to Upper Tak Fa Formation from rock strata as shown in figure 2.4, within limestone and shale including pyroclastic appearance. Sample from Bueng Sam Phan 1 and 2 and Chon Daen locations are considered to Middle Tak Fa Formation within argillaceous limestone appearance.

Table 3.1 Sampling location in Saraburi Group. All samples were corrected from Tak Fa Formation, which their locations cover three districts in Phetchabun province.

Sample ID	Lithology	Location		District
		UTM		
		X	Y	
BP1-1/1	Argillaceous limestone	0699930E	1759051N	Bueng Sam Phan
BP1-1/2	Mudstone			
CD-2/1	Argillaceous limestone	0700871E	1766638N	Chon Daen
NP-3/1	limestone	0708658E	1766638N	Nong Phai
NP-3/2	Shale			
NP-3/3	Shale			
NP-3/4	Limestone			
BP2-4/1	Argillaceous limestone	0699764E	1756635N	Bueng Sam Phan
BP2-4/2	Argillaceous limestone			

Four outcrops of the Tak Fa Formation in the Khao Khwang Platform covering in three districts of Phetchabun Province, including Bueng Sam Phan, Nong Pai and Chon Daen areas were collected for this study (figure 3.2). Sample types and UTM coordination system were collected and listed in Table 3.1. All outcrop samples were categorized into nine samples for geochemistry analysis due to variation of rock types in each outcrop. In addition, sample categorization is useful to interpret depositional environment of outcrop areas.
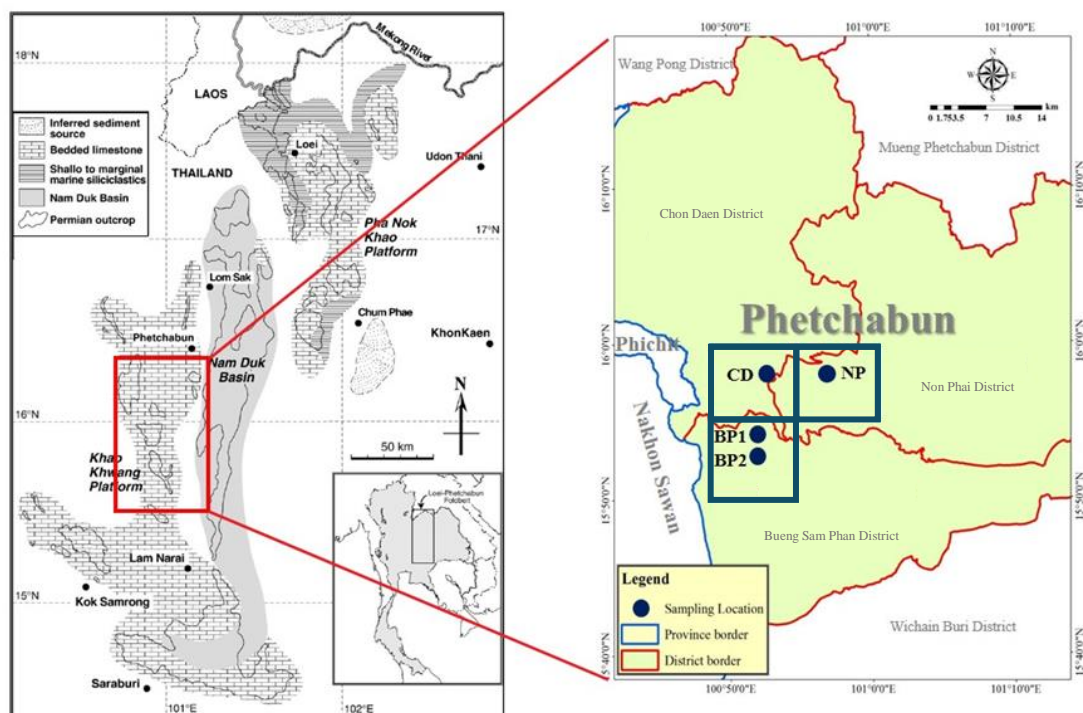
Figure 3.2 Sampling areas distribute over Khao Khwang Platform in Phetchabun province.

3.1.1 Bueng Sam Phan 1 (BP1)

Location: Ban Pho Sawan 1, Bueng Sam Phan area, Phetchabun Province

Both argillaceous limestone and calcareous mudstone of Tak Fa Formation were collected at this location. Fossil evidence from argillaceous limestone outcrop exposure includes brachiopods and gastropod, for example the mold brachiopod is appeared on argillaceous limestone sample (figure 3.3). The bed

thickness of argillaceous limestone is around 15-20 centimeters overlain bedded mudstone thickness around 10 centimeters.

Figure 3.3 Mold brachiopod evidence on argillaceous limestone sample.

3.1.2 Bueng Sam Phan 2 (BP2)

Location: Ban Pho Sawan 2, Bueng Sam Phan area, Phetchabun province

Only argillaceous limestone of Tak Fa Formation was collected at this location. Argillaceous limestone outcrop shows evaporitic sedimentary structure as teepee structure (figure 3.4). The bed thickness of argillaceous limestone is up to 50 centimeters.

Figure 3.4 Some evidence of minimal teepee structure appeared on bulk rock samples.

3.1.3 Chon Daen (CD)
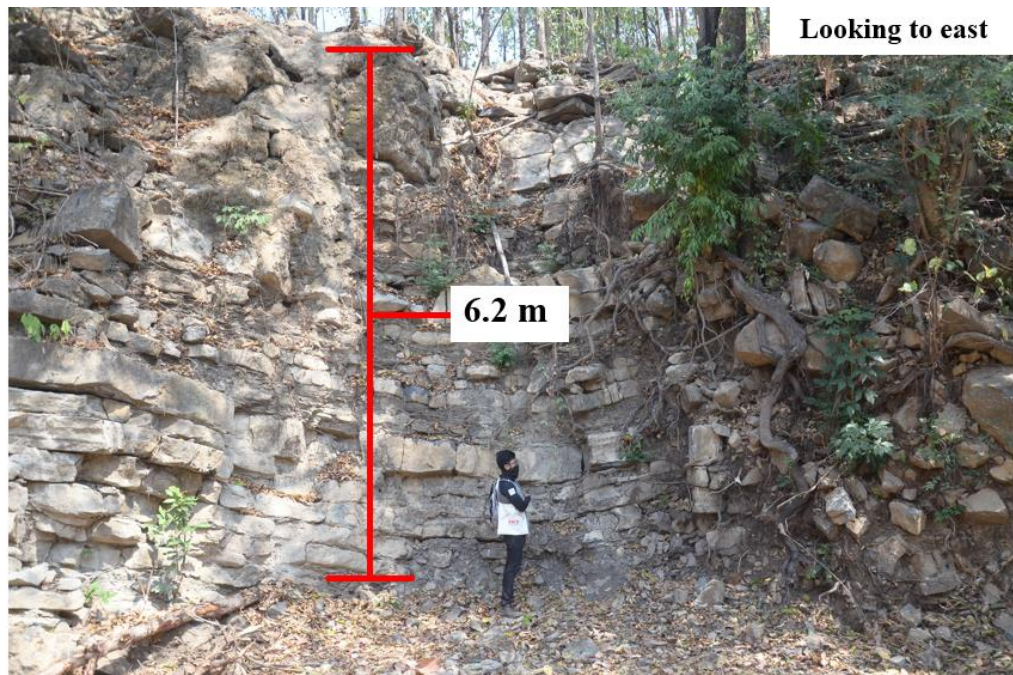
Figure 3.5 Bedded argillaceous limestone at Phu Pra That temple.

Location: Phu Pra That temple, Chon Daen area, Phetchabun province

Only argillaceous limestone of Tak Fa Formation was collected at this location. Outcrop exposure is bedded of argillaceous limestone at about 6 meters as presented in figure 3.5.

3.1.4 Nong Phai (NP)

Location: Nong Phai hill, Nong Phai area, Phetchabun province

Both shale and limestone were collected at this location. Bedded limestone is on top of bedded shale having thickness around 50 centimeters at exposure as shown in figure 3.6.

Figure 3.6 Limestone outcrop at the top of hill.

3.2 Sample preparation

Bulk samples were washed by distillated water, acetone, and dichloromethane, respectively, to eliminate contaminant. These washed samples were crushed into small pieces by hammer and jaw-crusher before being ground into powder by dish mill grinder. The powder samples were put into pre-washed glassware. All steps were proceeded at Department of Geology, Chulalongkorn University.

3.3 Geochemistry laboratory

3.3.1 Total organic carbon (TOC)

The pulverized samples were analyzed for TOC contents by SHIMADZU TOC analyzer with solid sample module (SSM-5000A) (Sleutel et al., 2007). The procedure is divided two steps including creating standard calibration curves and sample

measurement. This method has been carried out at by Center of Excellent on Hazardous Substance Management (HSM), Chulalongkorn University. Firstly, in standard calibration curves setup, standard calibration curves are detaching in two parts including standard total carbon curve (TC) and standard inorganic carbon (IC). The TC curve was set up by glucose ($C_6H_{12}O_6$: Glc; molecular weight: Mw = 180.156 g.mol^{-1}). They are prepared into five different concentrations including 5, 10, 20, 50, 100 mg. The weighted standards were put in cleaned ceramic boat. Prepared boats were combusted undergo 900° C in 2 minutes under atmospheric oxygen. While, sodium carbonate (Na_2CO_3; Mw = 105.988 g.mol^{-1}) has been used for producing IC curve. The IC standard concentration was weighted as same as TC, but IC was performed within different condition, IC step was used 2.5 molar (M) phosphoric acid (H_3PO_4) for neutralization reaction eq 3.1 that released carbon dioxide (CO_2) from material. Amount of CO_2 was purged at 200° C, then CO_2 is detected by non-dispersive infrared detector (NDIR). The last stage, the difference of two values from TC and IC curves were calculated into completed TOC curve.

$$3Na_2CO_{3(s)} + 2H_3PO_{4(aq)} \rightarrow 2Na_3PO_{4(s)} + 3H_2O_{(l)} + 3CO_{2(g)} \quad \text{(Eq. 3.1)}$$

After calibration setup, the sample measurements are carried out in two parts such a calibration part that measurement in two methods of TC and IC. Firstly, 10 mg of pulverized sample weigh into ceramic boat, prepares for two boats at the same sample, then two prepared boats were carried out by TC and IC mode, respectively. According to IC mode, the neutralization reaction for sample, 2.5 M H_3PO_4 reacted with calcium carbonate ($CaCO_3$) which chemical component in carbonate rock or calcite (eq. 3.2). The second, TC and IC data from samples were correlated to TOC data in accordance to difference of two values. Finally, TOC data from samples are received and reported in percentage per rock weight (% wt.).

$$3CaCO_{3(s)} + 2H_3PO_{4(aq)} \rightarrow Ca_3(PO_4)_{2(s)} + 3H_2O_{(l)} + 3CO_{2(g)} \quad \text{(Eq. 3.2)}$$
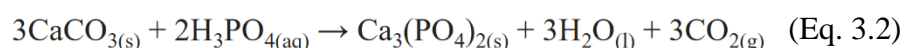
3.3.2 Rock-eval pyrolysis

The Rock-Eval-6 instrument provides a rapid (37 min/sample) source rock analysis on a small (50-70 mg) sample of rock by heating over temperature range of 300-650 °C, after an initial gas purge at 90 °C. This analysis quickly evaluates the concentration of volatile and soluble organic matter, the amount of pyrolysis organic matter and thermal maturity. The pyrogram is shown difference thermal for free hydrocarbon from pulverized rock sample. S1 corresponds to the quantity of hydrocarbon release during isothermal temperature step at 300 °C and shows the temperature of free hydrocarbons contained in the rock that possible methane migrating from the other resource. The maximum temperature with the peak of S_2 is called Tmax S_2 corresponds to the quantity of hydrocarbon release between 300°C and 650°C and represents the hydrocarbon generated from kerogen. The last one, S_3 corresponds to the quantity of hydrocarbon release between 300°C and 390°C and represents organic carbon dioxide release.

3.3.3 Extractable organic matter (EOM)

Organic matters within pore space in sedimentary rock are deformed under certain condition, they can be divided in 2 types: kerogen and bitumen. Bitumen or extraction organic matter from source rock sample reconstructed during organic sediment deposits with diagenesis, catagenesis and metagenesis processes which a tissue degradation as bio-polymer to bio-monomer of living organism deform geo-polymer into petroleum source rock (Tissot and Welte, 1984). Significant bitumen properties are fusion and dispersion in organic solvent that negative in kerogen. Normally, the bitumen and kerogen were packed within sedimentary rock such as shale or limestone, thus organic hydrocarbon compaction can be observed with naked eye to consider organic hydrocarbon quality. For example, black shale can be referred as organic rich shale while organic within brown shale is relatively less than black shale. Bitumen within rocks can be extracted by organic solvent by solid-liquid extraction technique (Chamchoy, 2014; Khositchaisri, 2012; Li et al., 2015; Sachse et al., 2011). The solid phase has contained solutes and bitumen can be dispersed and dissolve in the organic solvent. Then sediment and residues are removed by filtration then the extracted

organic matter is completely to collect. In the heart of parameters of solid-liquid extraction must be regarded as solvent property and duration that depending on quality and quantity of solute that attach on solid phase. This fact, the ancient rock is compatible for long term solid-liquid extraction which has two techniques including continuous-infusion and discontinuous-infusion. This study was selected discontinuous-infusion with soxhlet extractor due to its suitable for laboratory condition (Słowakiewicz et al., 2013). Basically, on the principle in soxhlet extraction is direct contact solvent in long term to solid phase in several times and solvent system recirculated undergo cooling system for repeating the extraction steps. In this study, the extraction solvent follows by Khositchaisri (2012) and Alkhafaji et al. (2015) they suggested to use dichloromethane (DCM; CH_2Cl_2) for bitumen extraction from rock sample including, this study, shale and limestone samples.

In procedure, firstly, 50 grams ground rocks sample was poured into cleaned cellulose thimble and cover the thimble with cleaned cotton wools, then transfer this prepared thimble into soxhlet apparatus (Khositchaisri, 2012). The second, 250 mL DCM was poured into prepared soxhlet from the previous step and prepared thimble have been soaked in 2 hours at least before extraction process. Next, after 2 hours, extraction apparatuses have connected them together including 1000 mL round bottom flask (take 200 mL of DCM into this glassware), prepared soxhlet apparatus and condenser for recirculating system. Then, all of this is setup on the heating mantle with 40-50 °C and cooling water temperature control at 10-12 °C. The extraction process was carried on this condition in 48 hours, since, the first distillation had been begun.

Finally, the extraction process was done, the massive solvent was removed from an extracted and collected for isolation step by rotary evaporator. For evaporation step, the extracted from 1,000 mL round bottom flask was transfer to 250 mL rotary flask then, connected them to condenser instrument part. The organic solvent (DCM) was eliminated from bitumen extraction with 40 °C and vacuum condition until final volume of extraction decreased to estimate 5 mL. Thus, the concentrated bitumen extracted was transfer into 5 mL pre-weighted cleaned vial and one-night stand in fume hood until, it was dried. Ensure all solvents have been removed from bitumen extraction then bring this dried extraction to post-weight for EOM record in part per million (ppm), which is equivalent to milligram of extractable organic matter per kilograms rock (mg/kg).

3.3.4 Cleanup by column chromatography

a

Saturated hydrocarbon

b

Aromatic compound

c

Hetero aromatic compound
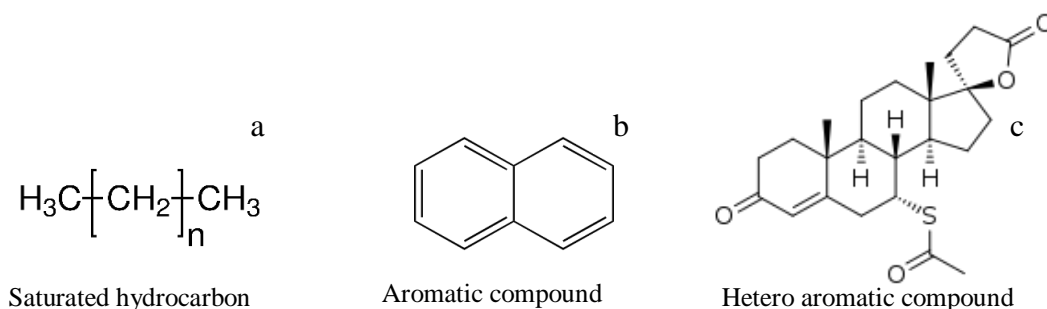
Figure 3.7 a) Saturated hydrocarbon refers non-polar organic structure because of stability electron in atom, b) aromatic compound refers to minor polar molecule due to electron delocalization phenomenon from conjugate double bond, c) hetero aromatic compound refers highest polar in this case because, oxygen, nitrogen and sulfur are the valence electron that effective polar in molecule.

EOM could be regarded as bitumen with variety of chemical composition. Bitumen are saturated hydrocarbon, aromatic hydrocarbon and hetero-aromatic compound (nitrogen, sulfur, oxygen compound; NSO compound) or resin as shown on figure 3.7. In addition, isolation imply petroleum quality from EOM, because the quality of petroleum product depends on chemical property or organic chemical structure. The EOM can be isolated or clean up into three sub-fractions by column chromatography method because, each fraction has different polarity. So, three sub-fractions are isolated by three eluents that different polarity, this method basis on intermolecular force such as dipole-dipole interaction and hydrogen bonding. Basically, the saturated hydrocarbon refers non-polarity compound, it can be eluted by non-polar solvent, for this study use n-pentane (C_5H_{12}). The aromatic compound refers low to moderate polarity compound, it can be dispersed by 60:40 (%v/v) of DCM and n-pentane. The hetero aromatic compound is the aromatic compound with oxygen, nitrogen, sulfur substituted in molecular structure thus, the eluent uses absolute methyl alcohol (CH_3OH) which was high polar eluent (Sachse et al., 2011).

The column chromatography is using for isolation technique by polarity of material or chemical compound, that use two elements phase are stationary phase and mobile phase. The most common stationary phase useful fine particle of silica (silicon dioxide; SiO_2). For this column chromatography method use silica gel 60 with a grain size of 0.063-0.200 mm and 70-230 mesh. These are inorganic materials and are very polar compared to nearly all organic structures. On the other hand, a mobile phase is the three eluents for eluting different polarity fraction. Figure 3.8 shows stationary phase was packed and while carried on by mobile phase.
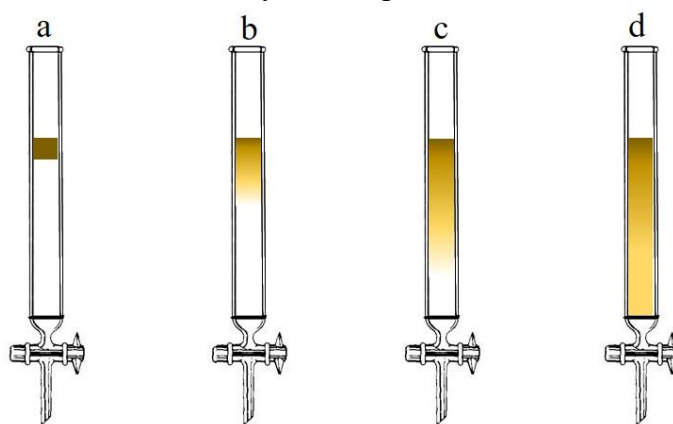
Figure 3.8 a) EOM loading on the top of column, b) the eluent loading and see the fraction getting a tail, that the first isolates step, c) shows duration time makes efficiency of isolation stage, d) first sub-fraction is running out from column then collected and recorded.

In this study, the stationary phase use activated silica gel 60; prepare from heat a silica gel at 120 °C for 8 hours and then keep it in a desiccator to prevent a humidity (Bastow et al., 2007). The amount of silica gel use for EOM purification depending on amount of sample at about ratio 20:1 weight of silica gel comparing to EOM sample in gram unit (Khositchaisri, 2012). 5 mL pasture pipet was taken to clean up process by small-scale column chromatography. Firstly, the pasture pipet was rinsed by distillated water, acetone and hexane, respectively and then was dried under room temperature condition. So, the cleaned pipet was setup on the clamp then take a small size of cotton wool for preventing silica gel running out from the pipet and then, the dried activated silica approximately 0.2 g (for example prepared 10 mg EOM sample; follow in 20:1 silica gel per sample weight ratios) was carried on dried packing method into pipet.

Next, hexane (analytical grade) is added into a prepared pipet and then use bulb for flushing air to increase flow rate for packing silica column (Still et al., 1978), however, carefully column crack during packing step because air bubble released from interspace of silica particle. Since, the column was packed, do not let a column to dry eluent, because column can be cracking by unstable pressure. The second, EOM sample was dissolved by c. 0.5 mL hexane and then dissolved sample is loaded on the top of packed column. First order eluent such a hexane is loaded with three bed volume. After, hexane elution, the second sub-fraction is carried on by 6:4 ratios of DCM: hexane, it uses to elute aromatic fraction from EOM. The final fraction use methyl alcohol for eluting organic polar fraction. Finally, each three fractions are evaporated for increasing concentration of fraction by rotary evaporator, carefully make a fraction volume in rotary flask approximately 2 to 5 mL and then, retain concentrated faction in 2 mL vial. After process, organic solvent was evaporated in receiving flask, it can be reused for cleaning up steps with green environment strategy and budget control. Saturated hydrocarbon fractions which received from cleanup step by n-pentane solvent was collected 1.5 mL adequate into 2.0 mL vial in n-pentane solvent, cap and seal vial, then retain sealed vial under -20 °C for preventing solvent evaporation.

3.3.5 Gas chromatography-mass spectrometry (GC/MS)

Gas Chromatography-Mass Spectrometry (GC-MS) is a usually instrumental technique for identifying molecular mass of organic compound by ionized composition. The sample solution is injected into the ionizing chamber by electron impact, ionized gas flows through the column and separated into compounds by polarity and molecular weight. The separated substances throughout from column and then flow into the mass analyzer equipment. Mass analyzer identifies compounds by the mass of the analysis molecule under electromagnetic field.

In this case, the saturated hydrocarbon fraction was dissolved in n-pentane and analyzed with Agilent 7890B GC and Agilent 7000C GC/MS (Triple quadrupole) at Scientific and Technological Research Equipment Centre (STREC), Chulalongkorn University, with the ion source temperature of 250 °C and ionizing energy of 70 eV. The column used in this study is a 30 m long DB-5 (5% Phenyl Methyl Siloxane) with

250 µm inner diameter and 0.25 µm film thickness. Starting temperature is 80°C and held for 3 minutes. The column temperature is heated from 80 °C to 310 °C at 4 °C/minutes and held for 30 minutes at 310 °C (Chamchoy, 2014; Khositchaisri, 2012). The total analysis time is 90 minutes. Data were acquired in scanning: 35-700 molecular weight and selected-ion-monitored (SIM) for compound identification and integration: n-alkane (m/z 85), terpanes and hopanes (m/z 191) and steranes (m/z 217) (Moustafa and Morsi, 2012).

Chapter IV

Results Interpretation

4.1 Lithological description

The collected samples from four locations cover some part of Permian limestone outcrop exposure of Tak Fa Formation in Phetchabun Province. The sampling locations are distributed in three districts in Phetchabun area including Bueng Sam Phan, Nong Phai and Chon Daen districts as shown in figure 3.1. Totally, nine samples were collected for the study, four samples in Bueng Sam Phan, four samples in Nong Phai and one sample in Chon Daen. General lithology of these nine outcrop samples were classified as limestone, shale and mudstone including argillaceous limestone and then ensure lithological details were proceeded by Core Laboratory, Malaysia. In advantage of lithological description coherence to quantify organic matter richness in different rock types which were determined to quantity criteria (Peters and Cassa, 1994).

The lithology of nine samples is shown in table 4.1 received from Core Laboratory of Malaysia. Northern Bueng Sam Phan (Bueng Sam Phan 1) was picked from two outcrop samples, named as code: BP1-1/1 and BP1-1/2. Southern Bueng Sam Phan (Bueng Sam Phan 2) was collected two bulk samples, named as code BP2-4/1 and BP2-4/2 divided from top and bottom outcrop exposure by BP2-4/1 and BP2-4/2, respectively. Chon Daen was collected only one outcrop sample, named as code CD-2/1. Nong Phai was collected for four samples from both shale and carbonate rocks, named as code NP-3/1, NP-3/2 NP-3/3 and NP-3/4.

Table 4.1 Lithological description and bulk sample figure.

Code	Figure	Lithology
BP1-1/1		• Argillaceous limestone • Light grey color

BP1-1/2		• Mudstone • Light olive grey color • Slightly calcareous
CD-2/1		• Argillaceous limestone • Light olive color
NP-3/1		• Limestone • Brownish grey color
NP-3/2		• Shale • Brownish grey color • Non-calcareous
NP-3/3		• Shale • Olive grey color • Non-calcareous

NP-3/4		• Limestone • Medium light grey color
BP2-4/1		• Argillaceous limestone • Medium light grey color
BP2-4/2		• Argillaceous limestone • Medium light grey color

4.2 Quantity of organic carbon

4.2.1. Total organic carbon (TOC)

TOC is usually primary screening method for revealing amount of organic carbon in material for defining hydrocarbon richness of petroleum source rock.

TOC contents of nine outcrop samples were obtained from HSM, Tak Fa Formation samples ranging from 1.42 wt. % to 4.58 wt.%. They can be classified in good to excellent petroleum potential by TOC contents referring to table 1.1 (Peters and Cassa, 1994). However, some different criteria for defining potential source rock is depended on rock types. According to Peters and Cassa (1994), they specified two criteria of source rock as shale and carbonate rocks by five levels; poor, fair, good, very good and excellent.

Table 4.2 Total organic carbon content and lithological description.

Sample ID	Lithology [a]	TOC (% wt.) [b]
BP1-1/1	Light grey argillaceous limestone	2.05
BP1-1/2	Greenish grey calcareous mudstone	2.18
CD-2-1	Light olive argillaceous limestone	4.05
NP-3/1	Brownish grey limestone	4.58
NP-3/2	Brownish grey shale	1.42
NP-3/3	Olive green shale	1.50
NP-3/4	Medium light grey limestone	3.88
BP2-4/1	Medium light grey argillaceous limestone	2.01
BP2-4/2	Medium light grey argillaceous limestone	2.01

a) Nine selected samples were determined lithological description at Core Laboratory, Malaysia

b) Adequate pulverized samples were analyzed amount of organic carbon content, proceeding at Hazardous Substance Management (HSM) laboratory, Chulalongkorn University

Only two shale samples were found and collected from same location in this study. TOC contents of shale samples are 1.42 wt. % and 1.50 wt.% (TOC fall to 1.0-2.0 wt.%; shale scale), suggesting a good petroleum potential source rock. Seven

carbonate rocks have range of 2.01 wt.% to 4.58 wt. % (TOC more than 2.0 wt.%; carbonate scale), 2.56 wt.% of average, suggesting excellent potential. TOC contents within same locations exhibit similar or almost the same values including between BP1-1/1 and BP1-1/2, between NP-3/1 and NP-3/4, and between BP2-4/1 and BP2-4/2 (table 4.2).

Table 4.3a The TOCs of seven carbonate rock samples from Tak Fa Formation.

Sample ID	TOC (wt. %)[a]	Potential scale (TOC)[b]
BP1-1/1	2.05	
BP1-1/2	2.18	
CD-2/1	4.05	Excellent
NP-3/1	4.58	(TOC content > 2.00 wt.%
NP-3/4	3.88	for carbonate rocks)
BP2-4/1	2.94	
BP2-4/2	2.01	

a) TOC content received from TOC analyzer at HSM

b) TOC richness scale was defined by Peters and Cassa, 1994

As a result, Permian Tak Fa carbonate samples, including limestone at north Bueng Sam Phan (Ban Pho Sawan 1), south Bueng Sam Phan (Ban Pho Sawan 2), Chon Daen (Phu Pra That temple) and Nong Phai areas, are defined as excellent petroleum potential source rock. The Nong Phai samples values between 3.88 and 4.58 wt. % showing high are in same potential scale with excellent petroleum potential source rock (table 4.3a).

Table 4.3b TOC content of two shale samples from Tak Fa Formation

Sample ID	TOC (wt. %)[a]	Potential scale (TOC)[b]
NP-3/2	1.42	Good
NP-3/3	1.50	(TOC range 1.00-2.00 wt.% for shale)

a TOC content received from TOC analyzer at HSM

b TOC richness scale was defined by Peters and Cassa, 1994

Shale samples were collected at only one location at Nong Phai area. Their values range from 1.42 wt. % to 1.50 wt. % as shown in table 4.3b indicating a good petroleum potential source rock. However, TOC contents can be only used to determine amount of organic matter in sedimentary rock. They cannot reveal type and origin of organic matter caused misunderstanding to interpret hydrocarbon potential source rock. Due to organic matter might be rework from another source that maybe inconsistent with depositional environment or sediment facies. Other parameters are used to support organic facies and origin of source rock to confirm organic matter type.

4.2.2. Extractable organic matter (EOM)

EOM or bitumen content was analyzed at geochemical laboratory of department of geology, Chulalongkorn university. The pulverized rock sample was extracted with dichloromethane. After extraction, dichloromethane was evaporated from extracted organic matter by vacuum evaporation, then EOM is isolated into three sub-fractions by cleaned up method with gravimetric and flash column chromatography using by n-pentane, n-pentane: dichloromethane (6:4 % v/v) gradient and methyl alcohol for saturated hydrocarbon, aromatic hydrocarbon and hetero aromatic hydrocarbon, respectively.

Table 4 4 The comparison between TOCs and EOMs

Sample ID	TOC (wt. %)	EOM (ppm)	Potential (EOM)[a]
BP1-1/1	2.05	79.97	Poor
BP1-1/2	2.18	99.28	Poor
CD-2/1	4.05	197.65	Poor
NP-3/1	4.58	197.11	Poor
NP-3/2	1.42	99.75	Poor
NP-3/3	1.50	76.84	Poor
NP-3/4	3.88	118.32	Poor
BP2-4/1	2.01	99.78	Poor
BP2-4/2	2.01	99.36	Poor
Average	**2.63**	**118.67**	Poor

a (Peters and Cassa, 1994)

The bitumen contents of pulverized rock from four studied areas can be extracted in range of 76.84 ppm to 197.65 ppm, the highest content appears on the carbonate rock sample of CD-2/1, on the other hand, the lowest is shale sample from NP-3/3 (Table 4.4). The average bitumen content of Tak Fa samples in this study is 118.67 ppm. According to bitumen contents less than 500 ppm based on (Peters and Cassa, 1994) ,are interpreted as a poor potential source rock due to amount of bitumen less than 500 ppm based on the EOMs criteria. In addition, EOM can be compared with TOC to define hydrocarbon potential of carbonate and shale source rocks as presented in figure 4.1a and figure 4.1b.
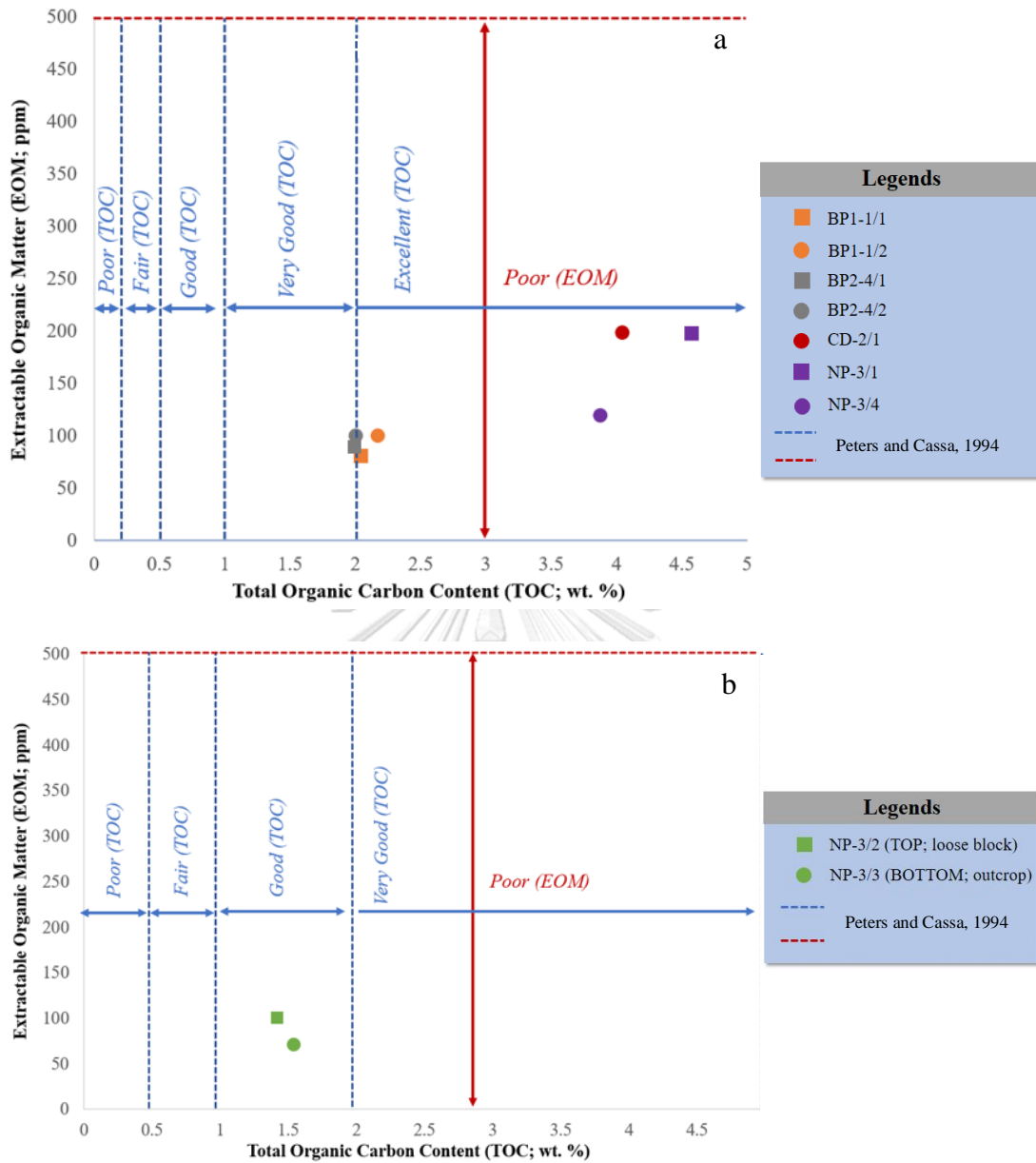
Figure 4.1   a) Diagram shows relationship of carbonate samples between TOC and EOM data; orange dots refers Ban Pho Sawan 1, grey dots refers Ban Pho Sawan 2, red dot refers Chon Daen (Phu-Phra Tat), purple dots refers Nong Phai area. b) Diagram shows relationship of shale samples between TOCs and EOMs data; top green dots refers shale loose block from Nong Phai, bottom green dots refers shale outcrop from Nong Phai area.

4.2.3 Rock-eval pyrolysis

Pulverized rocks 50-70 g were analyzed by Rock-eval 6 instrument at Core Laboratory of Malaysia with temperature program at 300°C to 600°C. The example of rock-eval pyrolysis is shown in figure 4.2a and figure 4.2b represented pyrogram of Phu-Phra Tat samples (CD-2/1).

Figure 4.2a shows the pyrolysis data of pulverized samples. Hydrocarbons are detected by FID detector and provided two parameters as S1 and S2. The first peak (S1) suddenly appear when running on temperature program, and second peak (S2) is raised up with increasing temperature. The first integrated peak area is amount of light-weight hydrocarbon from generated hydrocarbon of kerogen, or amount of EOM in a rock sample. The second integrated peak area is amount of decomposed hydrocarbon during thermal decomposition of kerogen in a rock (Hart and Steen, 2015). After FID detector have already detected hydrocarbons, the temperature program is carried on cooling gas chamber and purge pipeline, then both carbon monoxide (CO) and carbon dioxide (CO_2) are releasing from trapping chamber. Finally, they are detected by NDIR detector and provided S3 as presented in figure 4.2b. Figure 4.2b shows organic and organic O/C atomic ratios that are originate form o-functional group of organic compound and carbonate, respectively. The distribution of hydrocarbon and organic carbon in rock from pyrolysis data is listed in table 4.5.
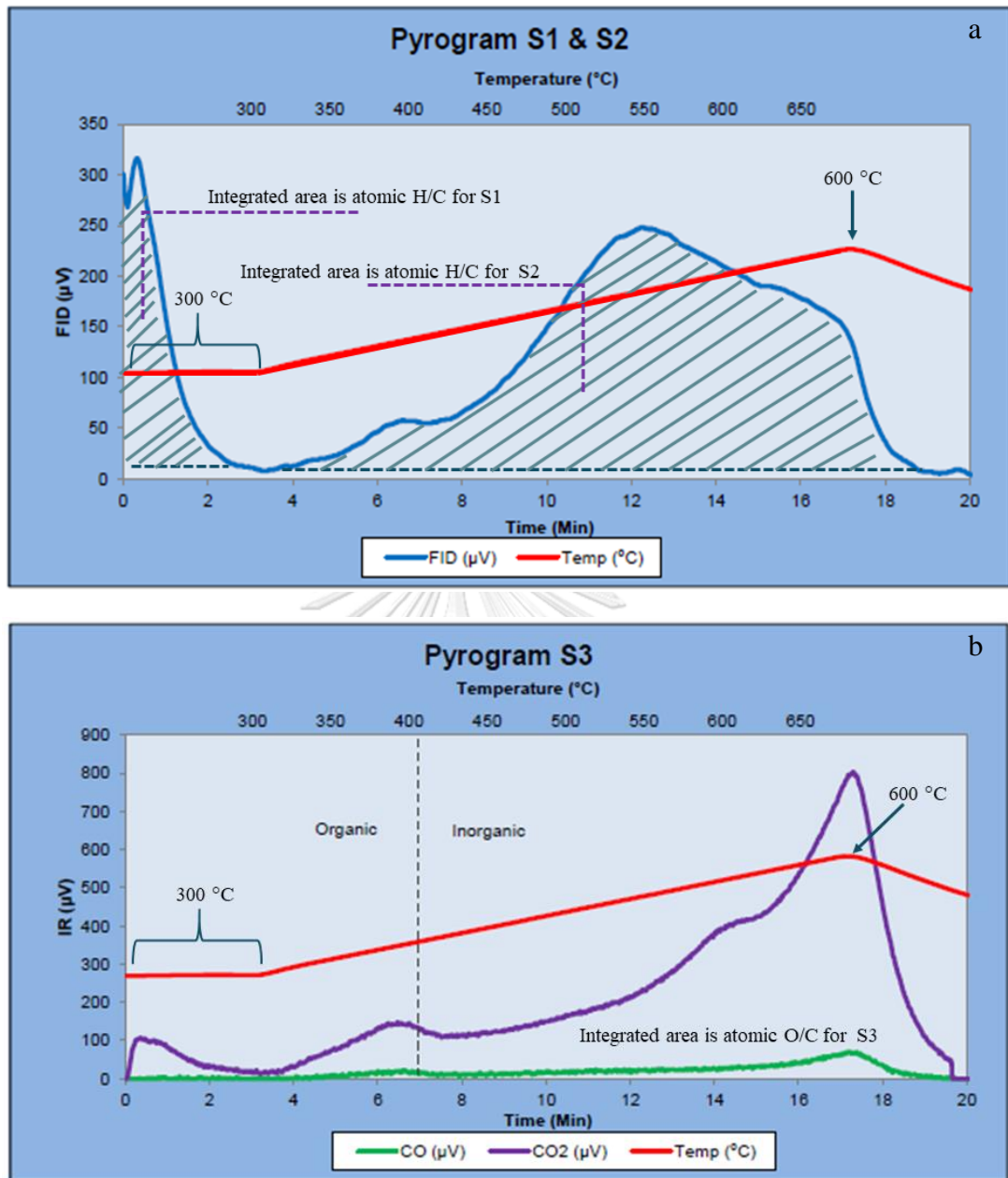
Figure 4.2 a) Pyrograms of carbonate rock sample from Chon Daen sample by FID
detector. b) Pyrogram of carbonate rock sample from Chon Daen sample by
NDIR detector

Table 4.5 The distribution of hydrocarbon and organic carbon in rock sample from
pyrolysis data modified from Jarvie (1991).

Parameters	Material
S1	Gas and oil or EOM
S2	Kerogen (convertible carbon)
S4	Kerogen (residual carbon)

Pyrolysis data consist S1, S2, S3 peaks that can be analyzed with TOC data and converted to be hydrogen index (HI) and oxygen index (OI) with pyrolysis parameters (Eq.4.1 and 4.2). Furthermore, maximum temperature (Tmax; °C) from pyrolysis data can be used to evaluate maturation level of source rock by using production index criteria (PI) as presented in Eq.4.3. Another analysis method, coherence of TOC data and pyrolysis data were used to define trend of kerogen types from organic matter in ancient sediments. Both TOC and pyrolysis parameters are used for kerogen classification by Pseudo Van-Krevelen plot.

$$Hydrogen\ index = \frac{S2\ (\frac{mg\ HC}{g\ rock})}{TOC\ (\%\ wt.)}\ x\ 100 \qquad \text{(Eq. 4.1)}$$

$$Oxygen\ index = \frac{S3\ (\frac{mg\ HC}{g\ rock})}{TOC\ (\%\ wt.)}\ x\ 100 \qquad \text{(Eq. 4.2)}$$

$$Production\ index = \frac{S1}{S1 + S2} \qquad \text{(Eq. 4.3)}$$

Table 4.6 Pyrolysis hydrocarbon parameters for classification source rock type (Peters
and Cassa, 1994).

S1 (mg HC/g rock)	S2 (mg HC/g rock)	Source rock type
<0.5	0-2.5	Poor
0.5-1.0	2.5-5	Fair
1.0-2.0	5-10	Good
>2.0	>10	Very good to Excellent

Table 4.7 Pyrolysis and calculated parameters of rock samples.

Sample ID	TOC (% wt.)	S1	S2	S3	Tmax (°C)	HI	OI	PI
		(mg/g rock)						
BP1-1/1	2.05	0.01	0.01	0.12	469	0	6	0.50
BP1-1/2	2.18	0.01	0.01	0.45	471	0	21	0.50
BP2-4/1	2.01	0.05	0.00	0.05	604	0	2	1.00
BP2-4/2	2.01	0.05	0.00	0.05	425	0	2	1.00
CD-2/1	4.05	0.05	0.26	0.44	485	6	11	0.16
NP-3/1	4.58	0.07	0.50	0.23	563	11	5	0.12
NP-3/2	1.42	0.07	0.45	0.09	565	32	6	0.13
NP-3/3	1.50	0.01	0.02	0.28	524	1	19	0.33
NP-3/4	3.88	0.01	0.02	0.02	600	1	1	0.33

4.2.4 Genetic potential

Genetic potential is amount of hydrocarbon that can be generated and remain in source rock by summation of light hydrocarbon (S1) and hydrocarbon cracking from kerogen (S2). Genetic potential is also used for determining a hydrocarbon potential level of source rock depended on types of organic materials in sedimentary rock.

Table 4.8 Genetic potential scale for source rock assessment (Peters and Cassa, 1994).

Genetic potential status	HC (mg HC/g rock)
Poor	2
Good	2-5
Very good	5-10
Excellent	>10

According to table 4.7, S1 and S2 of all samples in this study are relatively very low values; S1 range from 0.01 to 0.07 mg HC/g rock and S2 range from 0.01 to 0.50 mg HC/g rock that referring genetic potential criteria can be divided into four stages as follow in table 4.8. Figure 4.3a and 4.3b show associated petroleum generation by genetic potential and TOC contents (Abu Al-Atta et al., 2014; Adelzadeh et al., 2014; Hatampour, 2014). Both shale and carbonate rock sample plot into poor zone by low genetic potential. As a result, outcrop samples of Tak Fa Formation can be defined to poor petroleum source rock by genetic potential less than 2 mg HC/g rock.
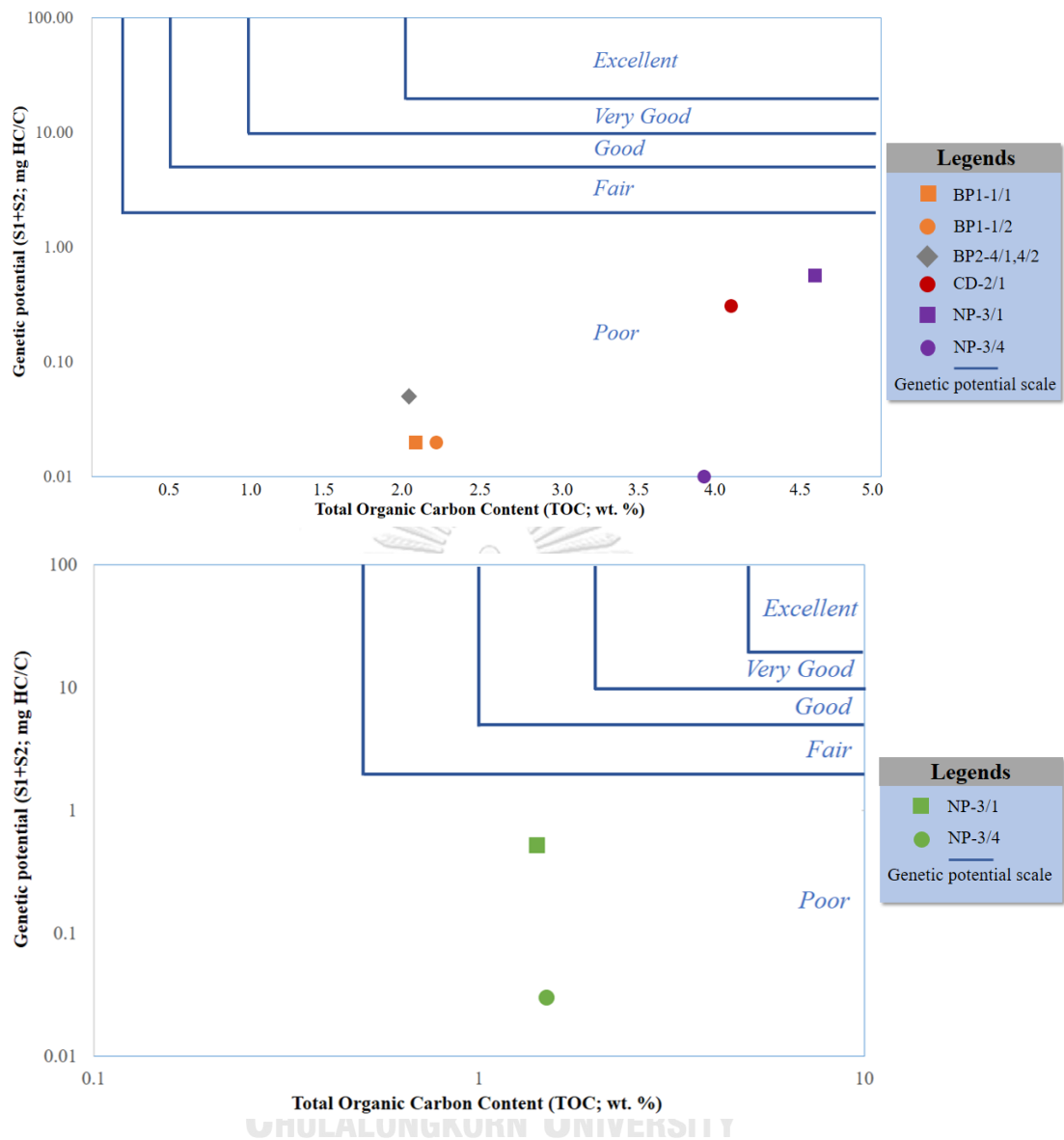
Figure 4.3 a) Bivariate plot for hydrocarbon potential in carbonate rock samples using genetic potential and TOC data. b) For shale sample depending on TOC criteria of shale

4.3 Quality of organic carbon (kerogen classification)

Type of organic matter can be defined by coherence of pyrolysis parameters and TOC contents for converting to HI and OI contents and used to plot in modified Van-Krevelen diagram. Moreover, the relevance of HI and OI depended on prototype of organic matter and condition for preserving of biomass. High HI content is proved that organic matter is deposited under anoxic condition while high OI content is oxidized

organic matter. According to Tissot and Welte (1974), the relationship of HI and OI is used to define type of organic matter or kerogen type including kerogen type I, II and III, moreover, when either organic matter was over mature or biodegradation by microbial, so it is turn into kerogen type IV as non-potential hydrocarbon generation which mostly nitrogen, sulfur and oxygen rich in molecular structure (NSO compound) like inertinite or asphalt as presented in table 4.9.

Table 4.9 HI and OI associate with scanning kerogen type (modified from Tissot and Welte, 1984).

HI (mg HC/ g rock)	OI (mg CO_2/ g rock)	Kerogen type	HC type
700	10-40	I	Paraffinic
350-700	20-60	II	Oil
200-350	40-80	II or III	Oil or Gas
100-200	50-150	III	Gas
0-100	20-200	IV	Some gas
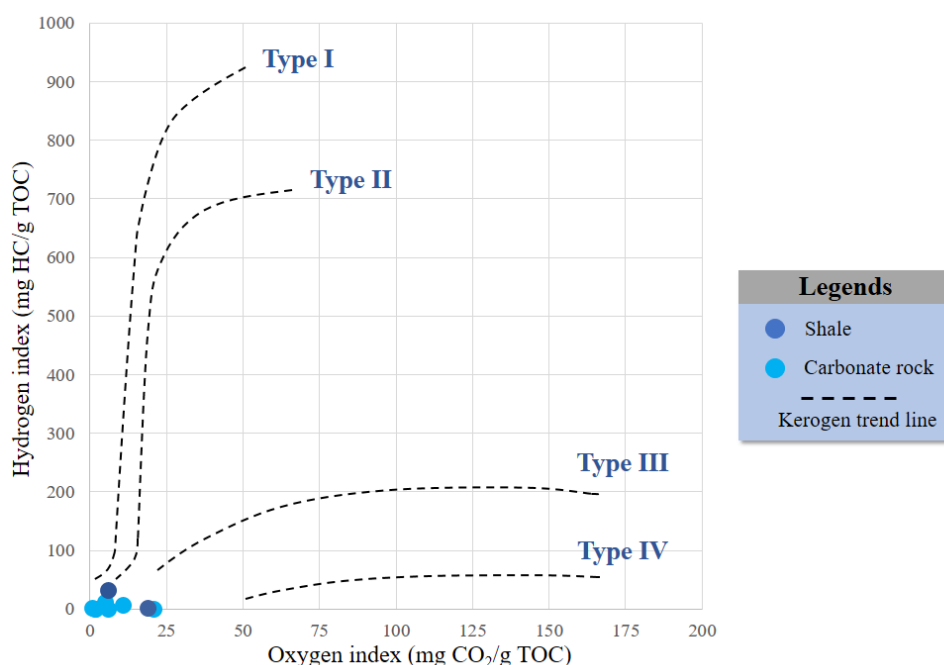
Figure 4.4 Pseudo Van –Krevelen or modified Van –Krevelen diagram, HI and OI used to define type of organic matter of Tak Fa Formation.

Pseudo Van-Krevelen diagram is unqualified kerogen classification of this study by low HI and OI, that are obtained determination error for classifying by quantity of organic matter. Thus, non-biomarker is quality of organic matter using kerogen classification by pristane (Pr)/n-C_{17} and phytane (Ph)/n-C_{18} diagram (Alkhafaji et al., 2015; Sachse et al., 2011; Shanmugam, 1985). As a result, non-biomarker diagram shows organic matter in rock samples of Tak Fa Formation as organic matter type II and III from marine source as shown in figure 4.5.

Figure 4.5 Non-biomarker diagram of Pr/n-C_{17} and Ph/n-C_{18}.

4.4 Maturation level

4.4.1 Maximum temperature (Tmax)

The hydrocarbon product from organism is not only depended on source of organic matter, but also burial pressure, heat and time that are important factors to decompose organic matter into oil and gas. For instance, if the burial depth i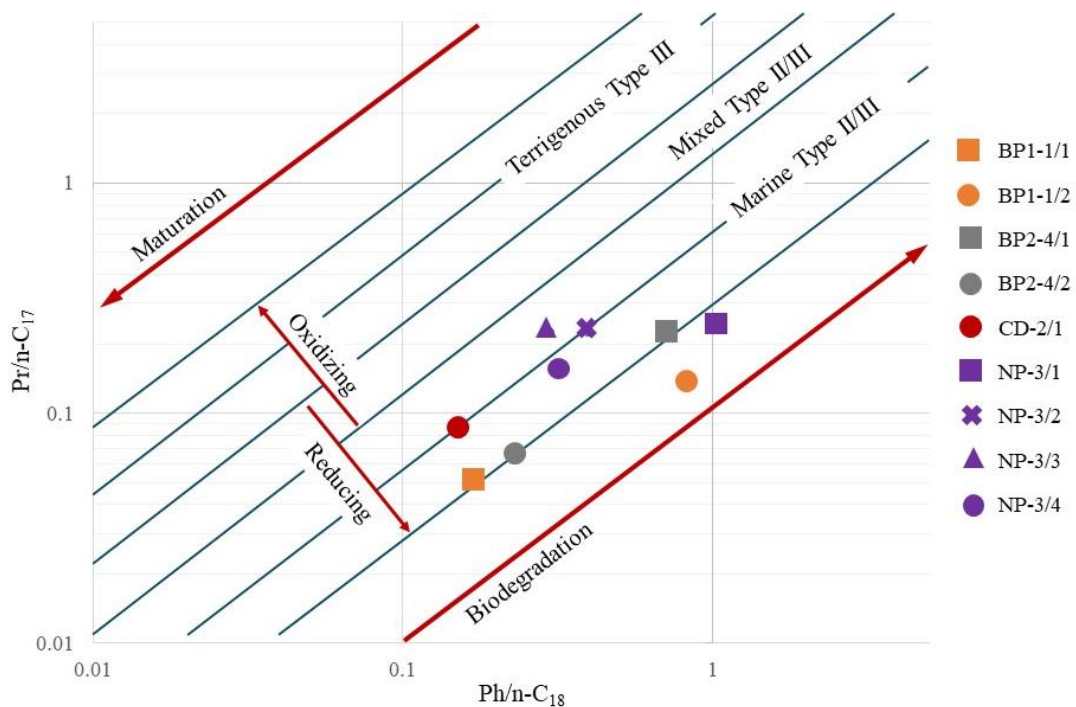s in over heat condition from pressure or geothermal gradient, then organic matter is metamorphosed to asphaltene or graphite. Furthermore, biodegradation of organic matter by micro-organism such as bacteria can be degraded organic molecular structure of organic matter into hetero-aromatic compound (NSO compound) or asphalts reducing amount of light hydrocarbon and petroleum potential in a sedimentary rock. The usage Tmax is usually compared with PI as follow table 4.10 (Tissot et al., 1987).

Table 4.10 Production index of petroleum associates with pyrolysis parameter as Tmax
(Tissot et al., 1987).

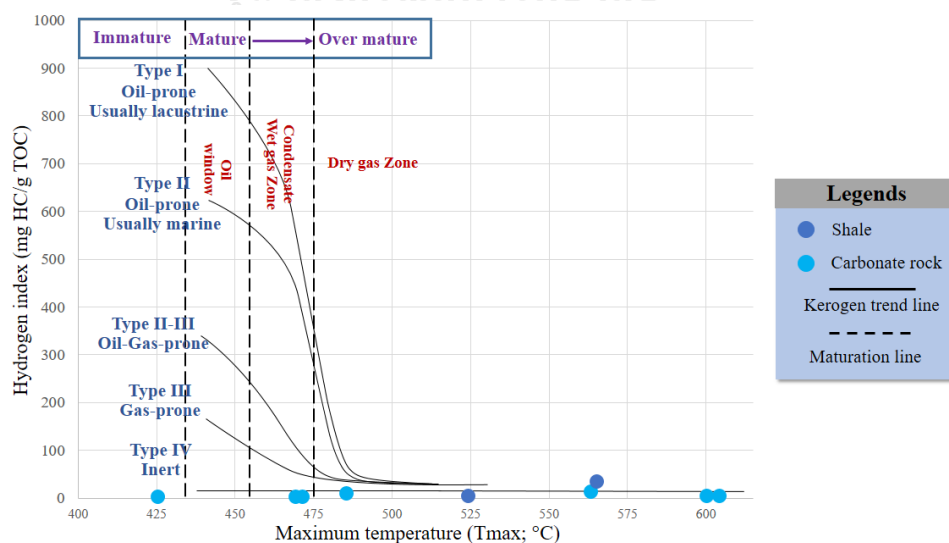| PI (S1/S1+S2)	Tmax (°C)	Maturation
<0.08	<430	Immature for oil
0.08	430-445	Top oil window
0.4	470	Bottom oil window
>0.4	>470	Over mature for oil

Figure 4.6 Coherence of HI and Tmax can be implied type of organic matter by using kerogen trend line from HI values.

As a result, Tmax can be implied maturity level of organic matter due to Tmax is the maximum temperature at S2 apex that used for decomposing hydrocarbon from kerogen in a sedimentary rock. Tmax also associates with transformation ratios (%TR) or production index (PI) of oil and gas products from source rock. However, maturity level can be evaluated by using HI and Tmax in cross plot as presented in figure 4.6 (i.e. Sommemberg, 2011; Hatampour, 2014; Adelzadeh, Hatampour and Ghiasi-Freez, 2014; Mashhadi, 2015). Figure 4.6 shows samples ranging in late to over mature stage except the sample from Bueng Sam Phan 2; Tmax at 325 °C and 425 °C implying immature source rock. In addition, PI and Tmax crossplot provides source rock maturation level as presented in figure 4.7. Figure 4.7 shows that both shale and carbonate rocks in this study have already been over mature at present day. However, the argillaceous limestone samples from Bueng Sam Phan 2 are immature based on Tmax below 435 °C.
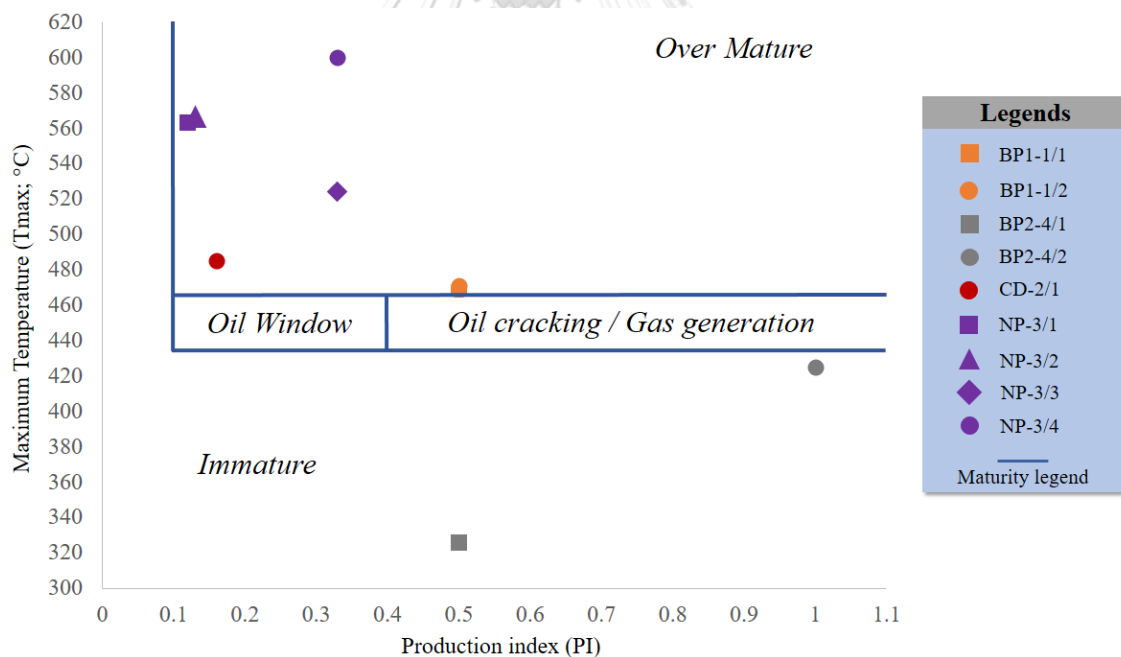

Figure 4.7 Coherence of HI and Tmax can be implied type of organic matter by used of kerogen trend line from HI reference values

4.4.2 Biomarker maturity indicator

Organic materials derived from several living organism have different provenance source. Thus, physical and chemical properties are also different. These properties depend on several factors such as environment of living organism and nutrient. However, physical property of organism is not appropriate for classification ancient materials due to physical degradation in shape of organism, while chemical composition is almost completely remaining the same. Thus, unique chemical composition of living organism is usually used for indicating source of organic matter also known biomarkers or biological markers. They are complex molecules, which mainly consist of carbon, hydrogen, and other elements such as nitrogen, sulfur and oxygen. They can be obtained from crude oils and extracted petroleum source rocks. Biomarkers are usually used to determine depositional conditions and maturity level by natural product. These biomarker structures can reveal more information about their origins than other compounds (Peters et al., 2005b). Biomarker parameters can be archived from GC-MS data.

Biomarkers maturity in sedimentary rock due to thermal alteration is based on measuring the relative concentrations of reactant (A) and product (B) in the following reaction (after Chamchoy, 2014);

$$A \underset{R2}{\overset{R1}{\rightleftharpoons}} B$$

Range from 0 to 1 or 0 to 100% is ratios of the concentration of B to the summarized of A and B (B/(A+B) ratio) associates increasing thermal maturity. R1 and R2 represent the rates of the forward and inverse reactions, respectively (Peters and Moldowan, 1993). Biomarker groups used in this study to estimate maturation stage are terpanes (m/z 191) and steranes (217).

Table 4.11 Maturity indicator by biomarker application from terpanes homologous
(m/z 191)

Sample ID	C_{31} 22S/(22S+22R)	Ts/(Ts+Tm)	Moretane/(Moretane+Hopane)
BP1-1/1	0.58	0.64	0.14
BP1-1/2	0.57	0.48	0.07
BP2-4/1	0.58	0.60	0.09
BP2-4/2	0.59	0.63	0.23
CD-2/1	0.58	0.65	0.10
NP-3/1	0.30	0.46	0.74
NP-3/2	0.59	0.55	0.09
NP-3/3	0.60	0.50	0.09
NP-3/4	0.61	0.54	0.09

4.4.2.1 C_{31}22S/(22S+22R) homohopane isomerization ratio

Homohopane isomerization ratio is used as a maturity indicator. It is measured from the m/z 191 mass chromatogram by selected-ion monitoring (SIM) mode. 22S/(22S+22R) homohopane ratio describes the isomerization conversion of the biological 22R to the geological 22S configuration of homohopane molecules, so this ratio has range 0 to around 0.6 at equilibrium during maturation. The ratio values ranging from 0.50 to 0.54 show maturity of organic matter almost reached to oil generation and the ratios from 0.57 to 0.62 indicate that the oil window has been reached (Moldowan et al., 1986). Homohopane isomerization ratio can be calculated from any or all the C_{31}-C_{35} homohopanes. However, this study uses only C_{31} due to barely appear in mass signal since C_{33} to C_{35}.

C_{31}22S/(22S+22R) homohopane isomerization ratios of Bueng Sam Phan, Chon Dean and Nong Phai areas have values ranging from 0.58 to 0.61 (table 4.11). These ratios suggest that organic matters in this study have been reached at mature stage, except samples from Nong Phai area. Black limestone from Nong Phai shows homohopane ratio at 0.30 indicated immature source rock.

Although C_{31}22S/(22S+22R) homohopane isomerization ratio of Tak Fa Formation samples are consistent with Tmax from pyrolysis data indicating that samples have been reached to over mature, only one black limestone sample from Nong Phai is not consistent with Tmax, because Tmax from NP-3/1 shows 563 °C that falls in over mature level.

4.4.2.2 Ts/(Ts+Tm)

Ts (C_{27} 18α(H)-22,29,30-trisnorneohopanes) and Tm (C_{27} 17α(H)-22,29,30-trisnorhopane ratios are used for Ts/(Ts+Tm) unit. This calculation can be used for maturity indicator in sedimentary rock. During catagenesis, Tm is less stable than Ts, so this ratio is reasonable to investigate organic maturity of sedimentary rocks (Seifert and Moldowan, 1986). Ts/(Ts+Tm) ratio can be calculated from the integrated peak area of Ts and Tm in m/z 191 mass chromatogram at SIM. Organic matter in sedimentary rock is mature when the values of Ts/(Ts+Tm) ratio are between 0.35 and 0.95 (Peters et al., 2005b). In addition, the ratio may also be influenced by variation in lithology, in which carbonate petroleum source rocks is significantly lower than mudstone source rocks (Chamchoy, 2014).

Ts/(Ts+Tm) ratios from this study ranging from 0.46 to 0.65 have been reached at mature stage. The result of Ts/(Ts+Tm) ratios in this study is coincide with Tmax data, only Bueng Sam Phan 2 samples are not consistent. Tmax of Bueng Sam Phan 2 indicates immature stage of organic matter in the rock sample, but Ts/(Ts+Tm) ratio shows in mature stage.

4.4.2.3 Moretane/(hopane+moretane) ratio

The ratio of 17β(H),21α(H)-moretanes and 17α(H),21β(H)-hopanes are used as maturity indicator by moretane/(hopane + moretane) ratio. It is measured from the m/z 191 mass chromatogram at SIM. Moretanes are less stable than hopanes under thermal condition, and the abundance of moretanes decreases relative to the corresponding hopanes with increasing thermal maturity. This ratio decreases with thermal maturity; about 0.8 indicate to immature source rocks, less than 0.15 to 0.05 indicates mature

source rocks (Seifert and Moldowan, 1986). The C_{29} and C_{30} compounds are used for moretane/(hopane + moretane) ratio (Peters et al., 2005b).

Moretane/(hopane+moretane) ratio range from Bueng Sam Phan 1, Bueng Sam Phan 2, Chon Dean and Nong Phai is 0.07-0.14, 0.09-0.23, 0.10 and 0.09, respectively. The ratio range suggests that the samples in this study have been reached at mature stage, except limestone from Nong Phai area. The black limestone from Nong Phai area shows moretane/(hopane+moretane) ratio at 0.74 indicated immature source rock. Moretane/(hopane+moretane) ratios and $C_{31}22S/(22S+22R)$ homohopane isomerization ratios of Tak Fa Formation from this study are consistent.

4.5 Depositional Environment

Biomarkers can provide information about organic facies and depositional environment of the rock samples. In this study, organic facies and depositional environment are interpreted by using pristane/phytane ratios, terpane (m/z 191) and sterane (m/z 217) distributions. In addition, non-biomarker parameters such as n-alkane and isoprenoid distribution, Pr/Ph, Pr/n-C_{17} and Ph/n-C_{18}, can be used to identify the source of organic matter and depositional environment (e.g. Shanmugam, 1985).

4.5.1 Hydrogen and oxygen indices.

The modern scanning method for rough indicating depositional environment of sediments is using HI and OI into Jone's diagram (Jones, 1987). Jone' s diagram can be used to provide the condition for organic matter accumulation .Jones (1987), divided HI and OI distribution into seven zones based on pseudo Van-Krevelen diagram. These zones indicate different deposition environments as followed; A refers to lacustrine environment severely oxidation state, AB refers to reducing marine environment, B refers relatively oxidation state of lacustrine or marine environment, BC refers to environments containing marine and terigenous organic matter in relatively oxidizing condition, C refers waters in oxidizing condition with moderate to rapid of sedimentation in reducing condition, CD refers to deep marines environments, and D refers to deep oceanic to severely oxidizing terrigenous environments. The cartoon in figure 4.8 illustrates the depositional environment based on Jone's diagram.
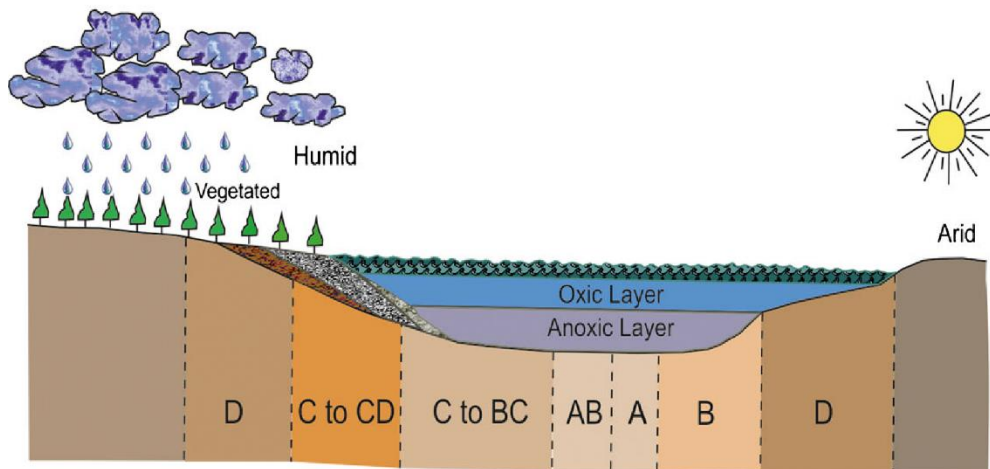
Figure 4.8 Organic facies modeling modified by Yalcın Erik (2015)
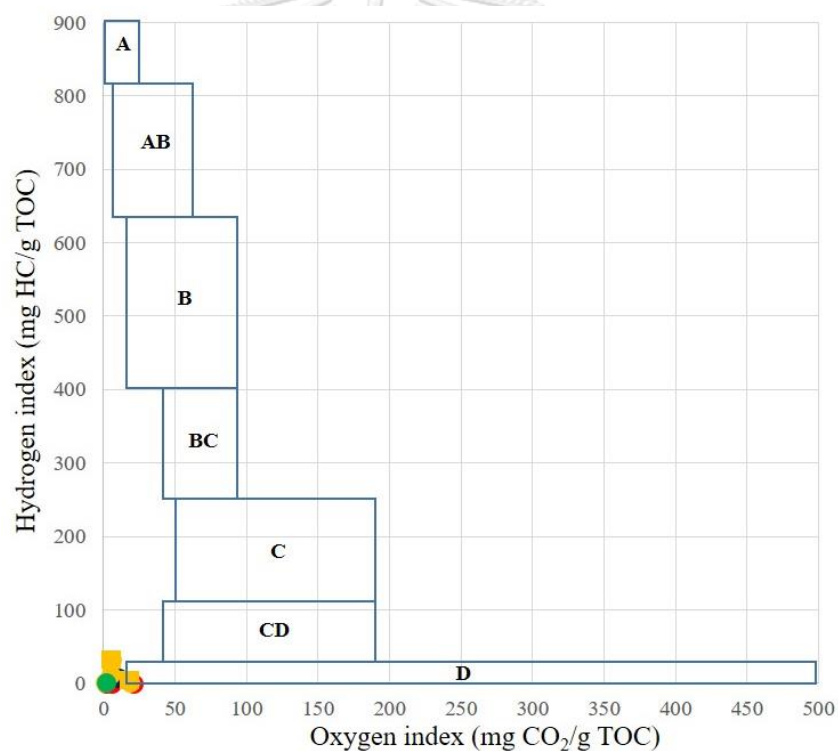

Figure 4.9 Samples from Tak Fa Formation gathering in D section of Jone's diagram

The depositional environment of organic matter from this study based on Jone's diagram indicated that organic materials are occurred within deep oceanic to severely oxidizing terrigenous environments as shown figure 4.9. Nevertheless, the data on this study is out of range from D border by low HI and OI, thus less accuracy for defining by this method.

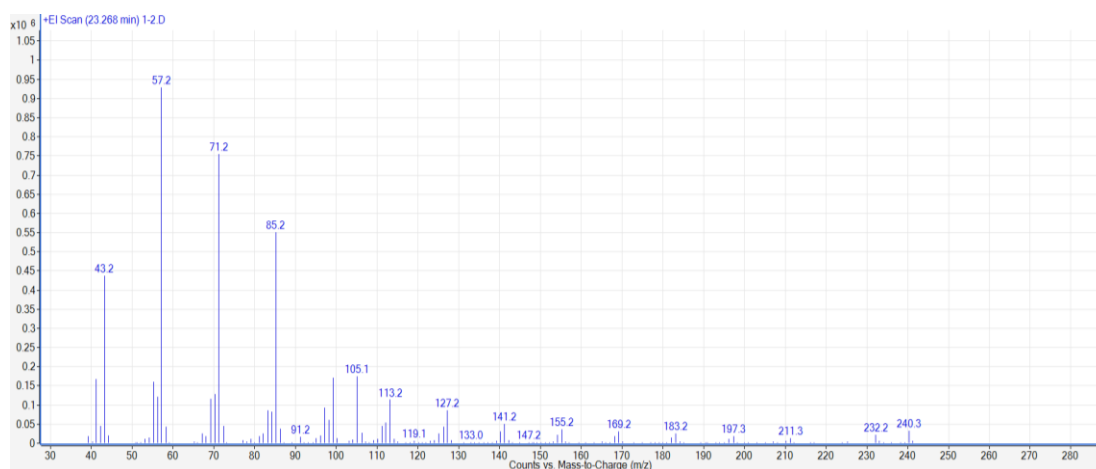4.5.2 Long-chain saturated hydrocarbon distribution (n-alkane)

Figure 4.10 Example of mass spectrum of n- alkane from BP1-1/2 (Ban Pho Sawan 1)

The distribution of n-alkanes from extracted bitumen can be used to indicate the organic matter source measured by GC-MS (m/z 85). The short chain n-alkanes (lower than C_{20}) are characteristic of microbial input. In addition, medium boiling point n-alkanes (nC_{11}-nC_{20}) are considered to indicate algal and/or bacterial origin for the organic material. The long chain n-alkanes (more than C_{20}), high boiling point n-alkane, are commonly attributed to the contribution of terrestrial waxes, especially in the C_{25}-C_{33} range (Peters and Moldowan, 1993).

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

Carbon preference index (CPI) is the ratio obtained from n-alkanes distribution, which divide the summation of the odd carbon-numbered alkanes to the summation of the even carbon numbered alkanes. CPI is specifically used for maturity indication but is also affected by source of organic matters and biodegradation (Tissot and Welte, 1984). CPI values above or below 1.0 indicate immature stage of oil or extract, while values approach to 1.0 indicates mature level (Peters and Moldowan, 1993). In very reducing environments, reduction of long chain fatty acids, alcohols from waxes, and

phytol is prevalent over decarboxylation, which results in predominance of even-carbon-number n-alkane molecules over odd molecules (CPI<1) and a predominance of phytane over pristane. In less reducing environments, decarboxylation results in a most odd n-alkanes (CPI>1) and a predominance of pristane over phytane. Moreover, CPI values less than 1.0 indicate carbonate facies, while CPI values higher than 1.0 indicate lacustrine environment or siliciclastic source rock (Tissot and Welte, 1984). CPI can be calculated as follow in eq. (4.4)

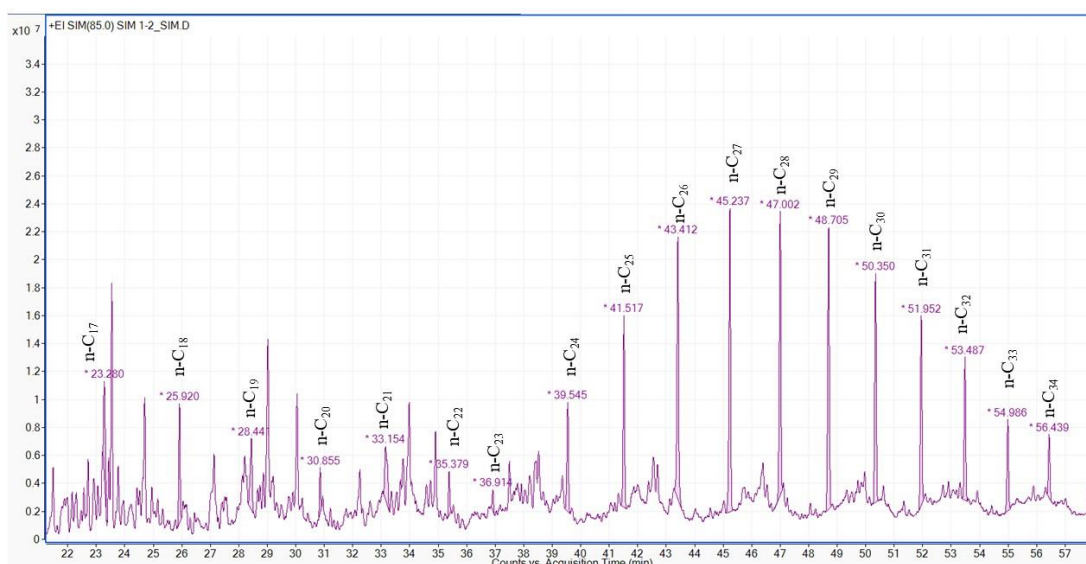$$CPI = \frac{2(C23 + C25 + C27 + C29)}{C22 + 2(C24 + C26 + C28) + C30} \qquad \text{(Eq. 4.4)}$$

Figure 4.11 Mass fragmentogram of normal alkane since n-C_{17} to n-C_{34} from BP1-1/2 (Bueng Sam Phan 1) by SIM mode 85 m/z

The mass spectrum of n-alkane in this study can be proved by using scan mode as shown figure 4.10, it is comparative to mass fragmentogram of SIM mode at 85 m/z for measuring quantity of n-alkane by integrated peak area (Wang et al., 1999), that show in figure 4.11. However, the signal to noise ratio of 85 m/z is very low, some n-alkane signal is near base line involving with low EOM of all samples.

Table 4.12 CPI is obtained from odd (C_{23} – C_{29}) and even (C_{22} – C_{30}) numbers of n-alkane, by CPI equation (Tissot and Welte, 1984)

Sample ID	Location	CPI
BP1-1/1	Bueng Sam Phan 1	1.00
BP1-1/2		1.01
BP2-4/1	Bueng Sam Phan 2	1.01
BP2-4/2		1.00
CD-2/1	Chon Dean	0.93
NP-3/1	Nong Phai	0.97
NP-3/2		1.81
NP-3/3		1.13
NP-3/4		1.29

Carbonate samples form Bueng Sam Phan 1 and Bueng Sam Phan 2 areas are almost similar in CPI values (table 4.12). The CPI from these two locations are around 1.00, because of organic matter has been reached in mature stage. Thus, they cannot be indicated source of organic matter. The argillaceous sample of Chon Daen (CD-2/1) and black limestone sample of Nong Phai (NP-3/1) respectively have CPI values of 0.93 and 0.97 which suggest a reducing environment. However, the other samples of Nong Phai, which are grey limestone (NP-3/4), brownish grey shale (NP-3/2) and olive grey shale (NP-3/3) show the CPI values 1.29, 1.82, and 1.29, respectively. In which, its indicated to less reducing environment or increasing of oxidation stage.

4.5.3 Pristane/Phytane ratio (Pr/Ph)

Pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$) are regular isoprenoid hydrocarbons, which both were derived from the phytol side chain of chlorophyll molecule (Miles, 1989). The phytol can be transformed into pristane of phytane depending on the depositional environment. So, pristane/phytane ratio (Pr/Ph) can be used to indicate oxic/anoxic conditions of depositional environment (Didyk et al., 1978). Anoxic or reducing condition in sedimentation promotes cleavage of the phytol side chain to yield phytol, which undergoes reduction to dehydrophytal and phytane. On the other hand,

oxic or oxidizing conditions promote the competing conversion of phytol to pristine by oxidation of phytol to phytenic acid, decarboxylation to pristene and then reduction to pristane (Peters et al., 2005b). Normally, pristane (Pr) and phytane (Ph) peaks in chromatogram appear as double peaks next to n-C_{17} and n-C_{18} normal alkanes, respectively.

Pr/Ph ratio above 3.0 suggests terrestrial organic matter input under oxidizing environment or oxic condition, and a ratio below 1.0 indicates the sediments were deposited undergo reducing depositional environment or anoxic condition. Whereas, Pr/Ph ratio between 1.0 and 3.0 suggests intermediate conditions or suboxic condition (Didyk et al., 1978). Moreover, Peters et al. (2005b) suggested that if Pr/Ph ratio is less than 0.8 may indicate anoxic condition, commonly saline to hypersaline conditions associated with evaporated and carbonate deposition. However, thermal maturity and type of organic matter in rock samples can be influent on the number of Pr/Ph ratio (Didyk et al., 1978). In addition, Lijmbach (1975) divided Pr/Ph ratios into three indicators that are 1) ratio lower than 2 indicating to reducing aquatic deposition (including marine, fresh water, and brackish water), 2) intermediate ratios 2 to 4 referring to fluvio-marine and coastal swamp and 3) ratio up to 10 and more indicating to peat swamp with oxidizing environment. The possible environment conditions of the rock samples interpreted from Pr/Ph ratio are illustrated in table 4.13.

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Table 4.13 Results of pristane and phytane ratios used for depositional environment
interpretation in this study

Sample ID	Pr/Ph	Environment	Condition
BP1-1/1	4.09	Swamp/Peat swamp	Oxic
BP1-1/2	15.10	Swamp/Peat swamp	Oxic
BP2-4/1	1.86	Aquatic deposition	Suboxic
BP2-4/2	4.64	Swamp/Peat swamp	Oxic
CD-2/1	2.48	Coastal swamp	Suboxic
NP-3/1	3.40	Coastal swamp	Oxic
NP-3/2	1.51	Aquatic deposition	Suboxic
NP-3/3	1.26	Aquatic deposition	Suboxic
NP-3/4	2.44	Coastal swamp	Suboxic

Bueng Sam Phan 1 (BP1) and Bueng Sam Phan 2 (BP2) areas can be classified
as an oxic condition within swamp or peat swamp deposits. Except the sample BP2-4/1
which indicates to a suboxic condition within aquatic deposits because phytane
predominant within ratio higher then 3.0 (table 4.13). The Chon Daen sample indicates
to a suboxic condition within coastal swamp. Both carbonate rock and shale samples
from the outcrop in Nong Phai areas indicate to a suboxic condition within coastal
swamp within aquatic depsotion (NP-3/2, NP-3/3 and NP-3/4 samples). However, the
black limestone sample (NP-3/1) from Nong Phai indicates to an oxic condition.

4.5.4 Pristane/n-C_{17} and Phytane/n-C_{18}

Pristane/nC_{17} and Phytane/nC_{18} ratios are usually used as indicators of
depositional environments, approximate organic matter maturation and level of
biodegradation (Peters et al., 2005b). When thermal is increased, n-alkanes are
generated faster than isoprenoids. Generally, isoprenoid hydrocarbons are more
resistant to biodegradation than n-alkanes, so the early stage of microbial degradation
can be monitored by the ratios of biodegradable to the less degradable compounds.
Thus, the ratio of Pr/nC_{17} is often used for scanning method to determine the relative

state of biodegradation. Moreover, this ratio decreases during weathering process through time (Moustafa and Morsi, 2012).

Pr/n-C_{17} and Ph/n-C_{18} diagram shows depositional environment of organic matter by coherence of n-alkane and isoprenoid distribution as presented in figure 4.12. Tak Fa rock samples from this study fall in marine type II and III, so they can be grouped into three zones based on this diagram. Zone A; Chon Dean (CD-2/1), Bueng Sam Phan 1 (BP1-1/1) and Bueng Sam Phan 2 (BP2-4/2) samples are interpreted to be marine reducing environment. Zone B; Nong Phai shale (NP-3/2 and NP-3/3) and Nong Phai carbonate samples (NP-3/4) are interpreted to be less reducing environment. Zone C; Bueng Sam Phan 1 (BP1-1/2), Bueng Sam Phan 2 samples and black limestone from Nong Phai (NP-3/1) is interpreted to be marine reducing environment. In addition, Bueng Sam Phan 1 and 2 samples including Nong Phai carbonate samples are approach to hypersaline environment (figure 4.12).
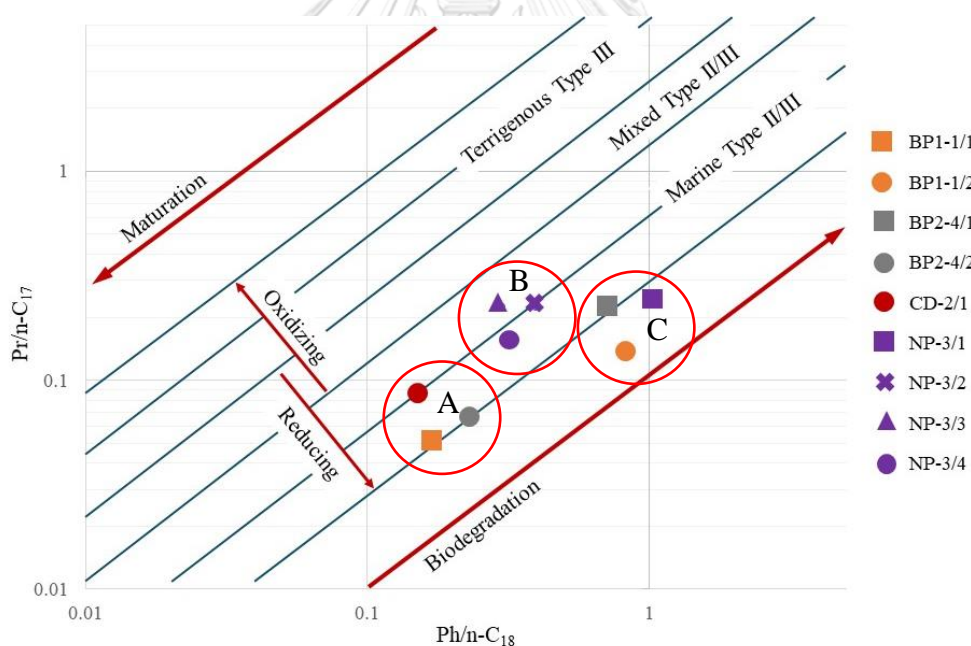
Figure 4.12 Pr/n-C_{17} and Ph/n-C_{18} diagram for interpretation depositional environment of organic matter of Tak Fa Formation indicating marine type II and III (modified from Shanmugam, 1985)

4.5.5 C_{31} 22R homohopane/ C_{30} hopane ratio

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

According to table 4.13, Most of Tak Fa carbonate rocks have C_{31} 22R homohopane/ C_{30} hopane ratio more than 0.25 ranging between 0.26 and 0.45 indicated marine environment, except shale sample form Nong Phai area that shows 0.21 referring to lacustrine environment. Furthermore, the highest C_{31} 22R homohopane anomaly is in NP-3/1 sample from Nong Phai area with 2.90 unit. However, NP-3/1 is also grouped in marine environment based on its value is over 0.25.

4.5.6 Gammacerane index

Gammacerane is C_{30} pentacyclic triterpene can be measured in m/z 191 mass chromatogram by SIM mode. Gammacerane is eluted after C_{31} homohopane 22S and 22R doublet. Gammacerane indicates as stratified water column in marine and non-marine depositional environments and is associated with increasing salinity of the depositional environment (Peters and Moldowan, 1993). The gammacerane index is shown as the ratio of gammacerane/ (gammacerane + C_{30} αβ-hopane).

If gammacerane index is below 0.1, it indicates freshwater depositional environment (Duan et al., 2006). While gammacerane index with a range of 0.1-1.0 suggests saline environment such as the Western Qaidam Oil Field, China and Taq Taq Oil Field, Northern Iraq (Baban and Ahmed, 2008; Duan et al., 2006).

The gammacerane index increase from 0 to 1.0, so that imply increasing of salinity in organic matter during sedimentation, all samples from Tak Fa Formation in this study have gammacerane occurrence that can predict organic matter accumulation under saline environment. Gammecerane index from this study is less than 1.0, around 0.16 to 0.29 at Bueng Sam Phan, 0.10 at Chon Daen and 0.13 to 0.15 at Nong Phai. NP-3/1 sample is considered to high value at 0.67.

Table 4.14 Other biomarker applications for depositional environment prediction of Tak Fa Formation samples in this study.

Sample ID	C_{31} 22R homohopane/ C_{30} hopane ratio	Gammacerane index	Regular steranes/17α- hopanes
BP1-1/1	0.45	0.24	0.26
BP1-1/2	0.39	0.16	0.33
BP2-4/1	0.44	0.19	0.19
BP2-4/2	0.43	0.29	0.47
CD-2/1	0.40	0.19	0.37
NP-3/1	2.90	0.67	1.57
NP-3/2	0.30	0.13	0.46
NP-3/3	0.21	0.15	0.58
NP-3/4	0.26	0.13	0.44

4.4.7 Regular steranes/17α-hopanes

The regular steranes/17α-hopanes ratio has been thought to be an indicator for organic matter sources (Moldowan et al., 1985). High concentrations of sterane and high sterane/hopane ratio ($\geq$1) suggest an aquatic algae and have been observed in many marine and evaporitic sediments. In contrast, low concentrations of steranes and low steranes/hopanes are more indicative of terrigenous and/or microorganism reworked organic matters (Tissot and Welte, 1984). The ratio can be expressed as eq. (4.5)

$$\frac{C27 + C28 + C29 \text{ regular steranes}}{C29 + \ C30 \text{hopanes} + C31 + C32 + C33 \text{homohopanes}} \quad \text{(Eq. 4.5)}$$

According to table 4.14, regular steranes/17α-hopanes ratio at Bueng Sam Phan is between 0.19 to 0.47 imply to terrigenous and/or microorganism reworked organic matters, Chon Daen at 0.37 imply to terrigenous and/or microorganism reworked organic matters, and Nong Phai around 0.44 to 0.58 imply to terrigenous and/or microorganism reworked organic matters, except black limestone sample NP-3/1 shows at 1.57 ratio of regular steranes/17α-hopanes imply to aquatic algae and/or marine and evaporitic sediment. The results from this study indicate that the depositional environment of the study area is more likely to be lacustrine environment based on Regular steranes/17α-hopanes ratio below 1.0. except NP-3/1, those are not consistent with C_{31} 22R homohopane/ C_{30} hopane. So, it is believed that low content of bitumen fraction can be affected leading to an error in some samples. This error may be explained by that regular steranes/17α-hopanes is depended on quantity of chemical composition.

4.4.8 C_{27}- C_{28}- C_{29} regular steranes

The distributions of steranes, C_{27}-C_{28}-C_{29} regular steranes, indicate distinguished different source rocks or organic facies of different facies of the same source rock (Peters and Moldowan, 1993). The relative abundance of C_{27}-C_{28}-C_{29} steranes was converted to a percentage and plotted in a ternary diagram, which peak area measurement was made in m/z 217 mass chromatogram. C_{29} steranes refers to terrestrial higher plants. The lacustrine environment is usually characterized by a higher relative concentration of C_{28} steranes. The presence of higher C_{27} steranes content suggests a marine influenced system from micro-plankton and micro-marine algae. In addition, some C_{28} and C_{27} steranes may derive from fresh water plankton and/or algae (Volkman and Maxwell, 1986).
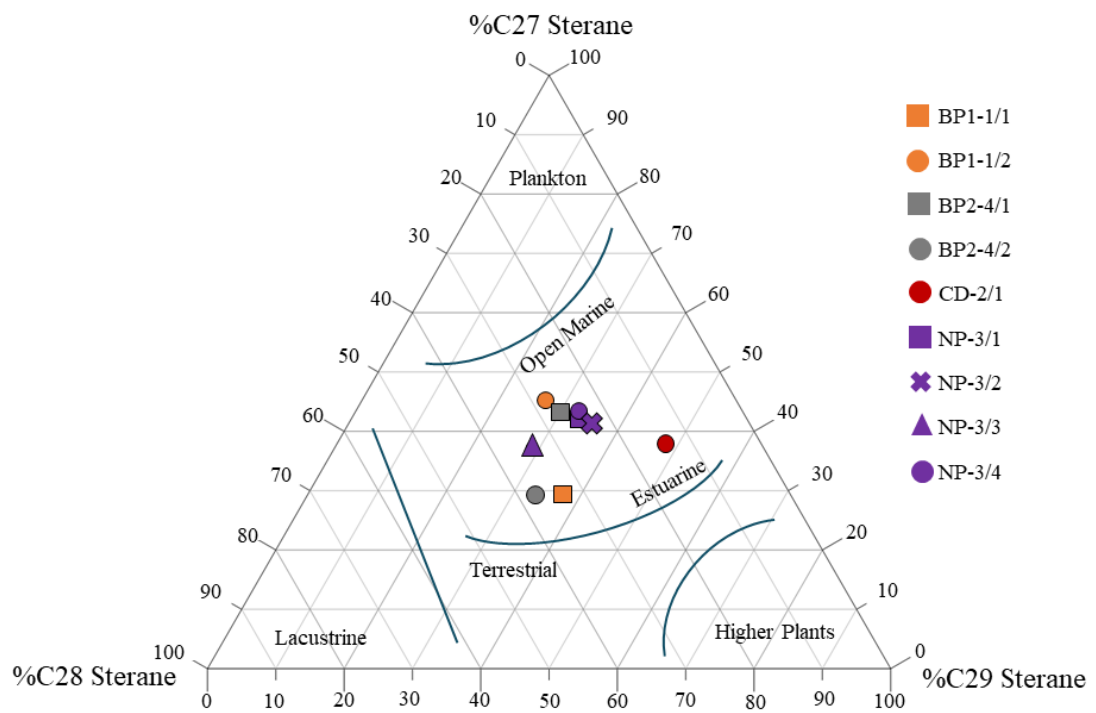
Figure 4.13 Ternary diagram of C_{27}- C_{28}- C_{29} regular steranes distribution of Tak Fa
Formation from this study.

Table 4.15 Relative abundance of C_{27}- C_{28}- C_{29} regular steranes from rock samples used in this study.

Sample ID	%C_{27}	%C_{28}	%C_{29}
BP1-1/1	37.12	29.53	33.35
BP1-1/2	26.81	45.30	27.89
BP2-4/1	47.90	38.11	13.99
BP2-4/2	33.06	42.19	24.75
CD-2/1	35.58	41.36	23.06
NP-3/1	28.88	37.17	33.95
NP-3/2	32.57	43.55	23.88
NP-3/3	29.79	43.38	26.83
NP-3/4	33.25	29.46	37.29
Average	**33.88**	**38.89**	**27.22**

The regular steranes distribution in figure 4.13 of Tak Fa samples can be indicated to hypersaline condition, because all data fall in around estuarine environment. According to table 4.15, the summarized relative abundance of C_{27}- C_{28}- C_{29} regular steranes are 33.88 %, 28.89 % and 27.22 %, respectively, it reveals the C_{28} steranes are higher than concentrations of C_{27} or C_{29} steranes ($C_{27} < C_{28} > C_{29}$). The predominance of C_{28} steranes in studied samples is interpreted as lacustrine environment. However, the predominance of C_{27} and C_{29} steranes in most of the samples is interpreted as strongly indicating a marine phytoplankton and terrestrial input respectively. Thus, it seems likely that there is a mixed source of organic matter within this study area and is coincide with lacustrine environment that sediments can be mixed between marine and terrestrial sources

Chapter V

Discussion

This study, several geochemical investigations are used for petroleum potential assessment and depositional environment of organic matter, including quantity of organic matter as TOC and EOM, petroleum biomarker for type of organic matter, and thermal maturation of organic matter of outcrop samples from Tak Fa Formation in Phetchabun province.

Table 5.1 Summarized of petroleum source rock assessment of Saraburi Group

Publication	Organic richness	Thermal maturation
This study	Poor to Fair	Over mature
Khositchaisri (2012)	Fair to good	Late mature to over mature
Chantong (2007)	Poor to good	N/A
Thongboonruang (2008)	Fair to excellent	Mature to over mature

Summary of petroleum potential assessment in Saraburi Group from previous studies is shown in table 5.1. Organic richness in the sedimentary rocks of Saraburi Group has variation in poor to excellent potential with thermal maturity at mature to over mature and can be predicted petroleum potential as a fair source rock by TOC at 0.37 wt.% and EOM at 534 ppm based on Peters and Cassa (1994). Petroleum source rock exploration of Saraburi Group has been study in several area including Tak Fa Formation in Bueng Sam Phan area Phetchabun Province (Khositchaisri, 2012).

5.1 Hydrocarbon potential

The preliminary method to define quantity of organic matter is TOC and EOM contents as kerogen and bitumen richness in a rock, respectively. The interpretation between TOC and EOM contents provides relevance hydrocarbon potential of source rock, in accordance with, chapter I bitumen is amorphous solid, so it can flow in source rock and reservoir. Thus, apart from TOC content imply overall organic hydrocarbon richness but bitumen content can be implied petroleum potential of source rock. Both

saturated hydrocarbon and aromatic hydrocarbon as bitumen sub-fraction can be interpreted absolute hydrocarbon potential that generated from bitumen or kerogen and provides to oil and gas product.

To date, insufficient information about petroleum source rock potential of Tak Fa Formation, only few sample locations were analysed by Khositchaisri (2012) from argillaceous limestone in Bueng Sam Phan area. (Khositchaisri, 2012) suggested that Tak Fa Formation shows 0.37 wt. % of TOC content indicated to fair petroleum potential as follow by Peters and Cassa (1994). Also, from her study, bitumen content shows 534 ppm falling in fair potential as follow by Peters and Cassa (1994). Thermal maturation is defined to late mature or gas window by Tmax at 463 °C. In which, S2 data form Tak Fa Formation lower than 1.0 mg HC/g rock (Khositchaisri, 2012) is confirmed low hydrocarbon content as well. However, low hydrocarbon and bitumen contents are occurred on outcrop sample by weathering process (Leythaeuser, 1973), especially, tropical zone like Thailand.
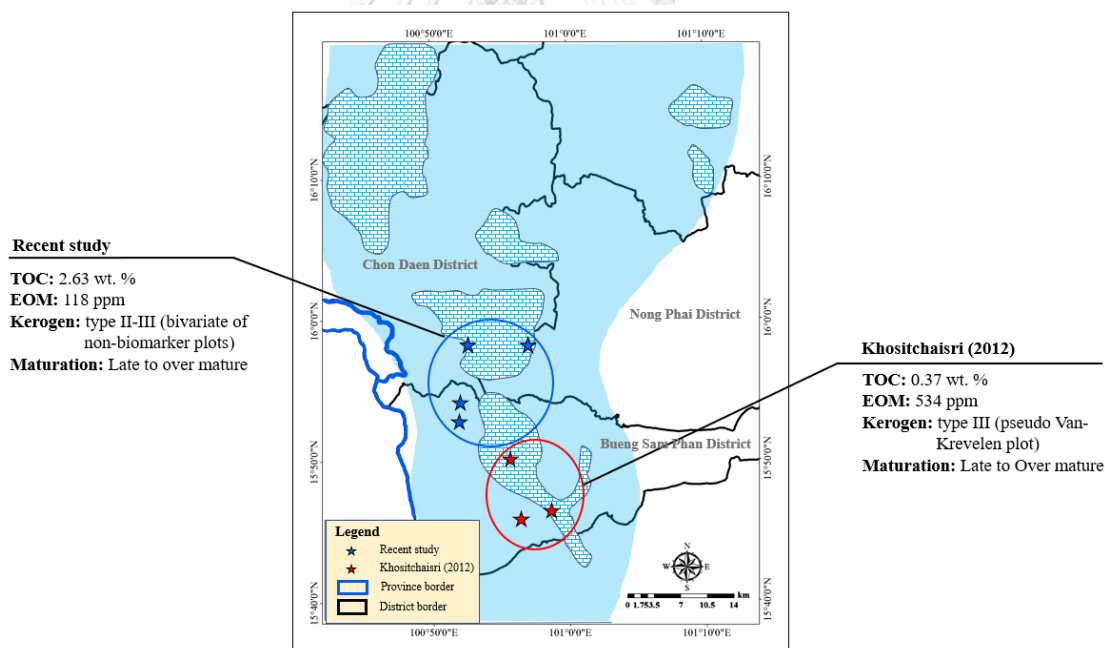
Figure 5.1 The comparison of geochemical data of Tak Fa Formation between this study and Khositchaisri, (2012).

This study, Tak Fa Formation samples have average TOC 2.63 wt. % to suggest excellent potential source rock by Peters and Cassa (1994). However, average EOM 118 ppm indicates poor potential by Peters and Cassa (1994) scale owing to outcrop

sample would be weathered by water flood and rainfall influence loss of organic matter. In addition, Tmax at least 470 °C were used to confirm late mature to over mature stage. To compare with Khositchaisri (2012) study as shown in figure 5.2, TOC content of this study is higher than her study. In addition, TOCs and EOMs intensity are increased from south to north of Khao Kwang Platform. However, high TOC content is appeared in this study, it can be predicted to high ratios of inert organic matter as high hetero aromatic compound that non-effective for petroleum production.

For this study, at the same of latitudinal, TOC values from carbonate rock in this study are similar values. TOCs intensity from the north of the study area is higher than the south with 4.05 wt. % at Chon Daen and average 4.23 wt. % at Nong Phai compared with 2.12 wt. % at Bueng Sam Phan 1 and 2.05 wt. % Bueng Sam Phan 2 figure 5.3. Also, the low bitumen contents located in Bueng Sam Phan 1 and Bueng Sam Phan 2 which are lower than Chon Daen and Nong Phi at northern area. However, the samples are defined to poor source rock by low bitumen content. In which, supporting by barely S2 appearance lower than 0.05 mg HC/ g rock that defines to low hydrocarbon cracking form kerogen.
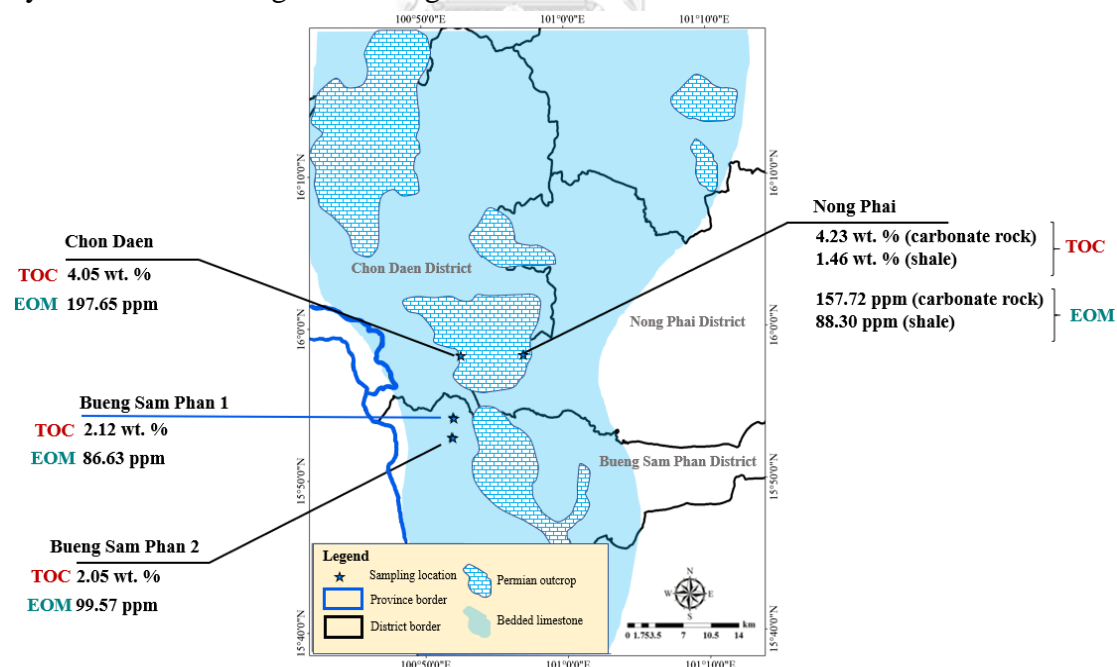
Figure 5.2 The result of TOCs and EOM from this study parted of Tak Fa Formation in Khao Khwang Platform, Phetchabun Province.

In summarized, Tak Fa Formation can be indicated to no petroleum potential at this time. In addition, in accordance with figure 4.3a and figure 4.3b represents hydrocarbon generation involved light hydrocarbon and decomposed hydrocarbon from kerogen or genetic potential with TOCs contents, that suggested to poor hydrocarbon generation also high production index.

5.2 Thermal maturation

Tmax and biomarkers including C_{31}22S/(22S+22R) homohopane isomerization ratio,Ts/(Ts+Tm), and Moretane/(hopane+moretane) ratio are indicated late to over mature Mostly Tak Fa samples are associated maturity indication with Tmax as physical parameter and biomarker, but some carbonate sample including BP2-4/2 and NP-3/1 are out of range for Tmax and biomarkers indication. However, thermal maturation of Tak Fa sample can be indicated late to over mature kerogen, that defines petroleum generation have already been expulsion form source rock. The conjugation of thermal maturity data, from both physical (Tmax) and chemical (biomarkers) as shown in table 5.2.

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Table 5.2 Assemblage of thermal maturation data of Tak Fa Formation in recent study.

Sample ID	Tmax (°C)		S2 (mg HC/g rock)	C31 22S/(22S+22R)		Ts/(Ts+Tm)		Moretane/(Hopane+Moretane)	
BP1-1/1	469	Late mature	0.01	0.58	Late mature	0.64	Late mature	0.14	Late mature
BP1-1/2	471	Late mature	0.01	0.57	Late mature	0.48	Mature	0.07	Late mature
BP2-4/1	604	Over mature	0.00	0.58	Over mature	0.60	Late mature	0.09	Late mature
BP2-4/2	425	Immature	0.00	0.59	Over mature	0.63	Late mature	0.23	Late mature
CD-2/1	485	Over mature	0.26	0.58	Over mature	0.65	Late mature	0.10	Late mature
NP-3/1	563	Over mature	0.50	0.30	Immature	0.46	Mature	0.74	Immature
NP-3/2	565	Over mature	0.45	0.59	Over mature	0.55	Mature	0.09	Late mature
NP-3/3	524	Over mature	0.02	0.60	Over mature	0.50	Mature	0.09	Late mature
NP-3/4	600	Over mature	0.02	0.61	Over mature	0.54	Mature	0.09	Late mature

5.3 Type of organic matter

According to table 4.7 in Chapter IV, HI and OI of all samples are too low values ranging from 0 to 32 mg HC/g rock of HI, while OI range from 1 to 21 mg CO_2/g rock. Cause of low HI and OI in sedimentary rocks is weathering on outcrop samples by sunlight, wind and rain, that effect to reworked material from origin source including hydrocarbon in molecular of organic matter also carbon oxide. For example, chemical weathering process carried on neutralization reaction show in eq. 3.1 in chapter III, carbonate rock can be reacted with acidic solution and release carbon dioxide from carbonate elements, thus this reaction affects to low OI in whole rock samples (Petsch et al., 2000). This is a problematic factor that causes to classify kerogen type. As a result, it seems like that Tak Fa carbonate and shale samples can be grouped in kerogen type IV (figure 4.4). Although HI is shown out less than 100 mg HC/g rock, OI index is not accorded to kerogen type IV due to OI less than 50 mg CO_2/g rock. Thus, Pseudo Van Krevelen diagram is not appropriate to classify kerogen type of Tak Fa samples in this study possibly due to quantity of HI and OI.

However, the quality of organic material can be used to typing organic matter of outcrop as non-biomarker. Although, organic matter was decomposed by thermal under burial depth and/or weathering process, the skeleton of organic compound maybe retains, and occurs in occasional trace element. Non-biomarker data for organic matter typing is Pr/n-C_{17} and Ph/n-C_{18}, both long-chain alkane and iso-alkane have obtained from m/z 85 by SIM mode or using reference standard, recent study receives both parameters by first suggestion. Figure 5.4 shows kerogen typing comparison between pseudo Van-Krevelen and iso-alkane/n-alkane ratios diagram.
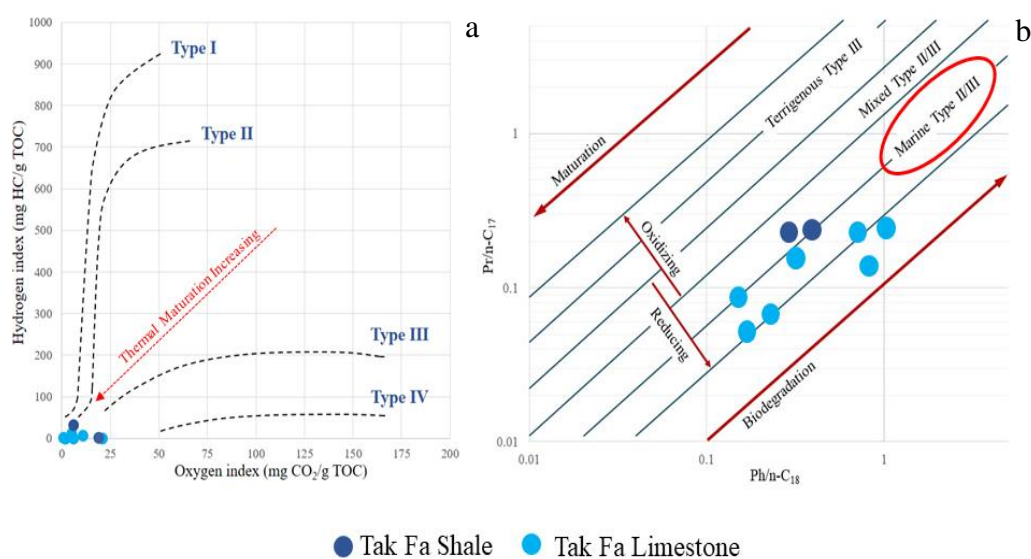
Figure 5.3 a) Pseudo Van-Krevelen plot and b) iso-alkane/n-alkane ratios plot.

The figure 5.4a is illustrate unpredictable kerogen type of both shale and limestone of Tak Fa Formation, because the data is out from kerogen trendline. In which cannot be suggested kerogen type owing to low HI and OI. On the other hand, figure 5.4b is presented organic matter of both Tak Fa rock types to kerogen type II/III that derived from marine sediment with organic matter possibly from marine algae and marine plankton.

In summarized, recent study of Tak Fa Formation consists clastics and carbonate rocks are showed non-potential source rock by over mature stage, and S2 content has lower than 1.00 mg HC/g rock that supporting kerogen already turn into free-hydrocarbon. Thus, in accordance with figure 5.4a on Pseudo Van-Krevelen plots were indicated kerogen type IV by low HI and OI. But, non-biomarker is used to indicate kerogen type II and III within diterpenoid and n-alkane evidences by chemical component residues.

5.4 Depositional evironment

According to Chitnarin (2007), Tak Fa Formation in Khao Khwang Platfrom at Bueng Sam Phan area is used to define depositional environment of carbonate platform by using ostracod study. Chitnarin (2007) suggested that the percentage of ostracod assemblages at superfamily/family level form fifteen ostracod species has been identified and that give evidence for a shallow marine, euryhaline, nearshore environment. Similarly to this study, the geochemical analysis indicated as estuarine environment by C_{27}, C_{28}, C_{29} regular steranes, that are consistent with ostracod species in Tak Fa limestone (Chitnarin et al., 2008).
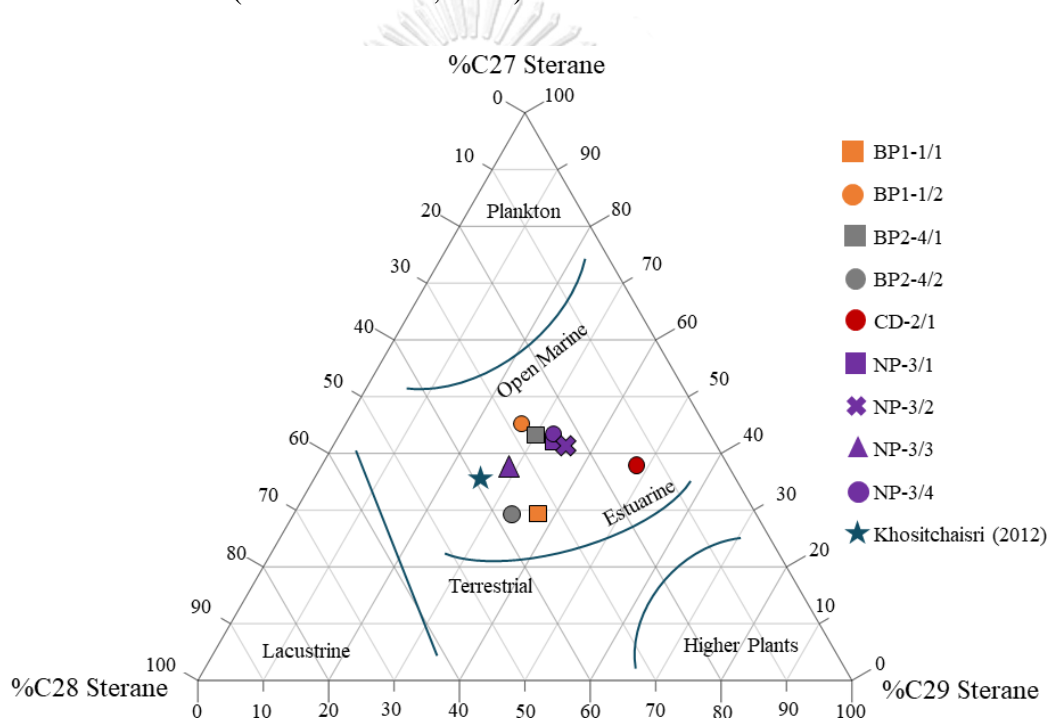
Figure 5.4 C_{27}, C_{28}, C_{29} regular steranes in this study compared to (Khositchaisri, 2012).

This study and Khositchaisri (2012) suggested Tak Fa Formation is in estuarine environment by C_{27} around 35%, C_{28} around 39 %, and C_{29} around 26 % as shown in figure 5.5. The estuarine environment refers to transitional zone, in which transition from fresh to saline water including tidal influence and water salinity lower than sea water. The geochemical data in part of terpanes homologous, all samples from this study show gammacerane occurrence at m/z 191 by SIM. Organic facies are confirmed by bivariate plot of non-biomarker (diterpenoid/n-alkane) between Pr/n-C_{17} and Ph/n-C_{18} as shown in figure 5.6.
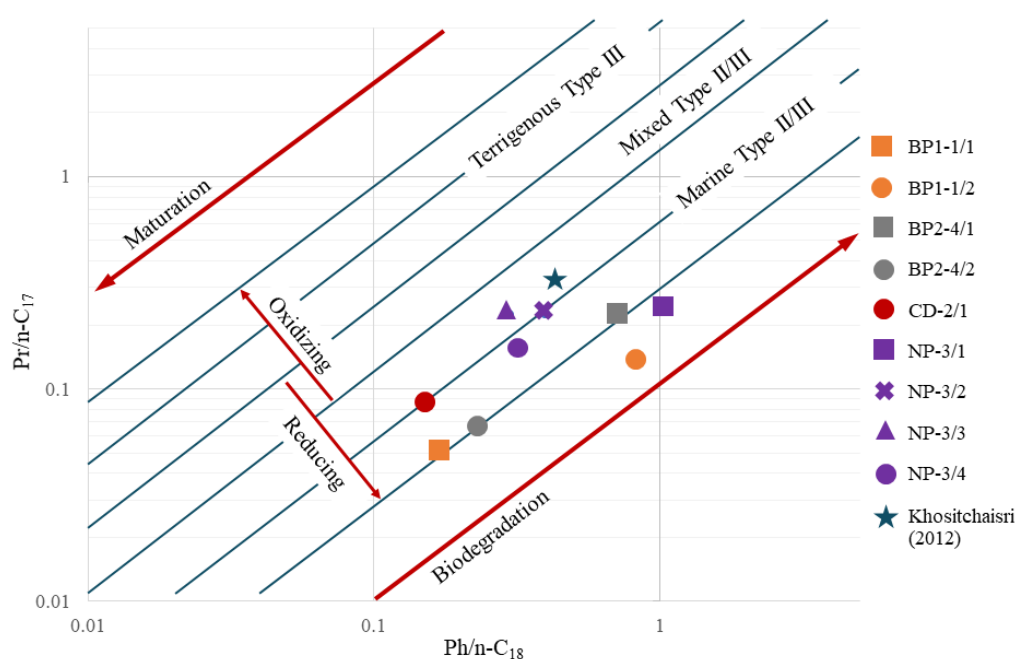
Figure 5.5 Organic facies from Tak Fa Formation comparison between (Khositchaisri, 2012) and this study.
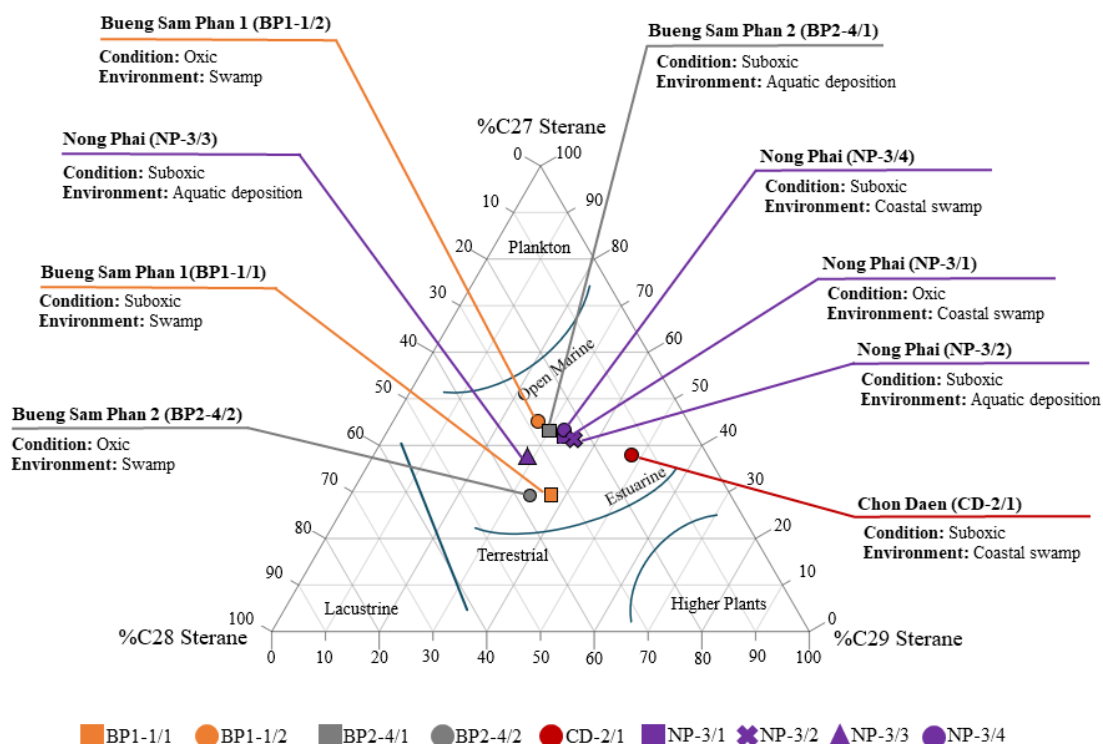
Figure 5.6 Biomarker and non-biomarker discuss depositional environment of Tak Fa Formation of current study.

Besides, in accordance with figure 5.6b, diterpenoid/n-alkane between Pr/n-C$_{17}$ and Ph/n-C$_{18}$ diagram revealed preliminary of depositional environment of organic matter. In which, organic matter accumulated under reducing-saline environment with marine influence. In addition, the depositional environment of Tak Fa Formaion can be discussed by biomarker as C$_{27}$, C$_{28}$, C$_{29}$ regular steranes and non-biomarker as Pr/Ph ratios as shown in figure 5.7 that can be discussed as follow:

1. Bueng Sam Phan 1 area can be defined to estuarine environment with swamp and oxic to suboxic condition.

2. Bueng Sam Phan 2 area can be defined to estuarine environment with swamp and aquatic deposition in oxic to suboxic condition.

3. Chon Daen area can be defined to estuarine environment with coastal swamp and suboxic condition

4. Nong Phai area (carbonate rock) can be defined to estuarine environment with coastal swamp in oxic to suboxic condition.

5.   Nong Phai area (shale) can be defined to estuarine environment with aquatic deposition in suboxic condition.
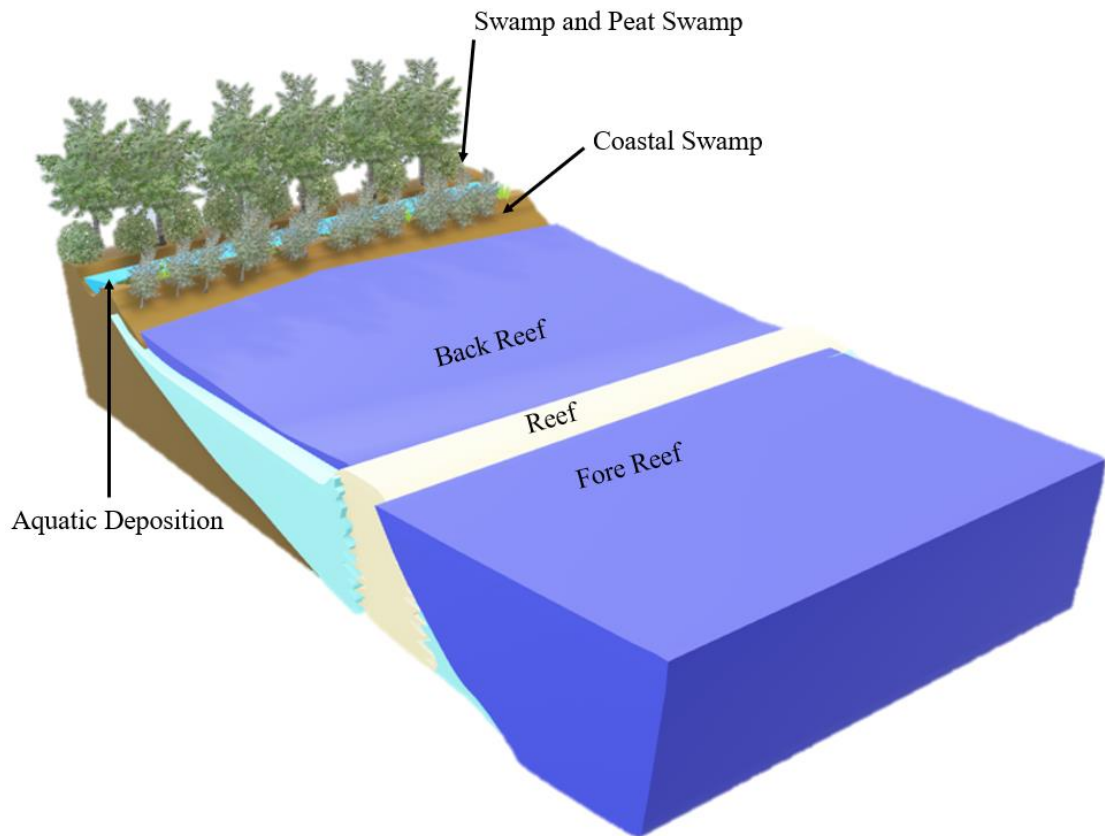
Figure 5.7 Estuarine depositional environment modified after Earle (2015).

Consequently, geochemical data show that Tak Fa Formation is in transitional zone, estuarine environment around back reef deposition. Figure 5.8 represents depositional zone for organic matter accumulation into two zones including swamp zone, and back reef zone. In accordance with swamp deposition can be found floating plant, which part of aquatic deposition.
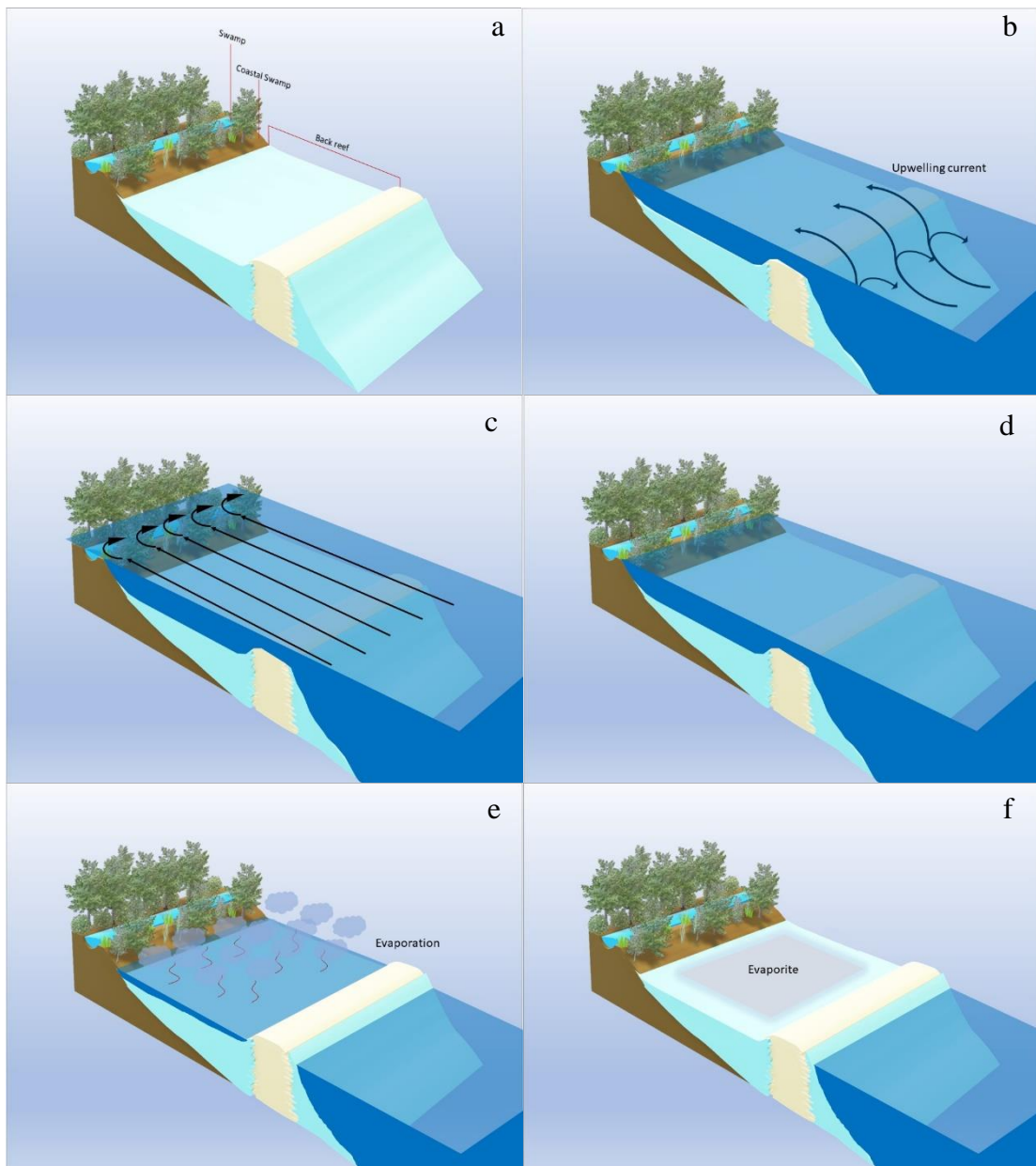
Figure 5.8 Transitional zone modeling of this study area with sea level fluctuations.

Three-dimensional model of transitional zone of the study area shows sedimentation events, which control by sea level fluctuations as shown in figure 5.9. The paleo-depositional environment of Tak Fa Formation, which setting in back-reef environment. When, sea level rises with upwelling current, fine-grain sediments and organic matters were transported into back-reef zone as shown in figure 5.9b. While sea level continuously rises, then sea water has been transgressed to swamp and aquatic zone, thus sediments in swamp is transported to back-reef zone by circulating wavy

current as shown in figure 5.9c. When sea level drops as shown in figure 5.9d and figure 5.9e, thus sea water is trapped in back-reef zone. Then sea water has been continuously evaporated by heat and turn into evaporite as shown in figure 5.9f. The evidence of evaporite in study area shows in argillaceous limestone in Bueng Sam Phan 2 as shown in figure 5.10 by teepee structure.

Figure 5.9 Teepee structure evidence occurred on argillaceous limestone.

In summarized, according to Jone's diagram from figure 4.9 represents organic matter was several oxidized from terrigenous source to deep marine source that widely source of sedimentation. Because of organic matter in swamp would be mixed from terrigenous sediments, and then sea level raised with circulating wavy current its transfer organic matter from swamp to back reef deposition as shown in figure 5.9c. Furthermore, upwelling current transgressed fine-grain sediment and organic matter from deep marine depositing into back reef as shown in figure 5.9b. Thus, diterpenoid/normal-alkane plots show organic matter is type II and III as shown in figure 4.5.

Chapter VI

Conclusion

Petroleum potential source rock assessment of Tak Fa Formation and adjacent area in Phetchabun Province of this study are reveal non-potential petroleum source rock. Even though, TOCs is high as excellent organic matter degree (more than 2.0 wt. % in carbonate rock), EOM or bitumen extraction in rock is lower than 500 ppm as poor petroleum source rock grade. Low bitumen contents involve pyrolysis parameter as genetic potential, that show all sample less than 1.00 mg HC/g rock. Indeed, organic matter in rock has already been generated hydrocarbon into petroleum product and no more in recently. Tmax from S2 is confirmed organic matter maturation in late to over mature by 469 °C to 604 °C also Moretane/(Hopane+Moretane), Ts/(Ts+Tm) and C31 22S/(22S+22R) ratios as well.

For kerogen classification, Pseudo Van-Krevelen diagram has been indicated sample to kerogen type IV by low HI and OI contents. In which, high thermal maturation and weathering outcrop sample. So, this study using bivariate non-biomarker plots that indicates source of organic matter by chemical components. The Pr/n-C$_{17}$ and Ph/n-C$_{18}$ plots indicated organic matter to kerogen type II/III.

The depositional environment of organic matter of Tak Fa Formation in this study reveal estuarine environment at overview by C$_{27}$, C$_{28}$ and C$_{29}$ regular steranes occurrence. Pr/Ph ratio is using for scope depositional environment by different isoprenoid genre as shown section below:

1. Bueng Sam Phan 1 area can be defined to swamp nearby estuarine.
2. Bueng Sam Phan 2 area can be defined to swamp and aquatic deposition nearby estuarine.
3. Chon Daen area can be defined to coastal swamp nearby estuarine.
4. Nong Phai area (carbonate rock) can be defined to coastal swamp nearby estuarine.
5. Nong Phai area (shale) can be defined to aquatic deposition nearby estuarine.

In summarized, geochemical data from sedimentary rock both clastic and carbonate rock of this study area can be defined to shallow marine in back reef zone supporting by high organic matter accumulation in this area.

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APPENDICES

APPENDIX A
(Rock-Eval Pyrolysis)
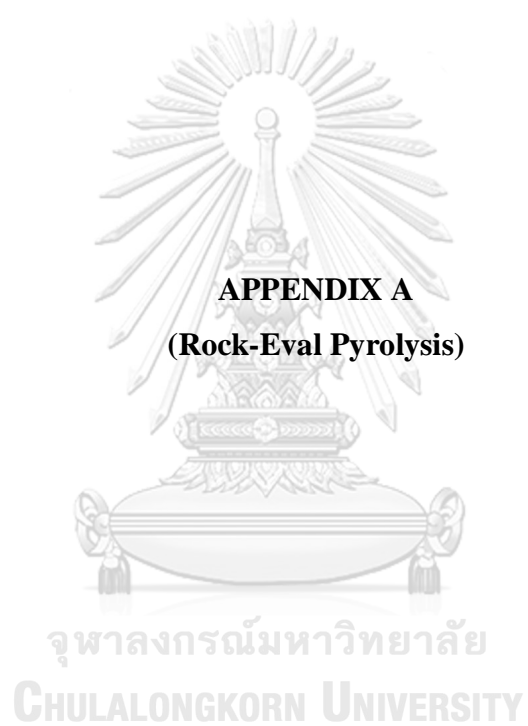
Rock eval pyrolysis

Sample ID: BP1-1/1

S1 = 0.01 mg HC/g rock   S2 = 0.01 mg HC/g rock   S3 = 0.12 mg CO_2/g rock

TOC = 2.05 wt. %   Tmax = 469 °C
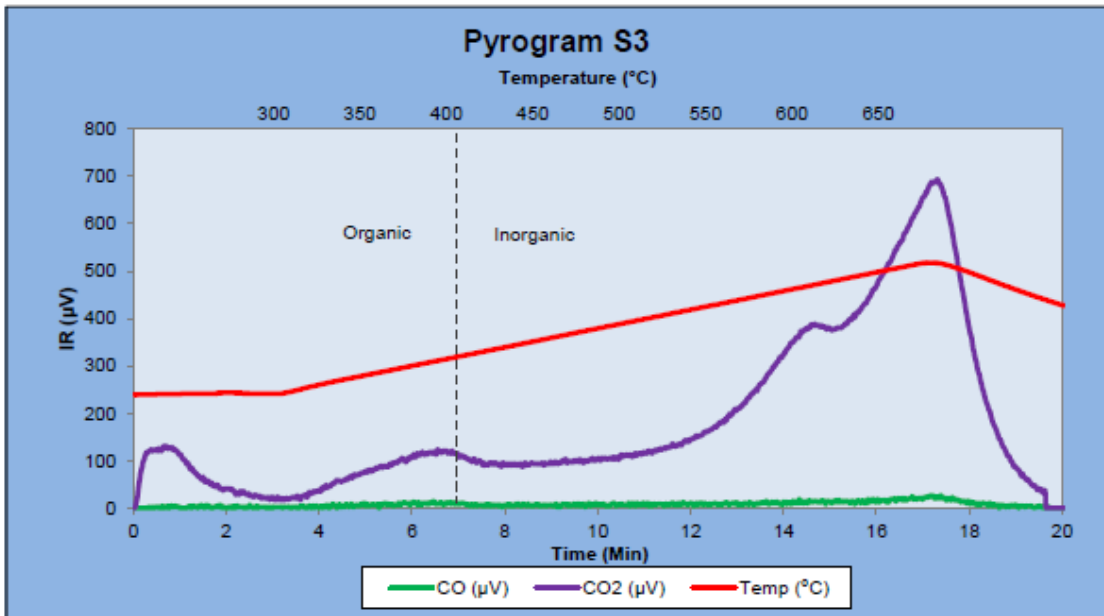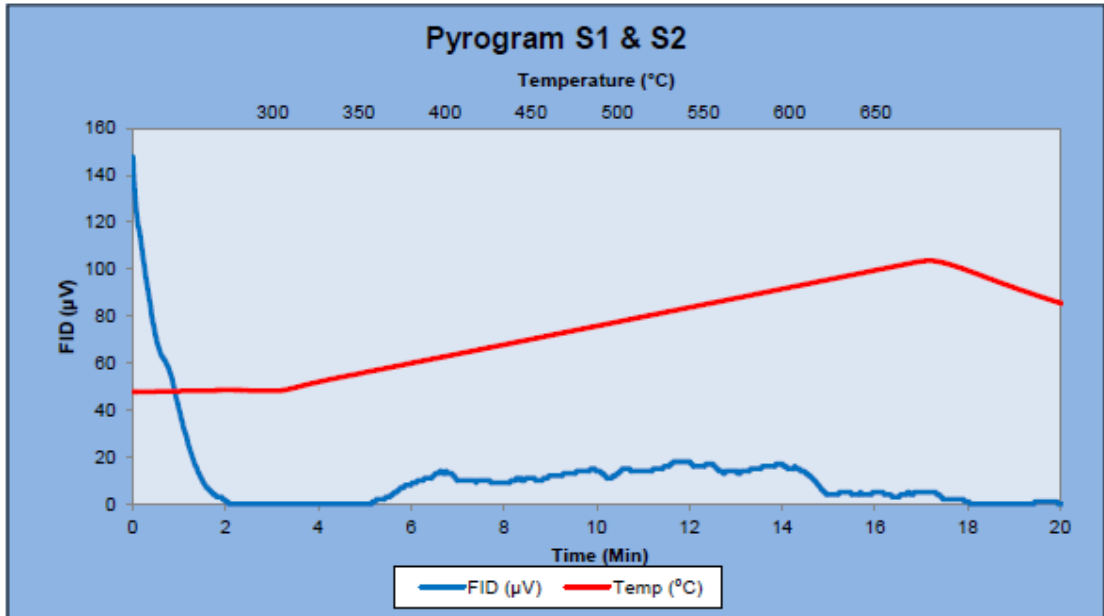
Sample ID: BP1-1/2

S1 = 0.01 mg HC/g rock   S2 = 0.01 mg HC/g rock   S3 = 0.45 mg CO₂/g rock

TOC = 2.18 wt. %   Tmax = 471 °C
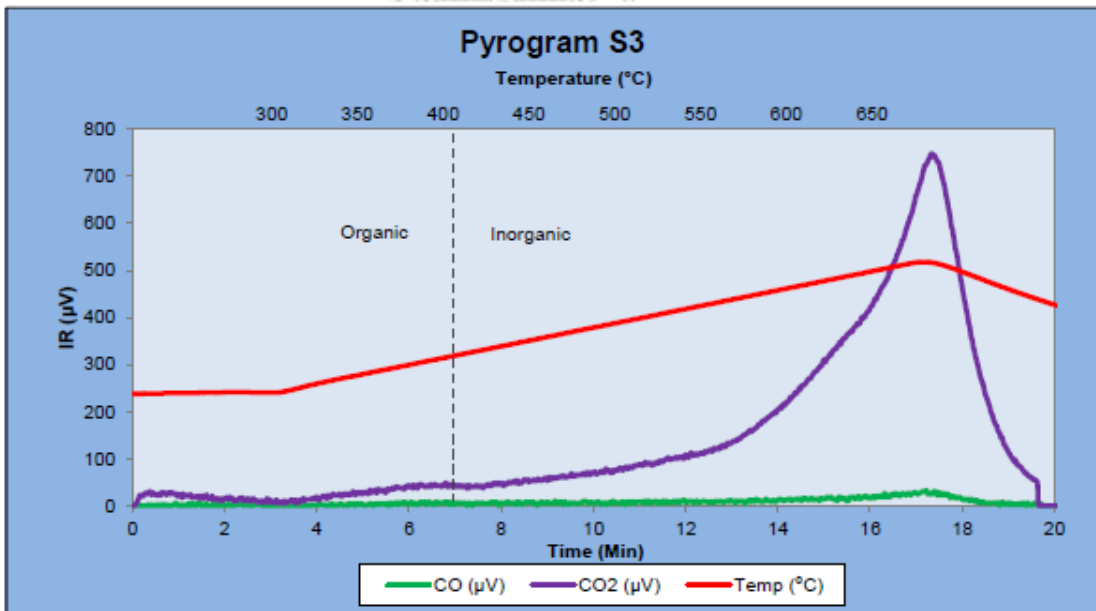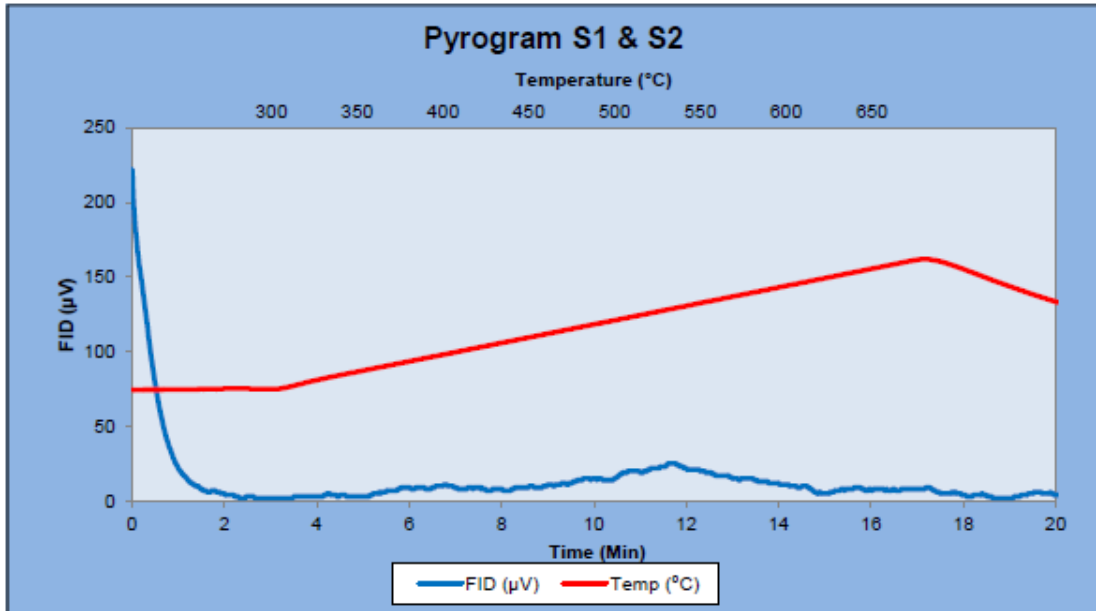
Sample ID: BP2-4/1

S1 = 0.04 mg HC/g rock   S2 = 0.00 mg HC/g rock   S3 = 0.14 mg CO_2/g rock

TOC = 2.01 wt. %   Tmax = 604 °C
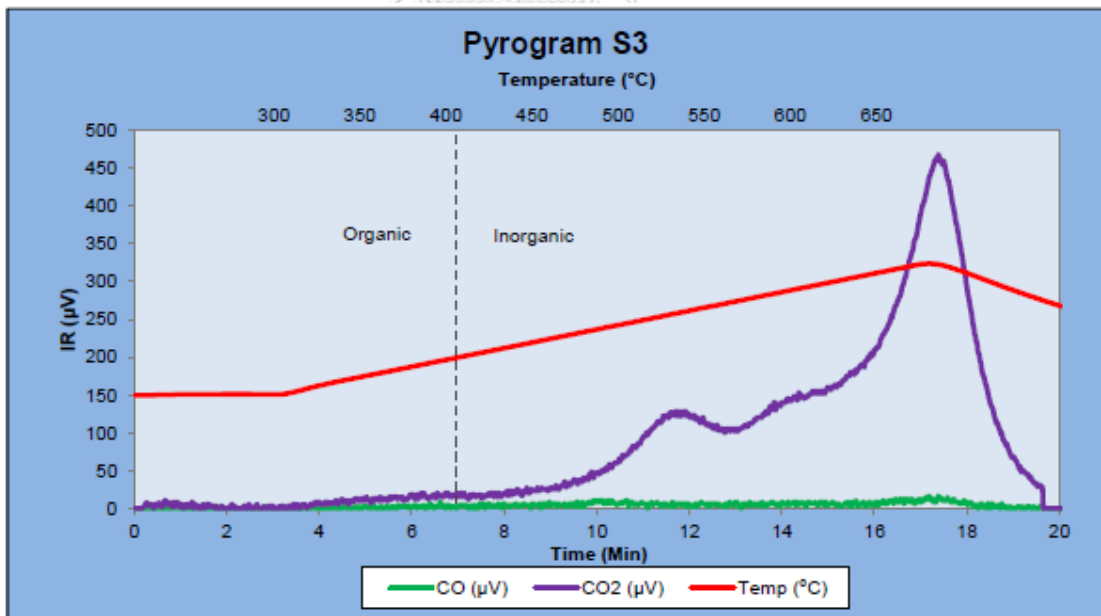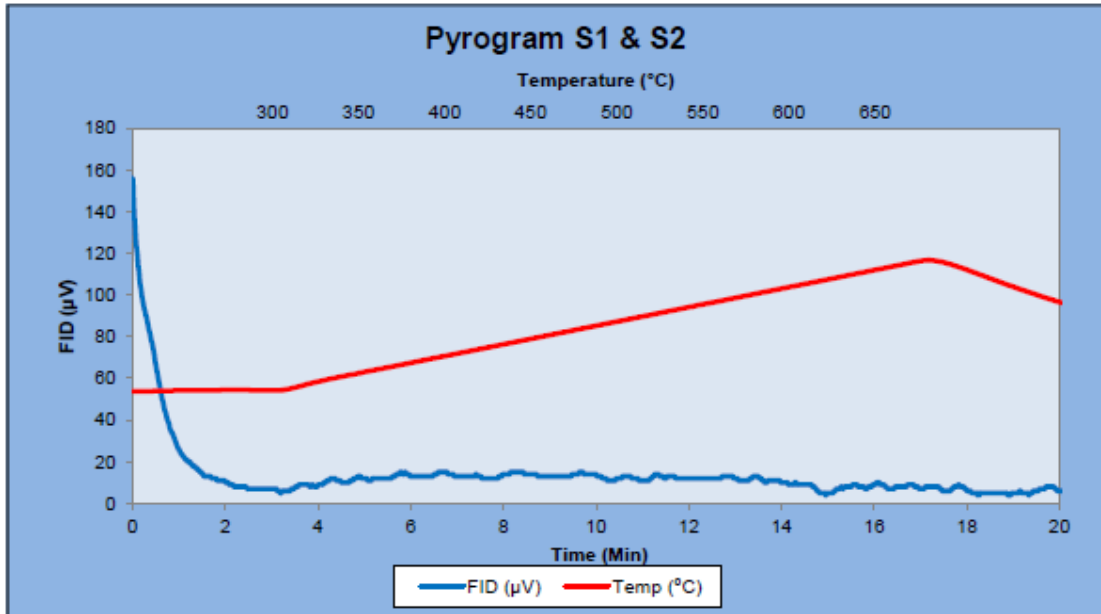
Sample ID: BP2-4/2

S1 = 0.05 mg HC/g rock   S2 = 0.00 mg HC/g rock   S3 = 0.05 mg CO_2/g rock

TOC = 2.01 wt. %   Tmax = 425 °C
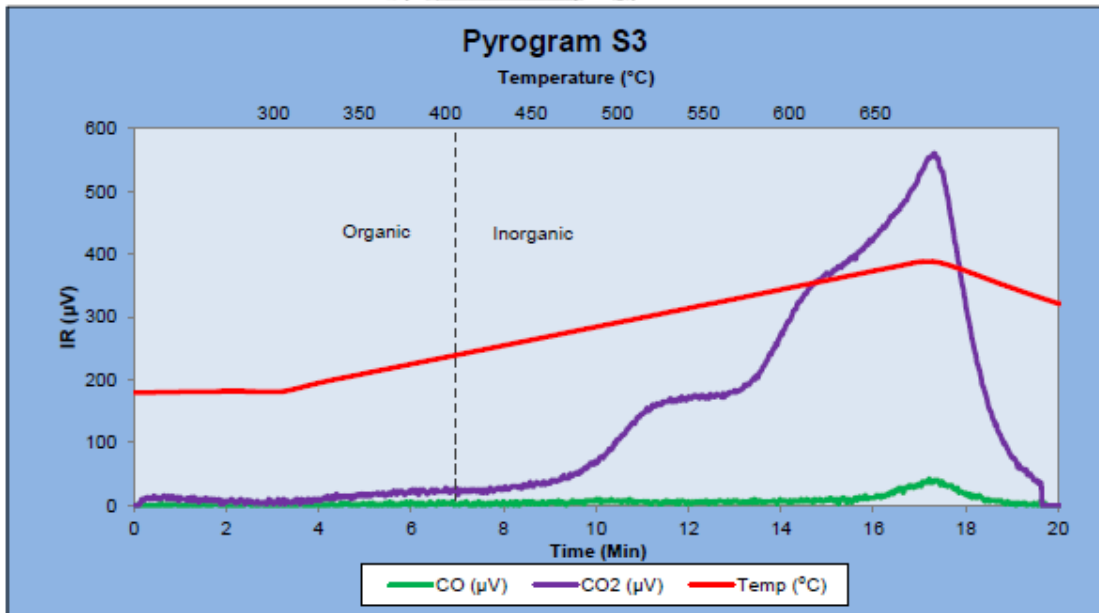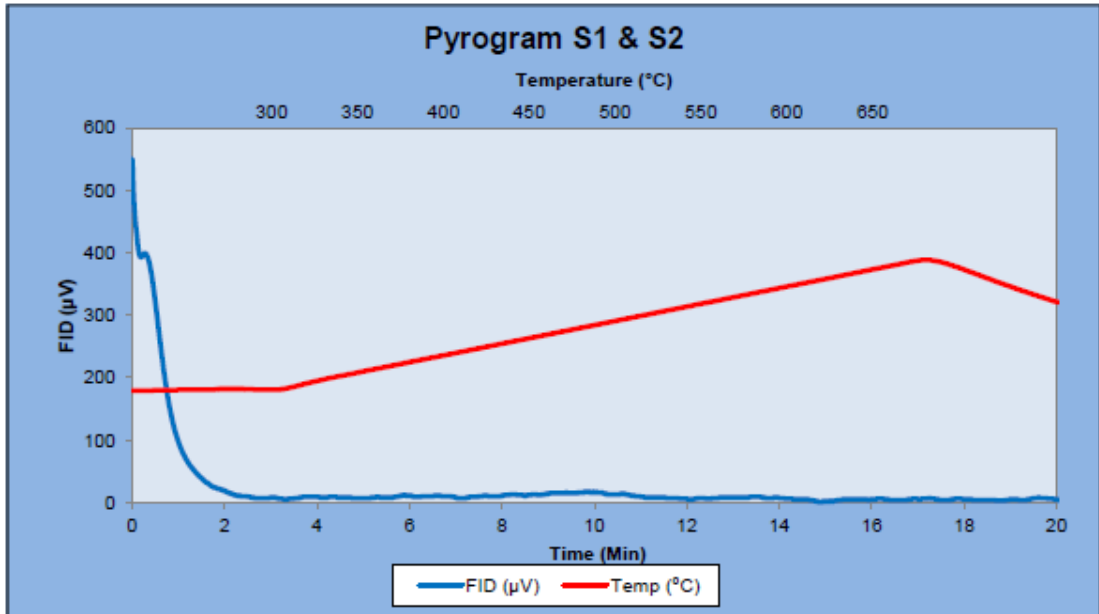
Sample ID: CD-2/1

S1 = 0.05 mg HC/g rock   S2 = 0.26 mg HC/g rock   S3 = 0.44 mg CO_2/g rock

TOC = 4.05 wt. %   Tmax = 485 °C
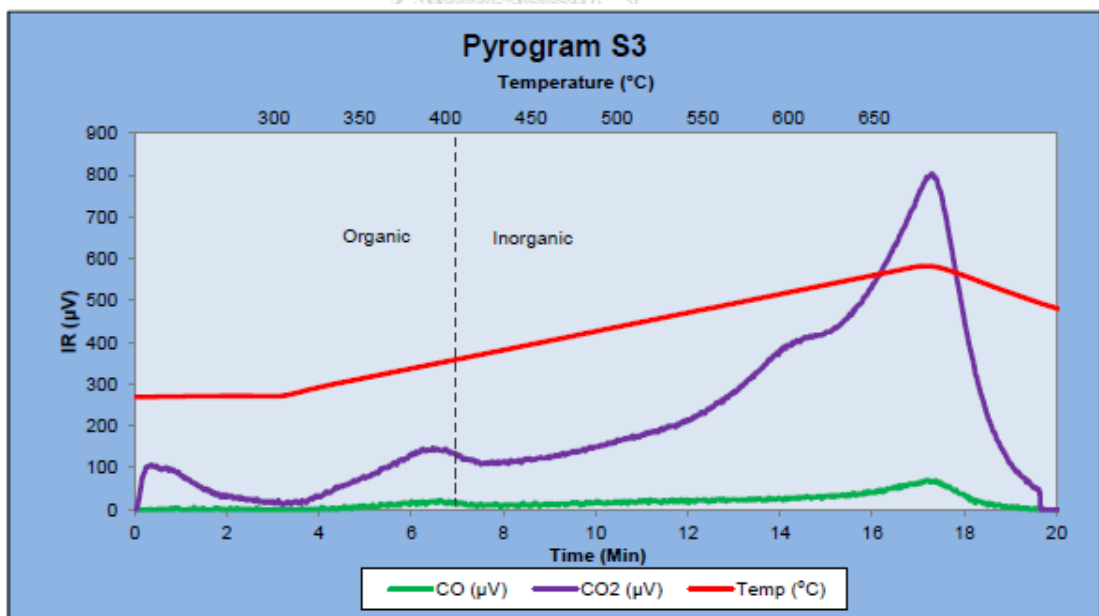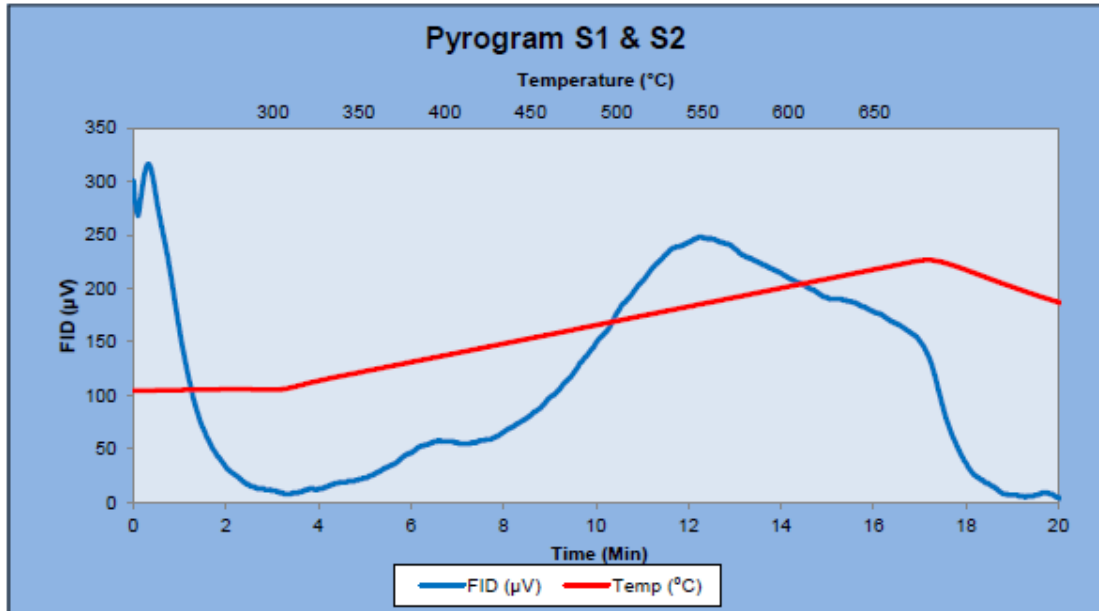
Sample ID: NP-3/1

S1 = 0.07 mg HC/g rock   S2 = 0.50 mg HC/g rock   S3 = 0.23 mg CO_2/g rock

TOC = 4.58 wt. %   Tmax = 563 °C
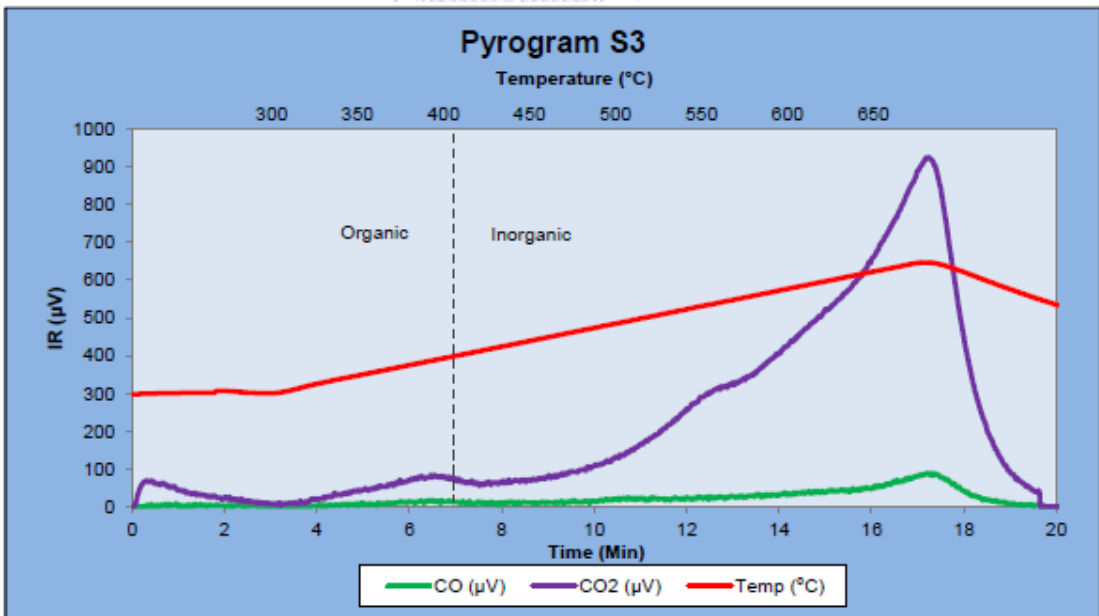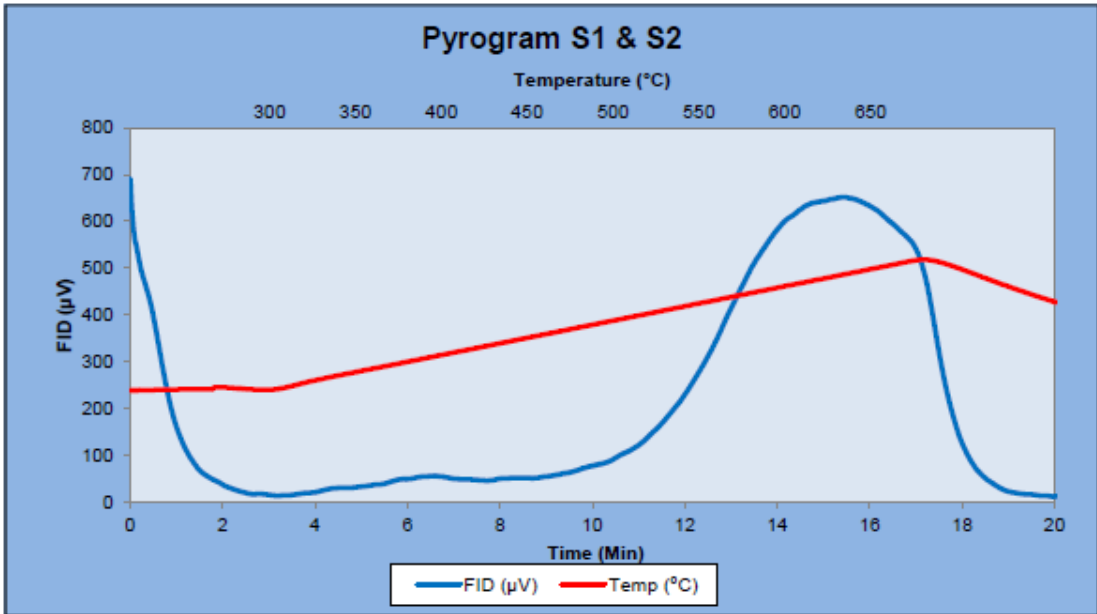
Sample ID: NP-3/2

S1 = 0.07 mg HC/g rock   S2 = 0.45 mg HC/g rock   S3 = 0.09 mg CO_2/g rock

TOC = 1.42 wt. %   Tmax = 565 °C
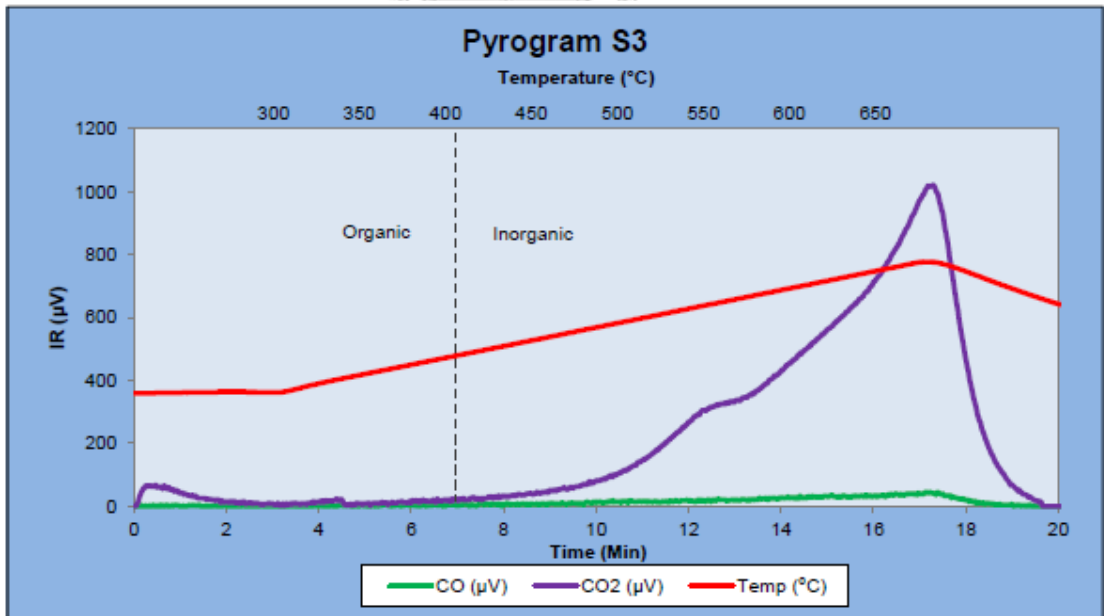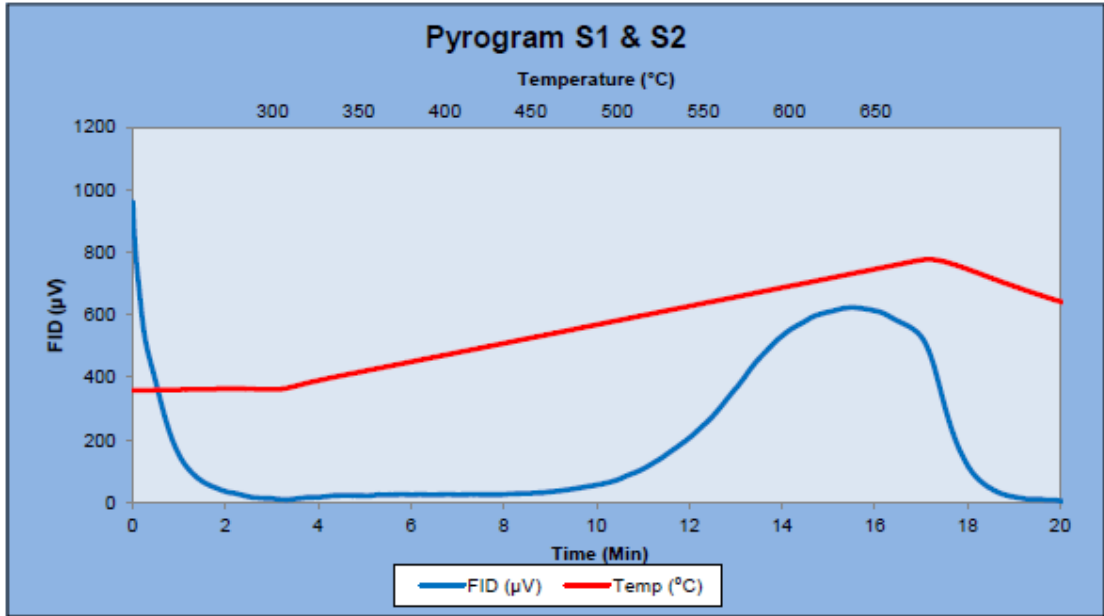
Sample ID: NP-3/3

S1 = 0.01 mg HC/g rock   S2 = 0.02 mg HC/g rock   S3 = 0.28 mg CO_2/g rock

TOC = 1.50 wt. %   Tmax = 524 °C
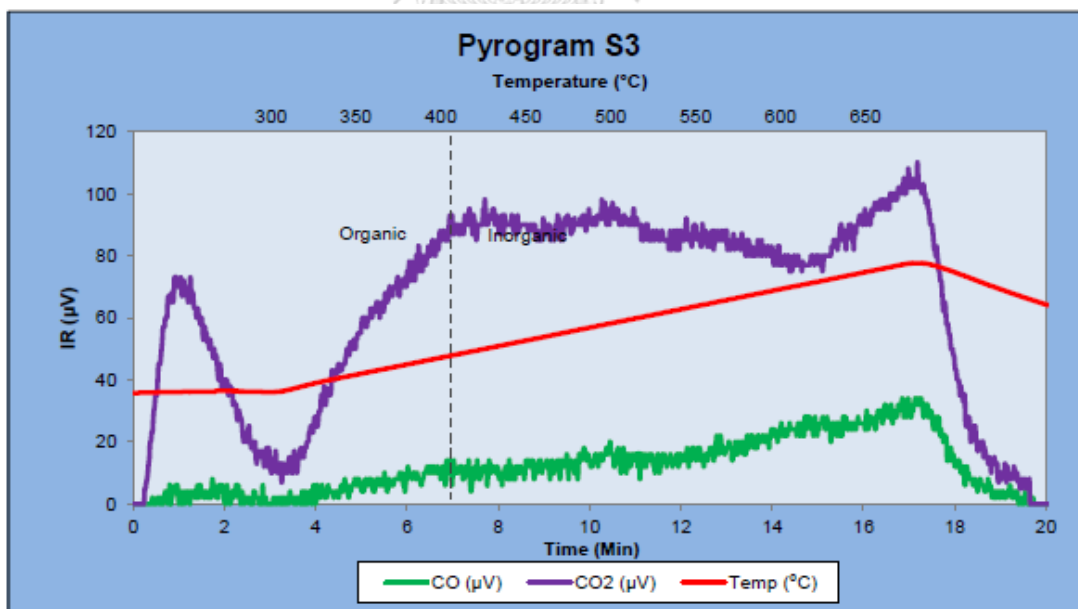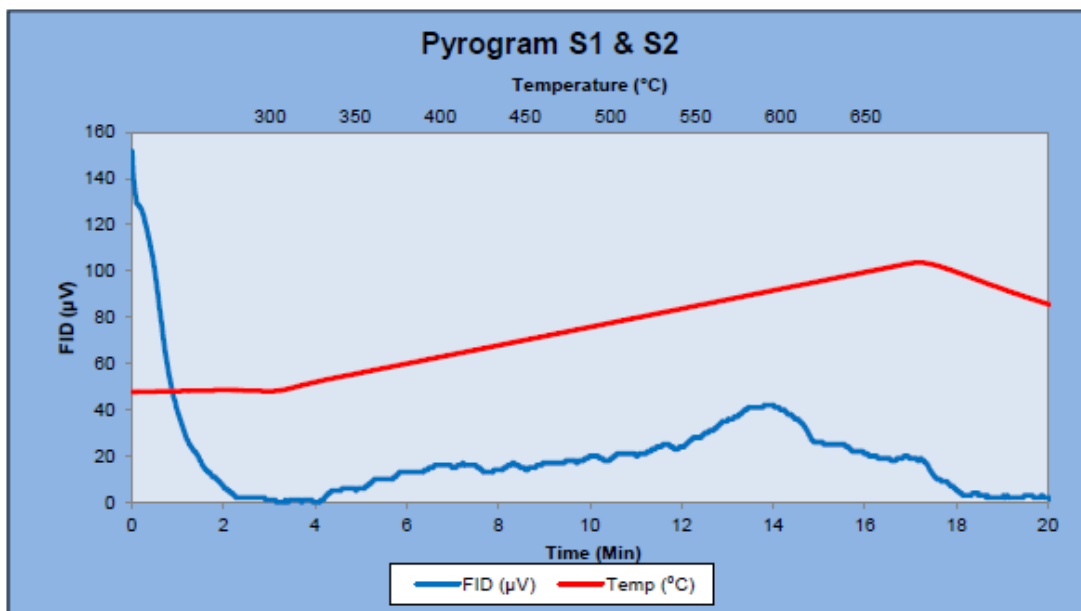
Sample ID: NP-3/4

S1 = 0.01 mg HC/g rock   S2 = 0.02 mg HC/g rock   S3 = 0.02 mg CO_2/g rock

TOC = 3.88 wt. %   Tmax = 600 °C

APPENDIX B

(Gas Chromatography – Mass Spectroscopy)
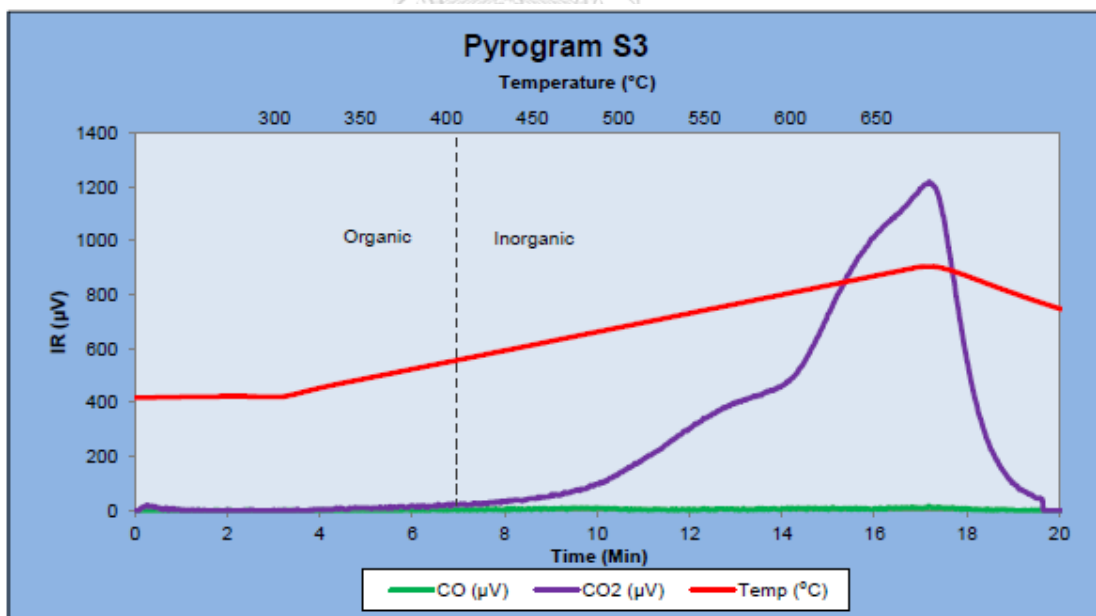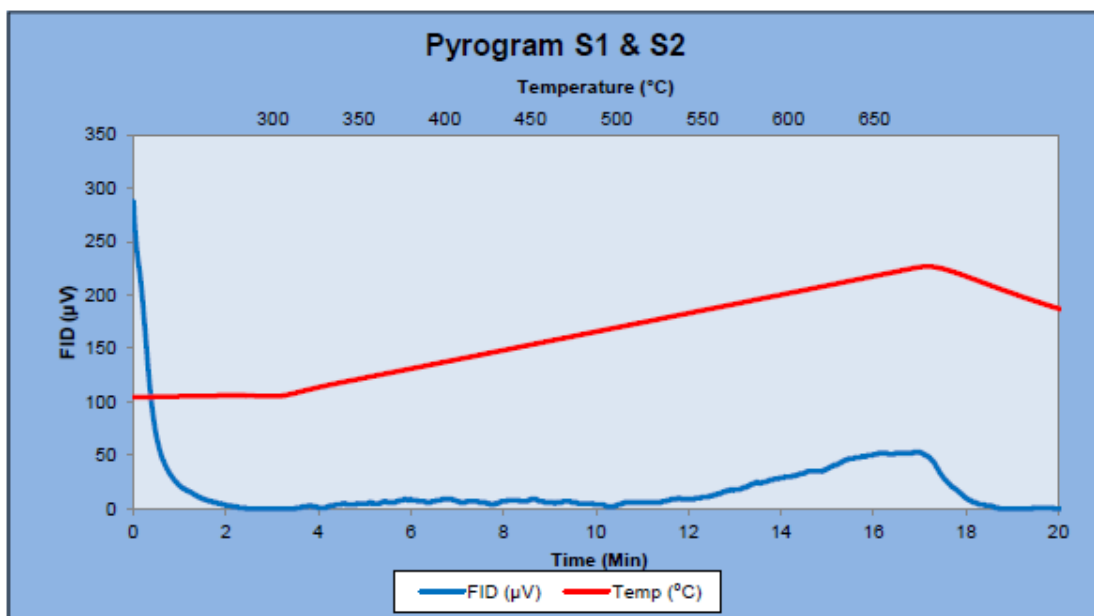
Gas chromatogram m/z 85 (normal alkane homologous and isoprenoids)

Peak No.	Name	IUPAC
1	n-C_{15}	Pentadecane
2	n-C_{16}	Hexadecane
3	n-C_{17}	Heptadecane
Pr	Pristane	2, 6, 10, 14-tetramethylpentadecane
4	n-C_{18}	Octadecane
Ph	Phytane	2, 6, 10, 14-tetramethylhexadecane
5	n-C_{19}	Nonadecane
6	n-C_{20}	Icosane
7	n-C_{21}	Heneicosane
8	n-C_{22}	Docosane
9	n-C_{23}	Tricosane
10	n-C_{24}	Tetracosane
11	n-C_{25}	Pentacosane
12	n-C_{26}	Hexacosane
13	n-C_{27}	Heptacosane
14	n-C_{28}	Octacosane
15	n-C_{29}	Nonacosane
16	n-C_{30}	Triacontane
17	n-C_{31}	Hentriacontane
18	n-C_{32}	Dotriacontane
19	n-C_{33}	Tritriacontane
20	n-C_{34}	Tetratriacontane

จุฬาลงกรณ์มหาวิทยาลัย

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Location: Bueng Sam Phan 1 (Ban Pho Sawan 1 area), Phetchabun Province

Sample ID: BP1-1/1

Pr/n-C$_{17}$ = 0.17   Pr/n-C$_{18}$ = 0.05   Pr/Ph = 4.09   CPI = 1.00

n-alkane series
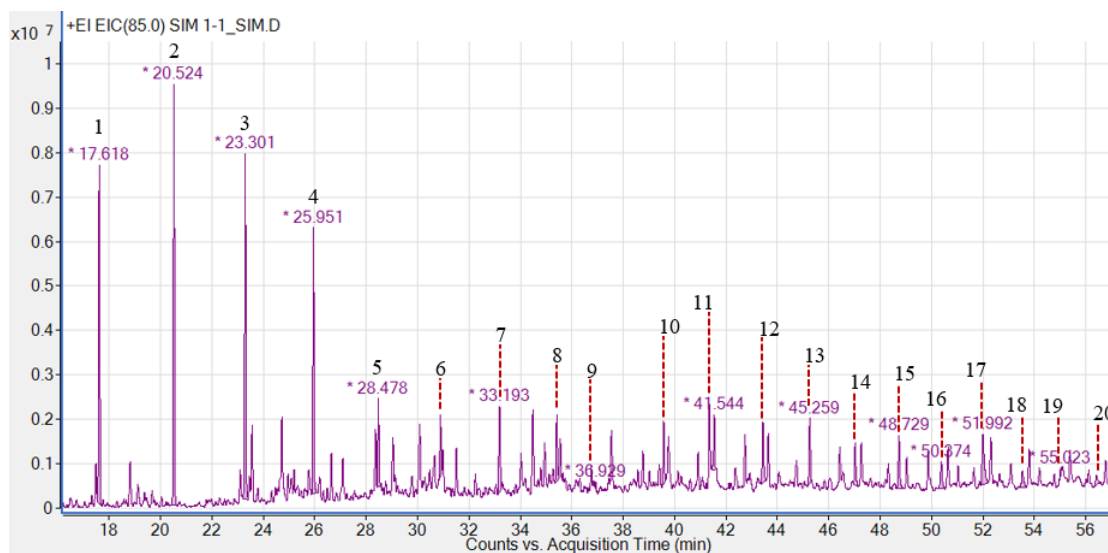
n-alkane and isoprenoids
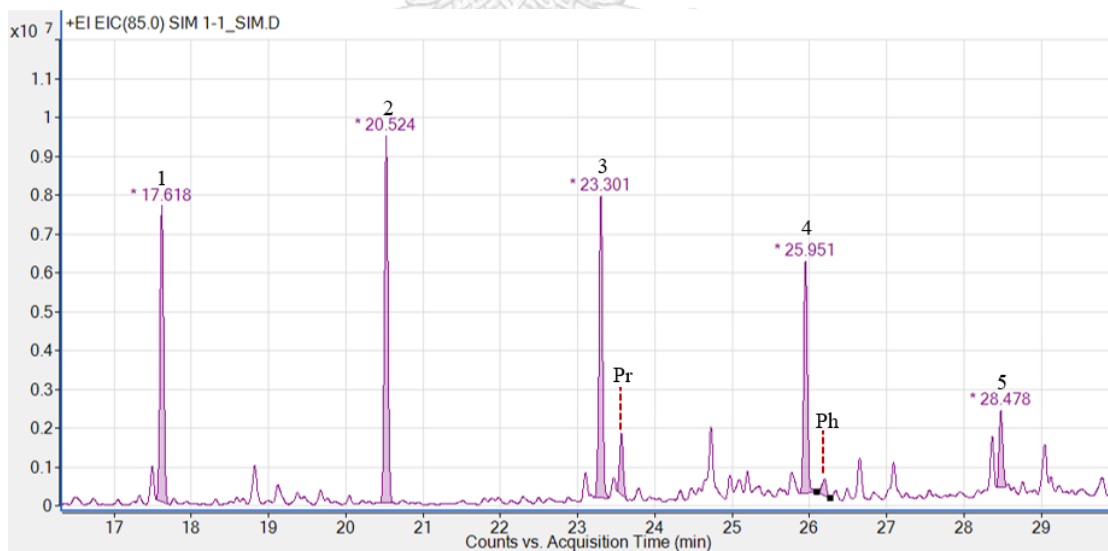
Location: Bueng Sam Phan 1 (Ban Pho Sawan 1 area), Phetchabun Province

Sample ID: BP1-1/2

Pr/n-C$_{17}$ = 0.82   Pr/n-C$_{18}$ = 0.14   Pr/Ph = 15.10   CPI = 1.01

n-alkane series
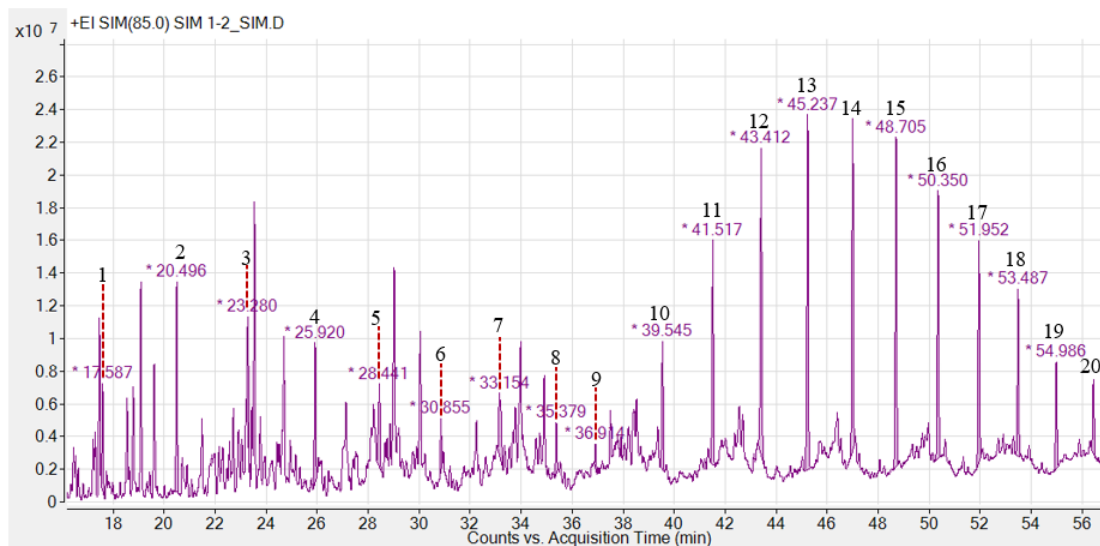
n-alkane and isoprenoids
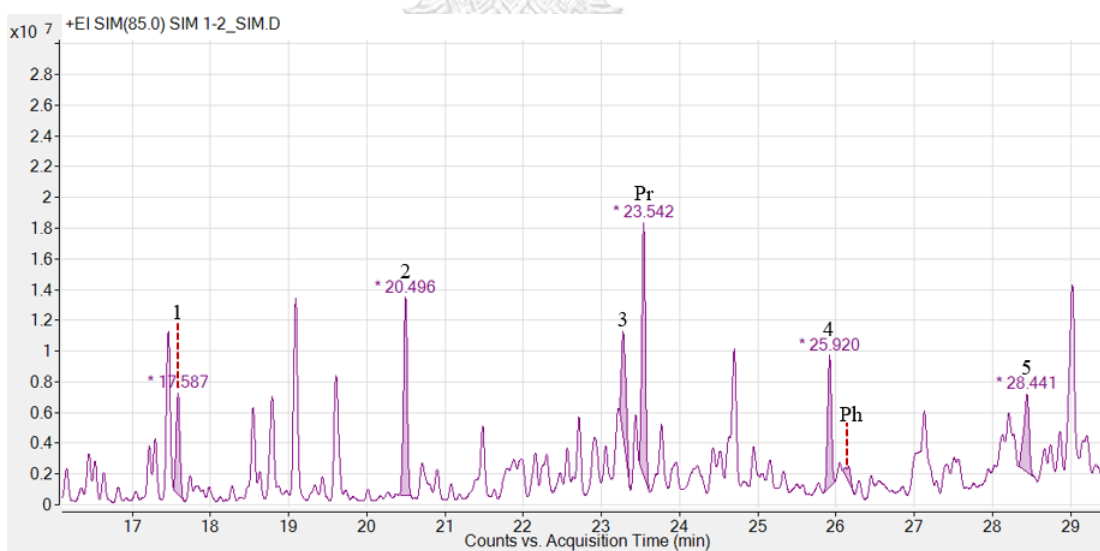
Location: Bueng Sam Phan 2 (Ban Pho Sawan 2 area), Phetchabun Province

Sample ID: BP2-4/1

Pr/n-C$_{17}$ = 0.69   Pr/n-C$_{18}$ = 0.23   Pr/Ph = 1.86   CPI = 1.01

n-alkane series
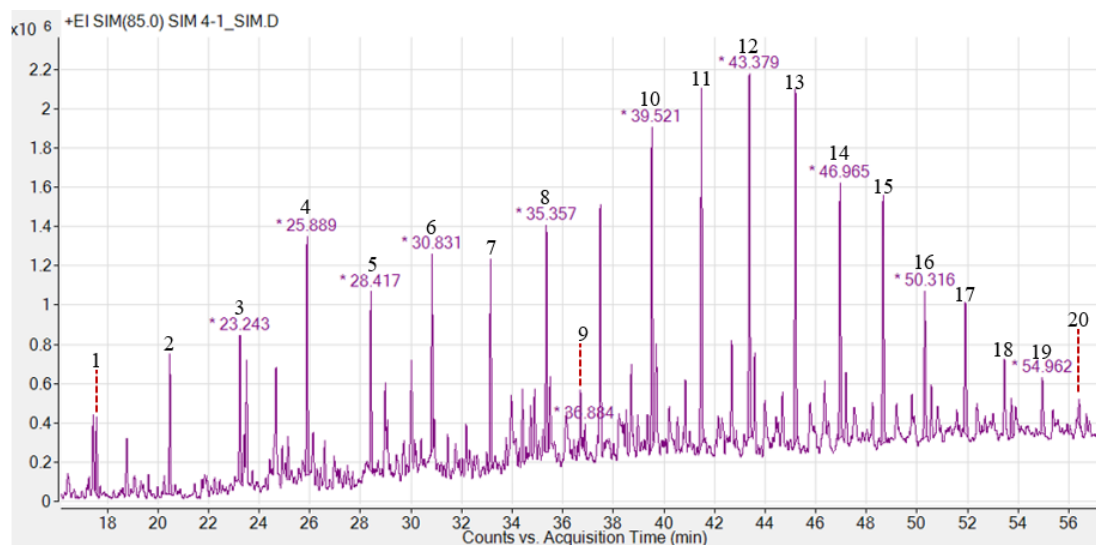
n-alkane and isoprenoids
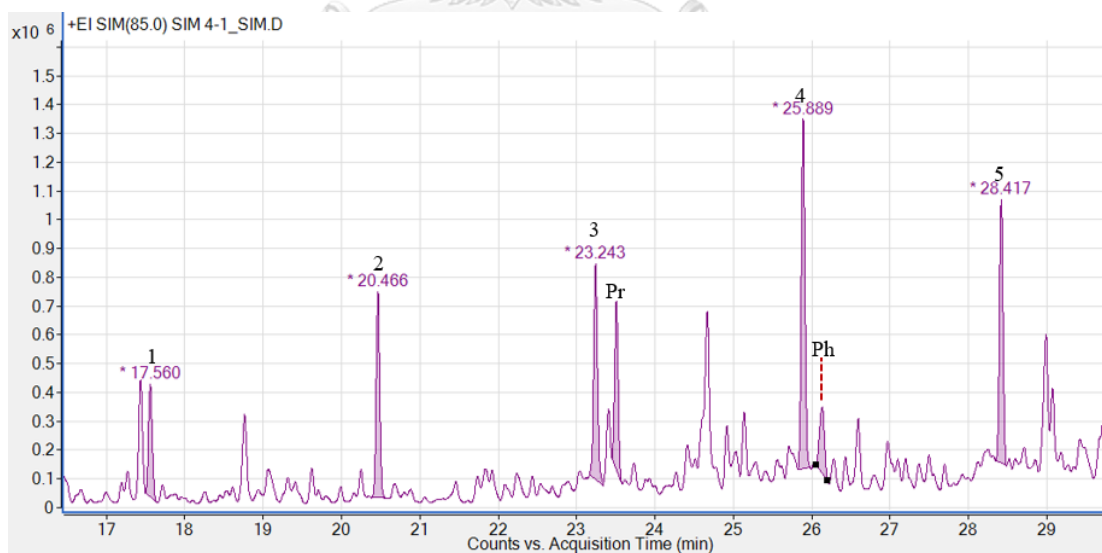
Location: Bueng Sam Phan 2 (Ban Pho Sawan 2 area), Phetchabun Province

Sample ID: BP2-4/2

Pr/n-C_{17} = 0.23   Pr/n-C_{18} = 0.07   Pr/Ph = 4.64   CPI = 1.00

n-alkane series
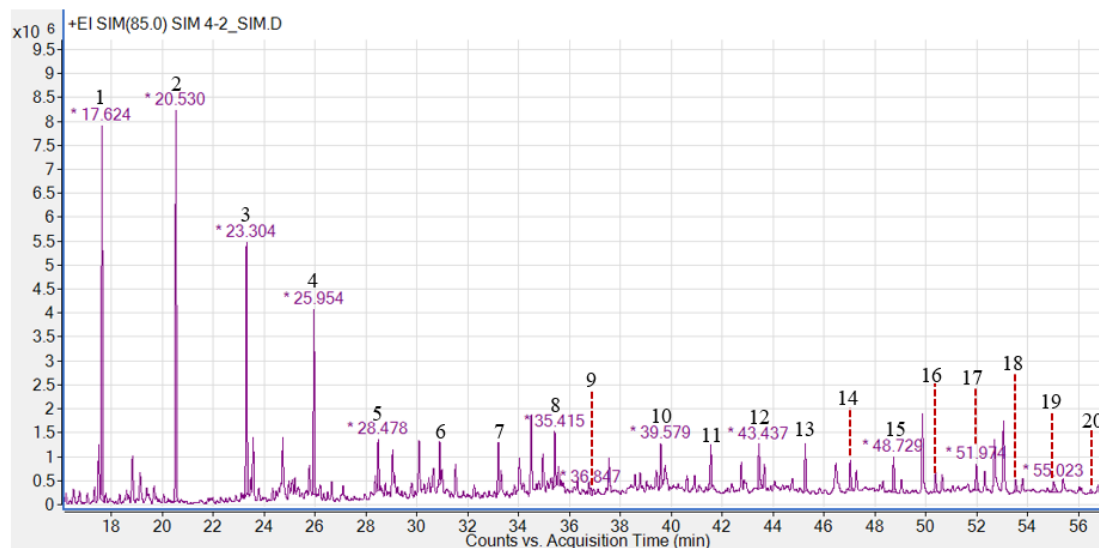
n-alkane and isoprenoids
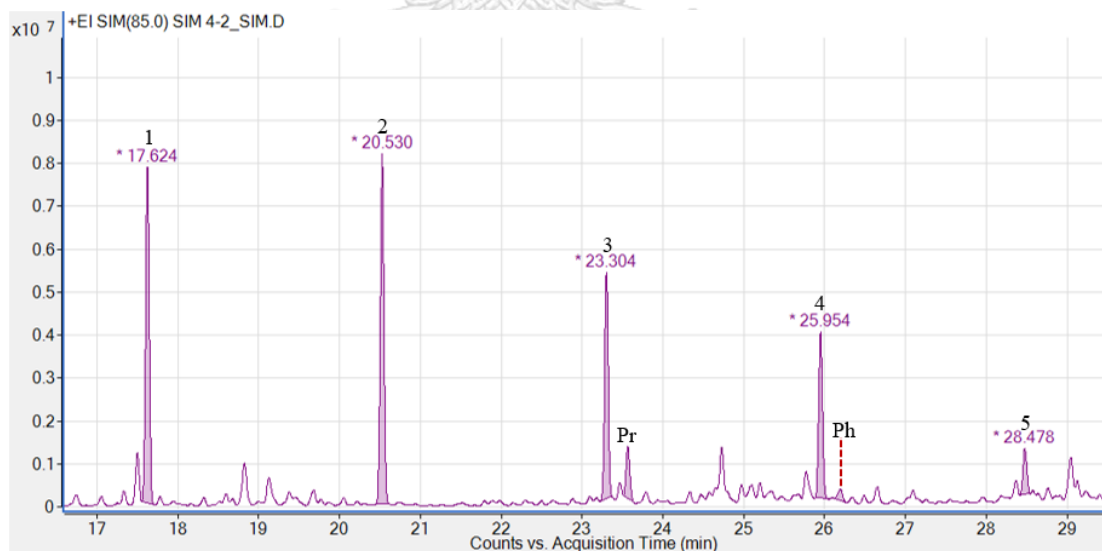
Location: Chon Daen section (Phu Pra That temple), Phetchabun Province

Sample ID: CD-2/1

$Pr/n-C_{17} = 0.15$ $\qquad$ $Pr/n-C_{18} = 0.09$ $\qquad$ $Pr/Ph = 2.48$ $\qquad$ CPI = 0.93

n-alkane series
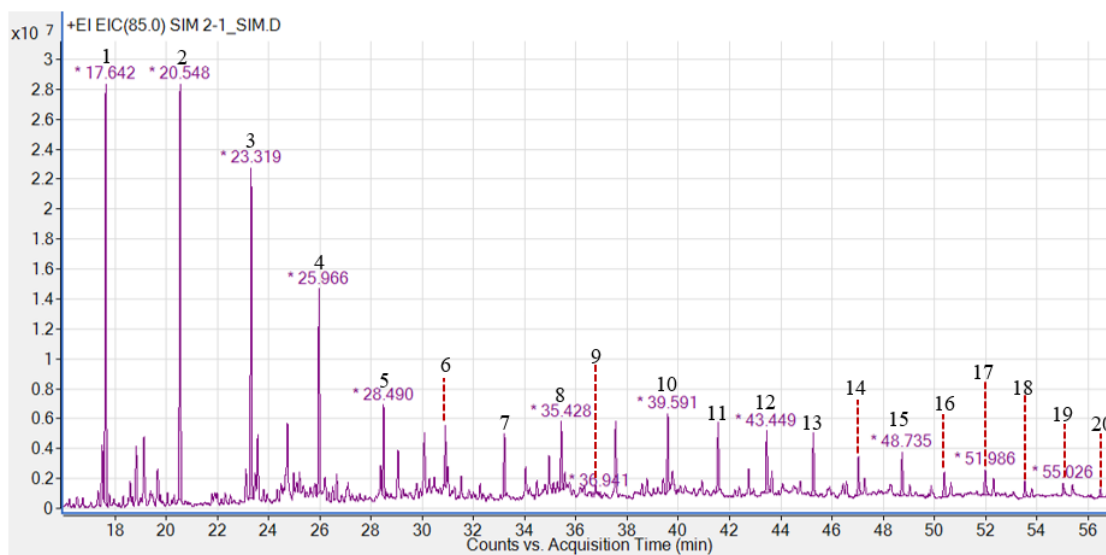
n-alkane and isoprenoids
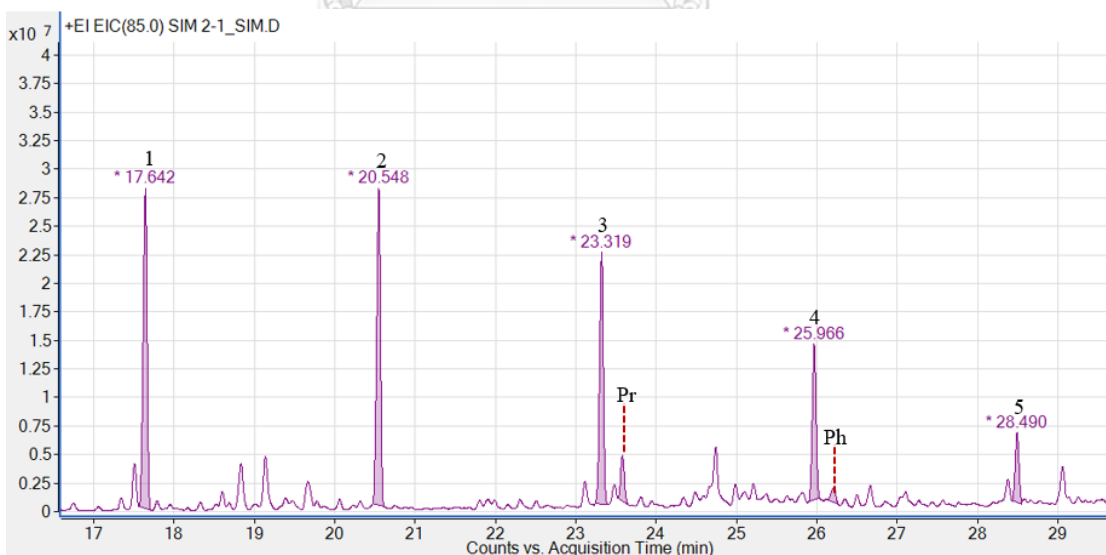
Location: Nong Phai section, Phetchabun Province

Sample ID: NP-3/1

Pr/n-C_{17} = 1.02   Pr/n-C_{18} = 0.25   Pr/Ph = 3.40   CPI = 0.97

n-alkane series
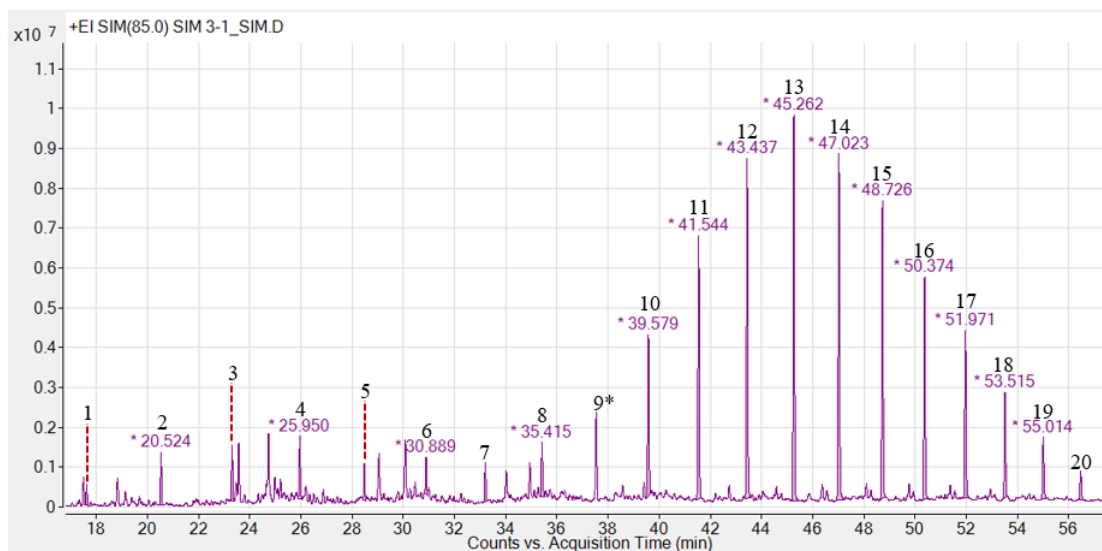
n-alkane and isoprenoids
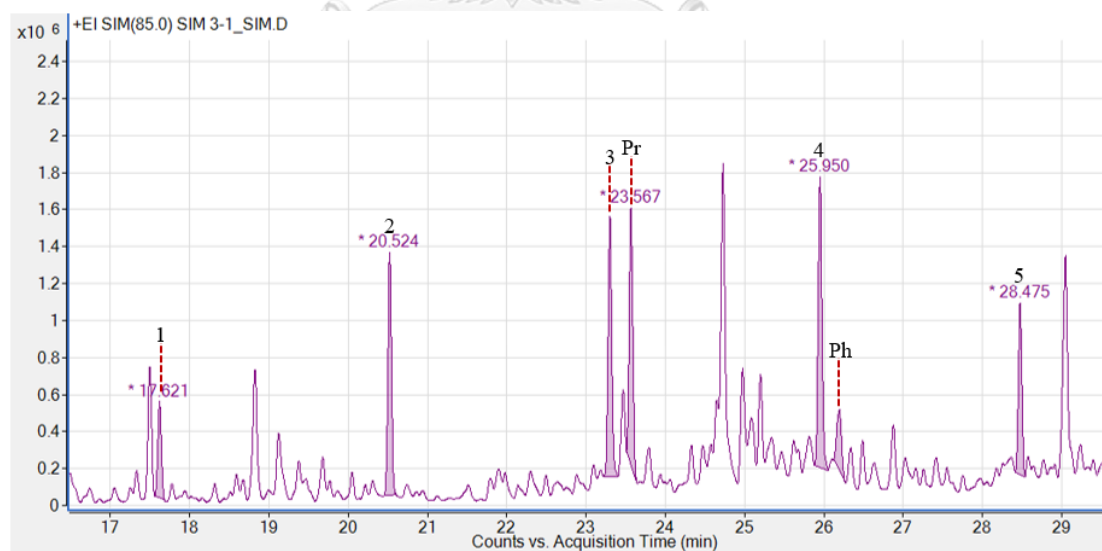
Location: Nong Phai section, Phetchabun Province

Sample ID: NP-3/2

Pr/n-C$_{17}$ = 0.39   Pr/n-C$_{18}$ = 0.23   Pr/Ph = 1.51   CPI = 1.81

n-alkane series
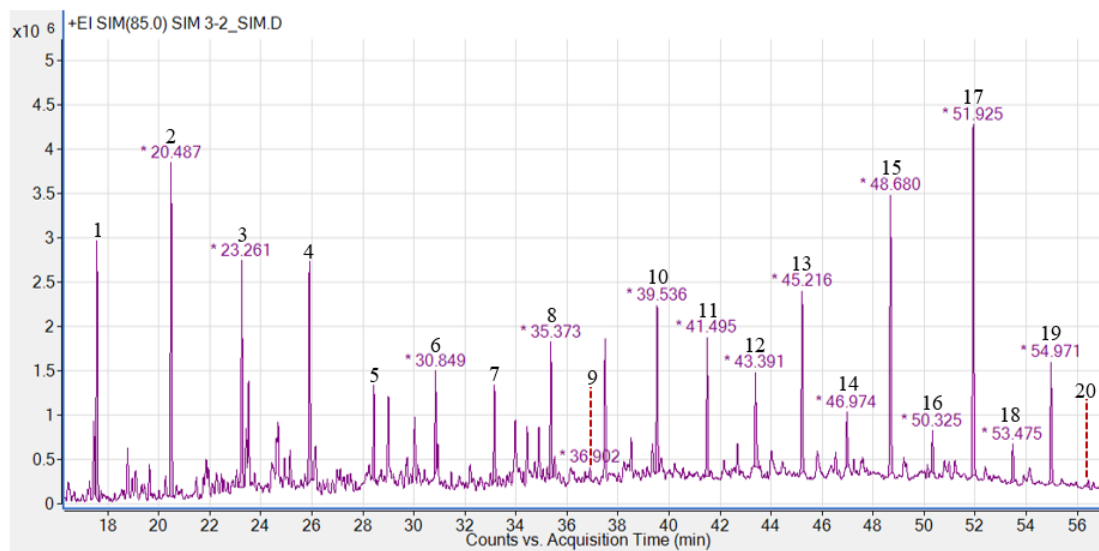
n-alkane and isoprenoids
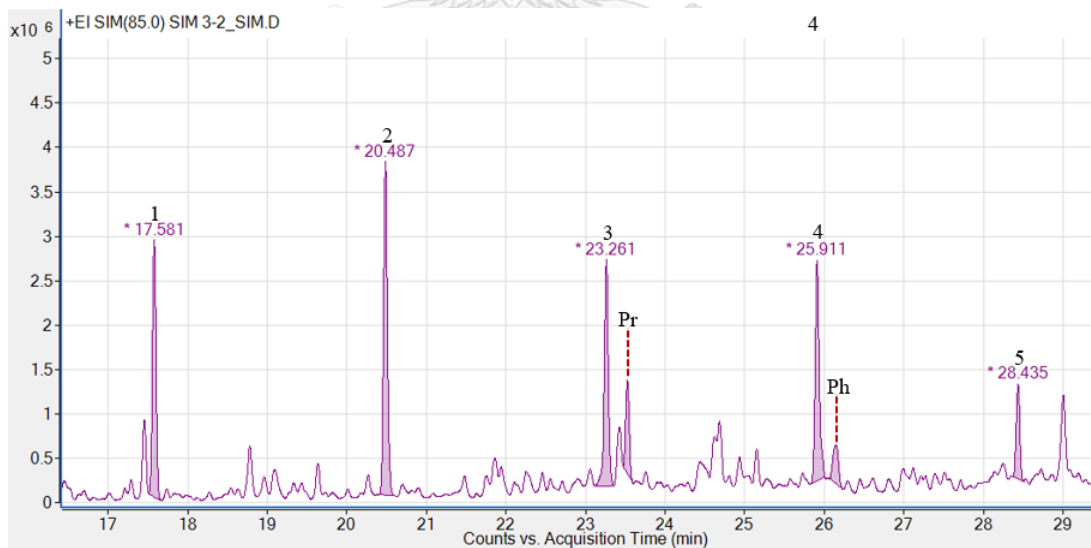
Location: Nong Phai section, Phetchabun Province

Sample ID: NP-3/3

Pr/n-C$_{17}$ = 0.29   Pr/n-C$_{18}$ = 0.23   Pr/Ph = 1.26   CPI = 1.31

n-alkane series
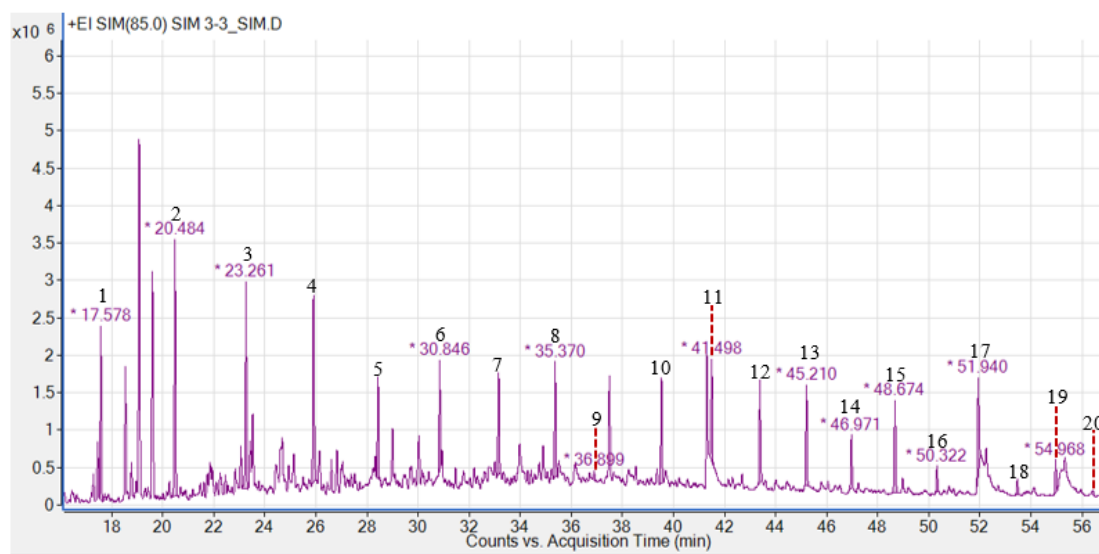
n-alkane and isoprenoids
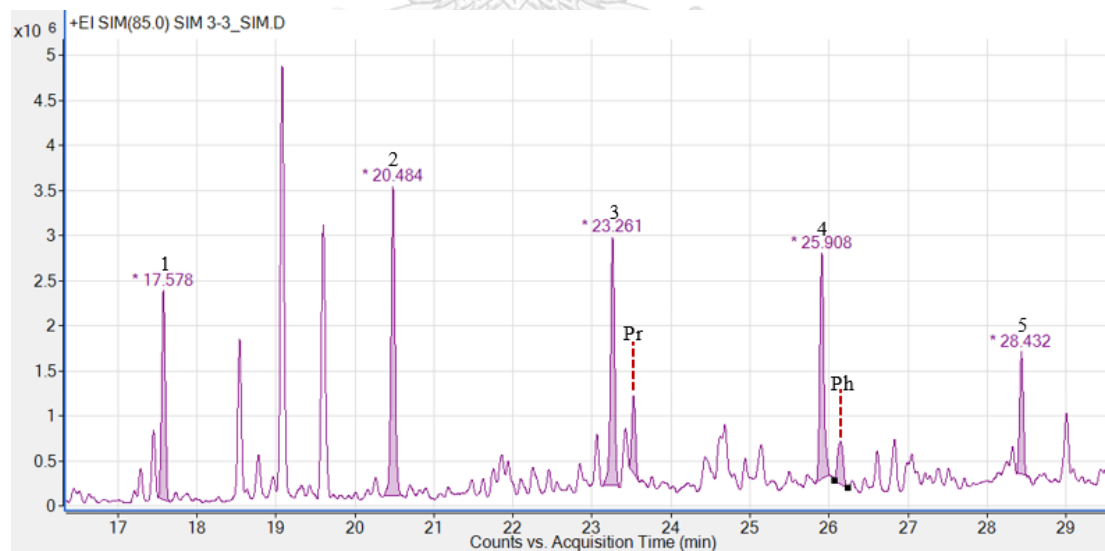
Location: Nong Phai section, Phetchabun Province

Sample ID: NP-3/4

Pr/n-C$_{17}$ = 0.32   Pr/n-C$_{18}$ = 0.16   Pr/Ph = 2.44   CPI = 1.29

n-alkane series
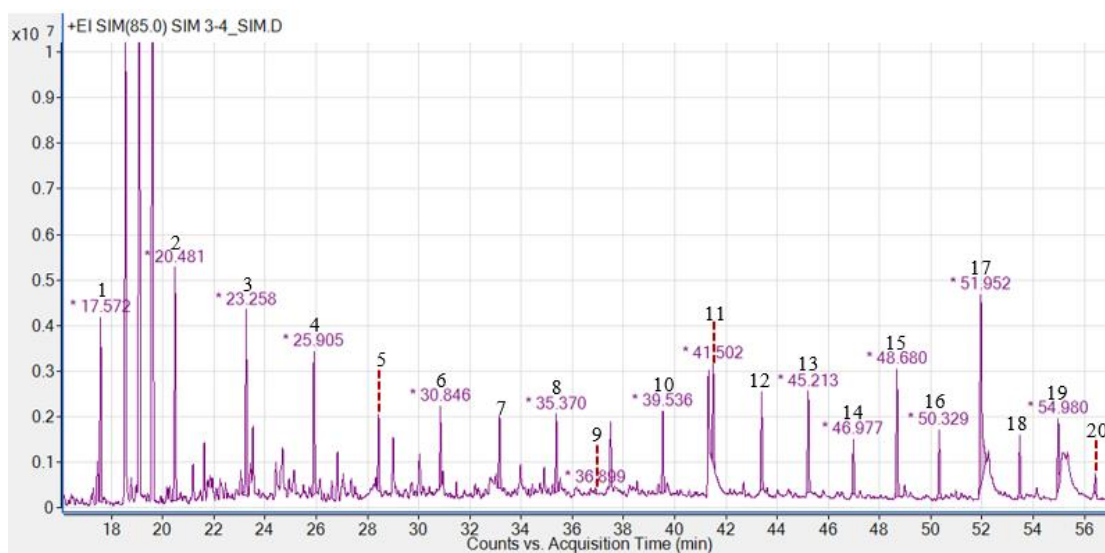
n-alkane and isoprenoids
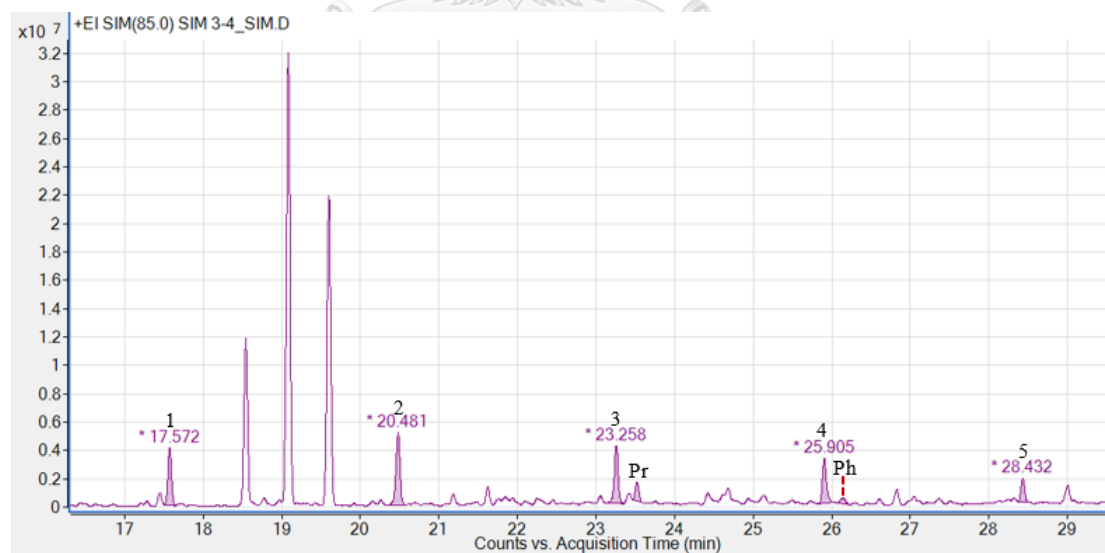
Gas chromatogram m/z 191 (Hopane homologous)

Peak No.	Abbreviate name	Name
1	Ts	C27 18α(H)-22,29,30-Trisnorhopane
2	Tm	C27 17α(H)-22,29,30-Trisnorhopane
3	C29Hop	C29 17α(H),21β(H)-Hopane
4	C30Hop	C30 17α(H),21β(H)-Hopane
5	Moretane	C30 17β(H),21α(H)-Moretane
6	C31S	C31 αβ-Homohopane (22S)
7	C30R	C31 αβ-Homohopane (22R)
8	Gammacerane	C30 Gammacerane
9	C32S	C32 αβ-Homohopane (22S)
10	C32R	C32 αβ-Homohopane (22R)
11	C33S	C33 αβ-Homohopane (22S)
12	C33R	C33 αβ-Homohopane (22R)
13	C34S	C34 αβ-Homohopane (22S)
14	C34R	C34 αβ-Homohopane (22R)
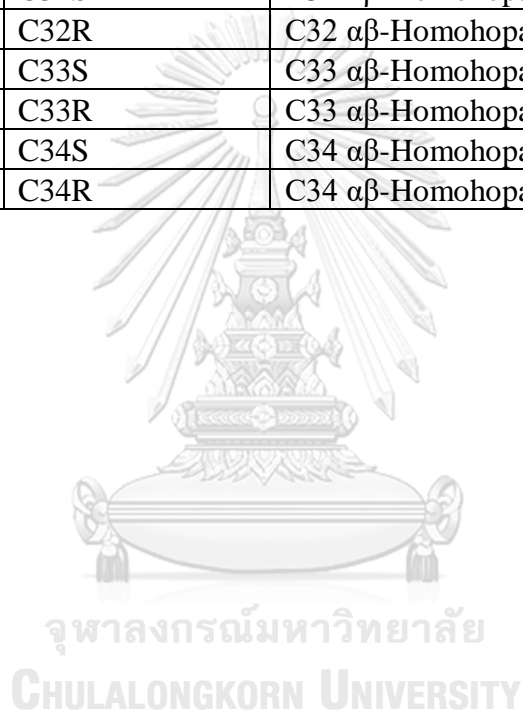
Location: Bueng Sam Phan 1 (Ban Pho Sawan 1 area), Phetchabun Province
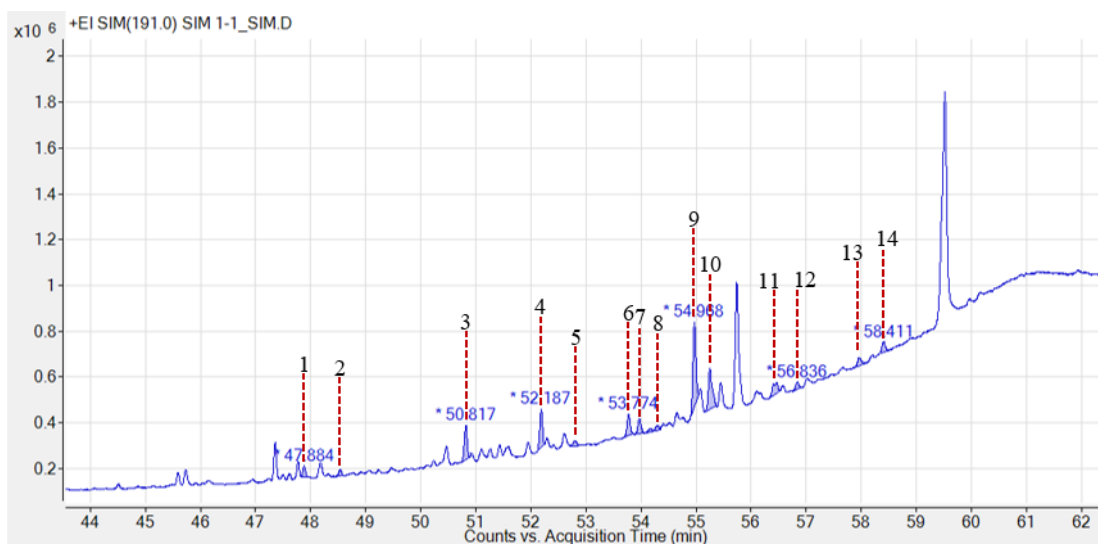
Sample ID: BP1-1/1
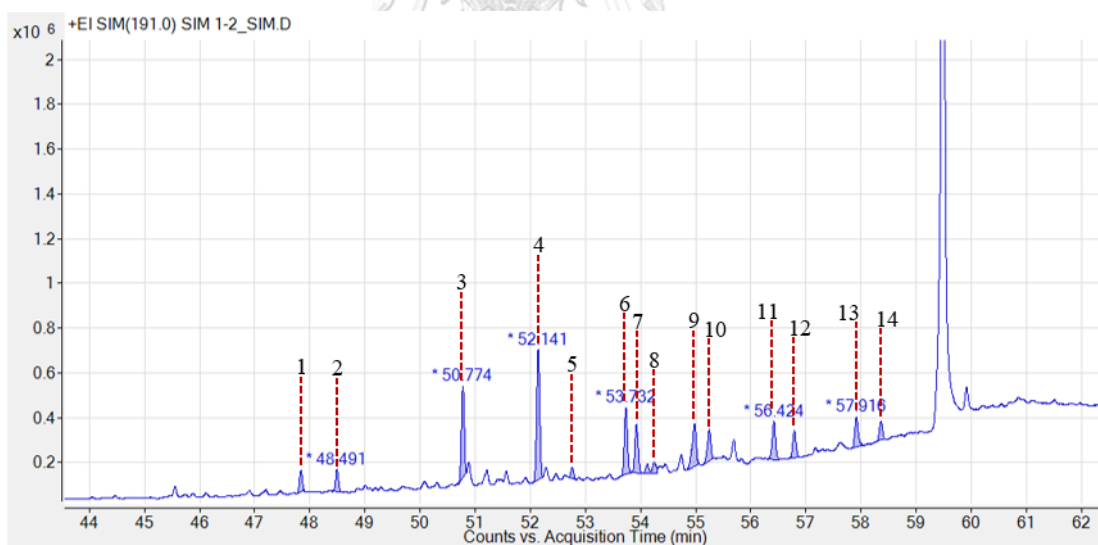
Sample ID: BP1-1/2

Location: Bueng Sam Phan 2 section (Ban Pho Sawan 2 area), Phetchabun Province
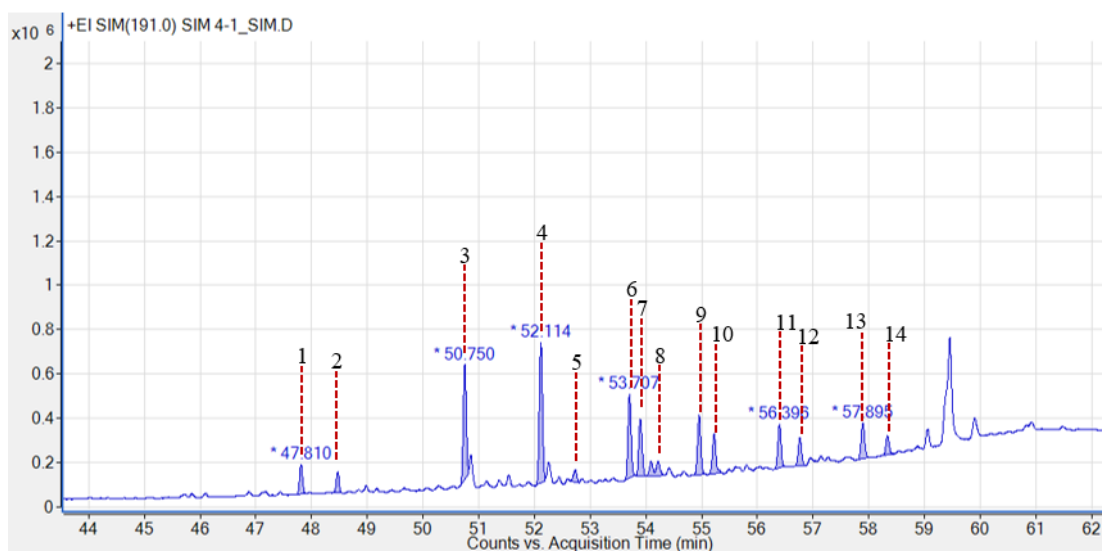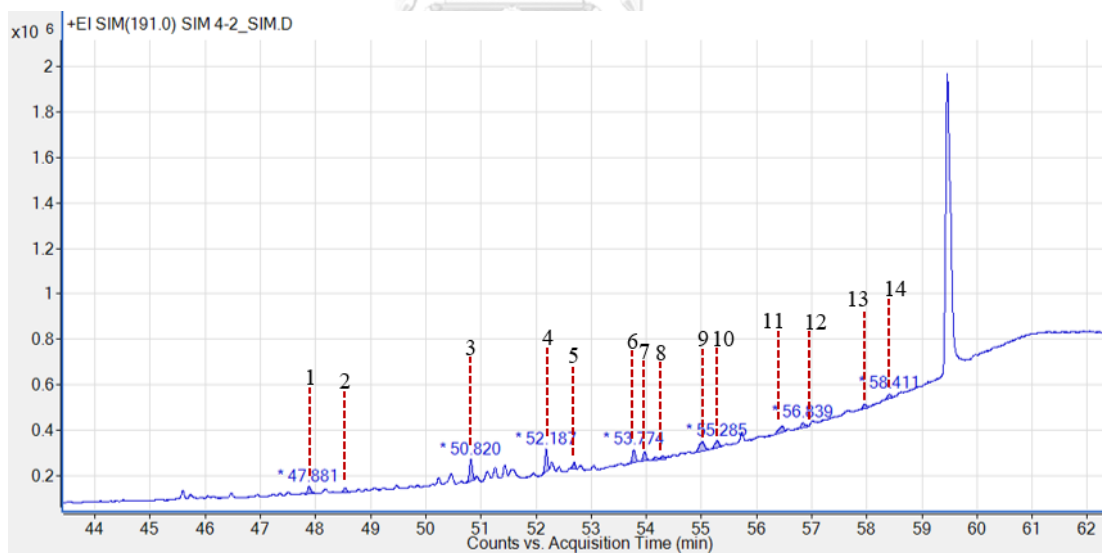
Sample ID: BP2-4/1

Sample ID: BP2-4/2

Location: Chon Daen section (Phu Pra That temple), Phetchabun Province

Sample ID: CD-2/1
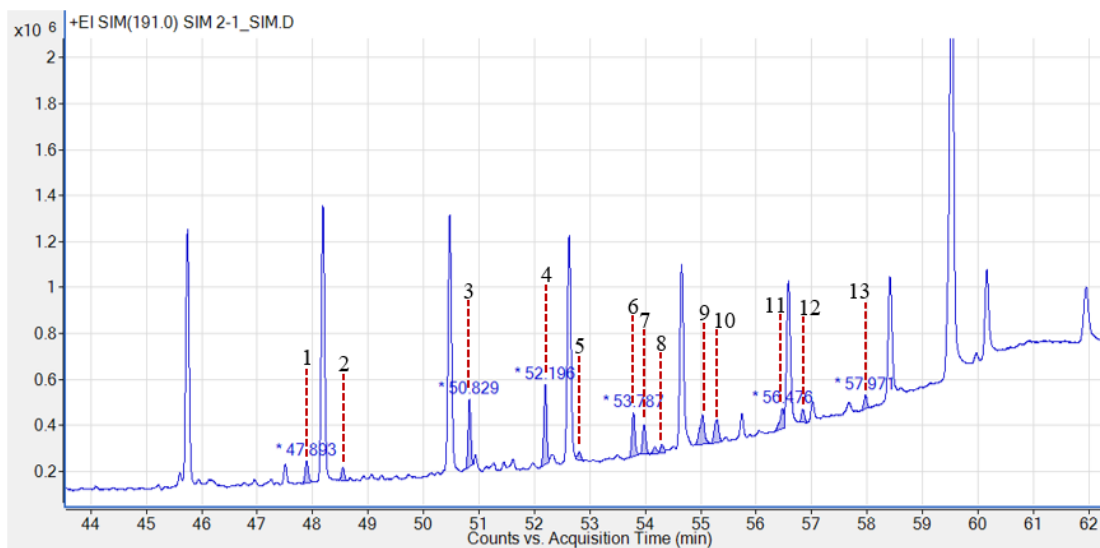
Location: Nong Phai section, Phetchabun Province

Sample ID: NP-3/1 (limestone)
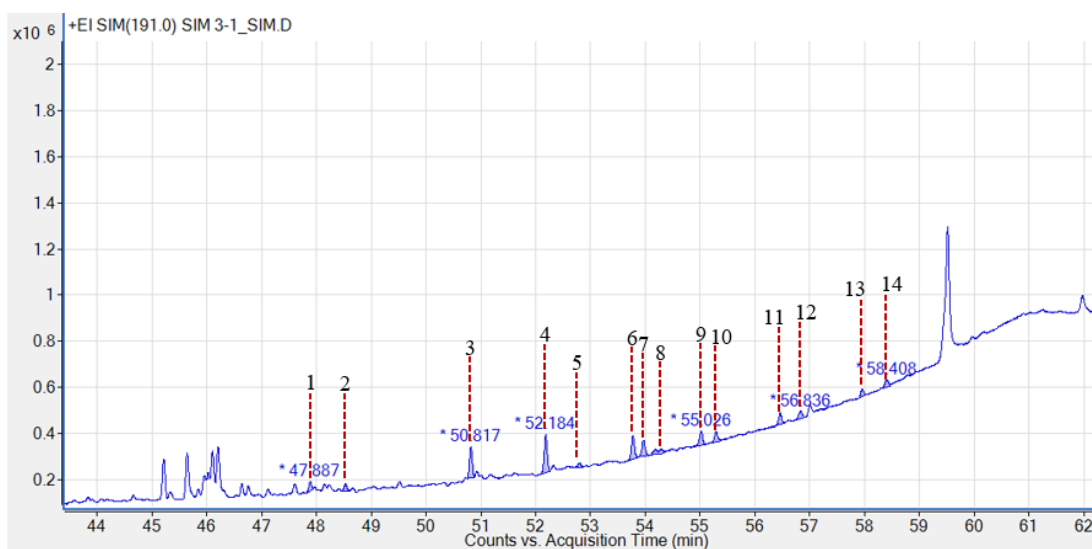
Sample ID: NP-3/4 (limestone)
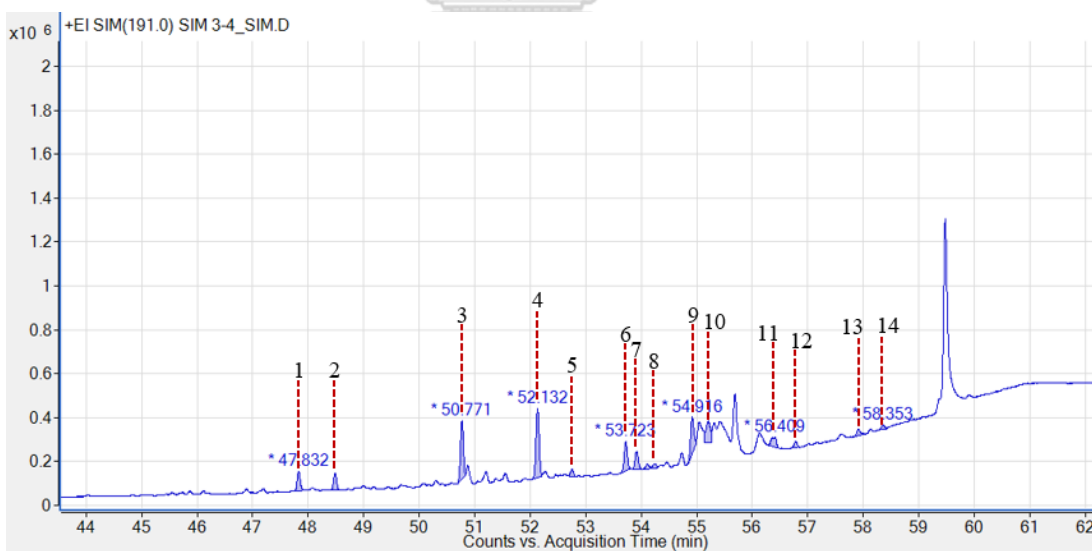
Sample ID: NP-3/2 (shale)
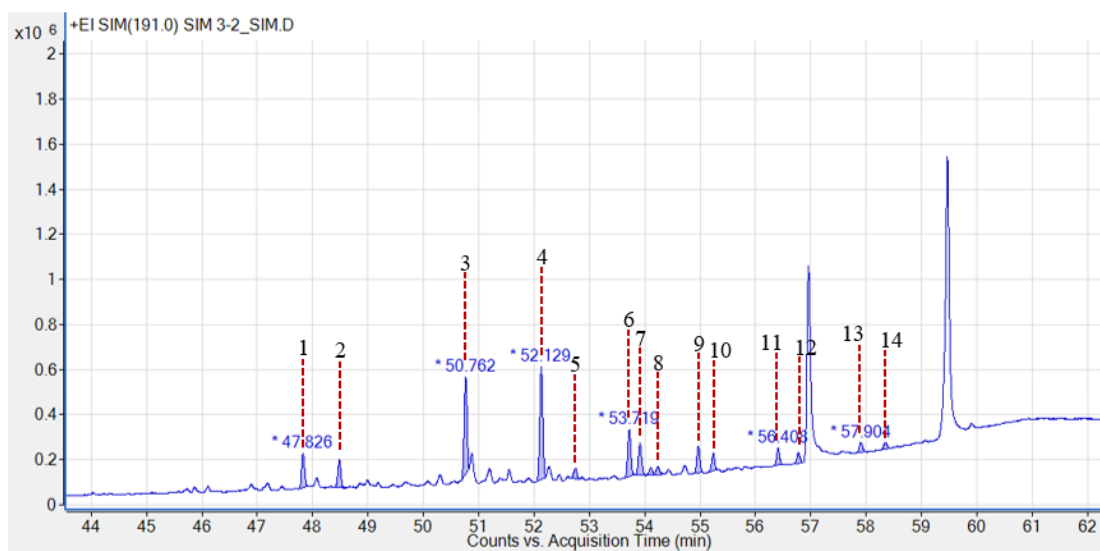
Sample ID: NP-3/3 (shale)
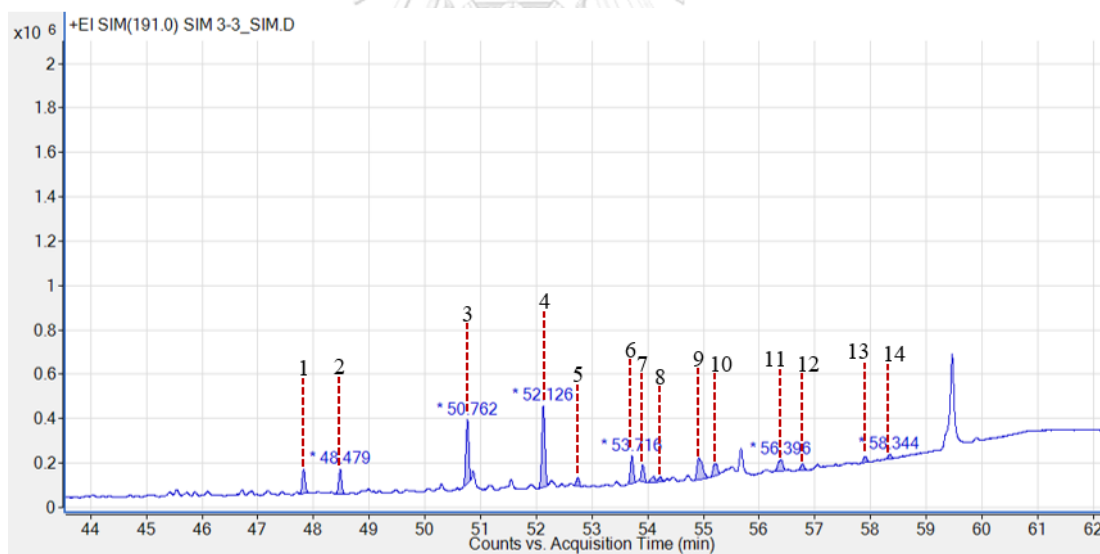
Gas chromatogram m/z 217 (Regular steranes)

Peak name	Carbon number	Identification
ααα-C_{27}(20S)	C_{27}	5α, 14α, 17α(H)-Cholestane 20S
αββ-C_{27}(20R)	C_{27}	5α, 14β, 17β(H)-Cholestane 20R
αββ-C_{27}(20S)	C_{27}	5α, 14β, 17β((H)-Cholestane 20S
ααα-C_{27}(20R)	C_{27}	5α, 14α, 17α (H)-Cholestane 20R
ααα-C_{28}(20S)	C_{28}	5α, 14α, 17α (H)-Ergostane 20S
αββ-C_{28}(20R)	C_{28}	5α, 14β, 17β (H)-Ergostane 20R
αββ-C_{28}(20S)	C_{28}	5α, 14β, 17β (H)-Ergostane 20S
ααα-C_{28}(20R)	C_{28}	5α, 14α, 17α (H)-Ergostane 20R
ααα-C_{29}(20S)	C_{29}	5α, 14α, 17α (H)-Stigmastane 20S
αββ-C_{29}(20R)	C_{29}	5α, 14β, 17β (H)-Stigmastane 20R
αββ-C_{29}(20S)	C_{29}	5α, 14β, 17β (H)-Stigmastane 20S
ααα-C_{29}(20R)	C_{29}	5α, 14α, 17α (H)-Stigmastane 20R

Location: Bueng Sam Phan 1 (Ban Pho Sawan 1 area), Phetchabun Province
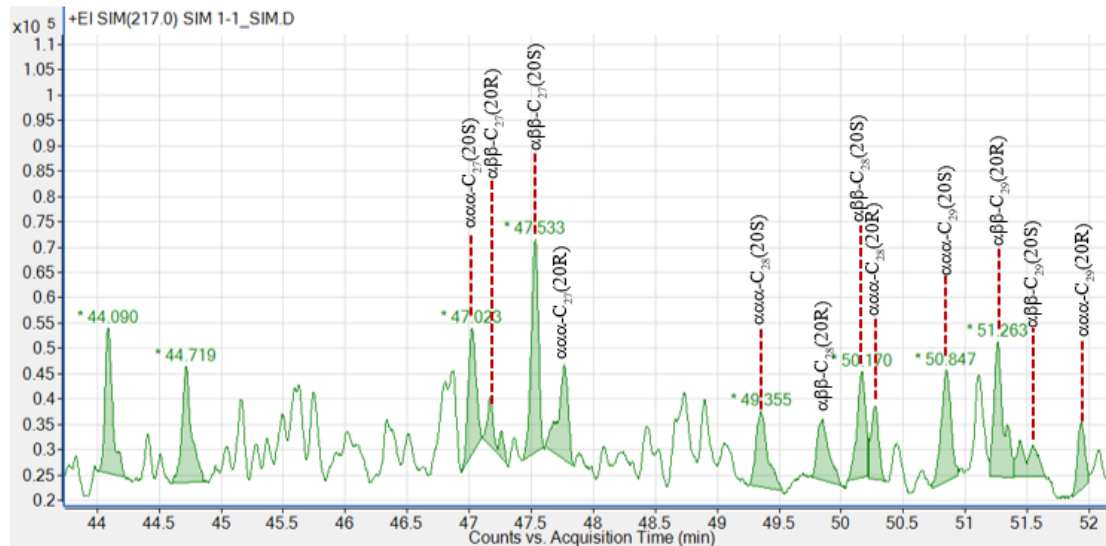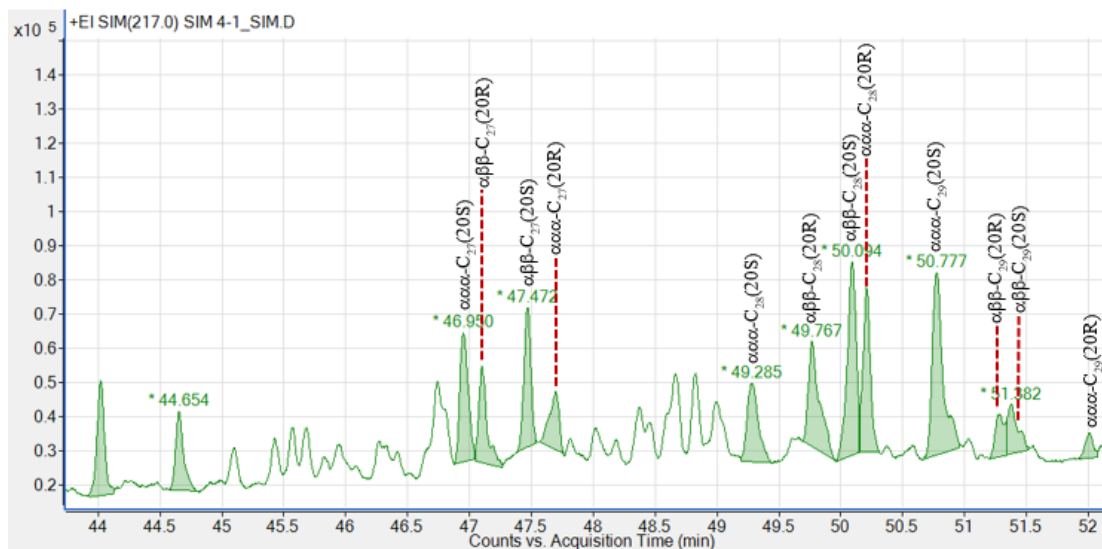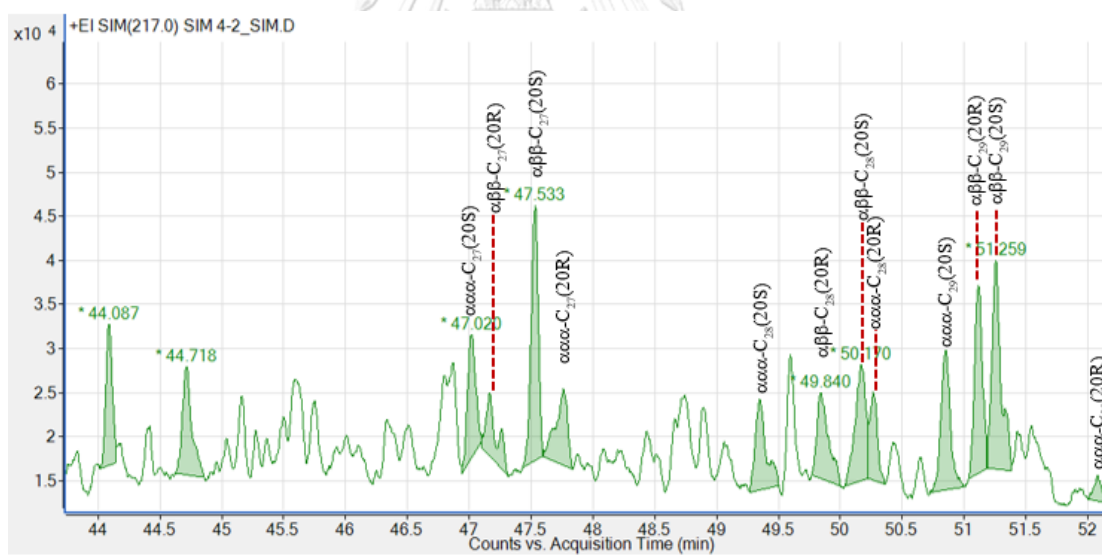
Sample ID: BP1-1/1
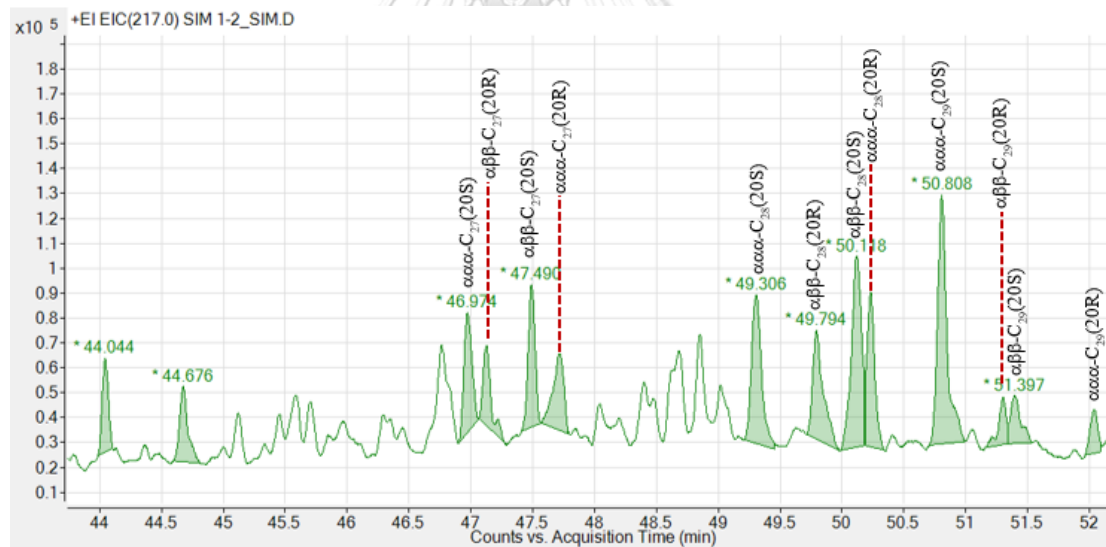
Sample ID: BP1-1/2

Location: Bueng Sam Phan 2 (Ban Pho Sawan 2 area), Phetchabun Province
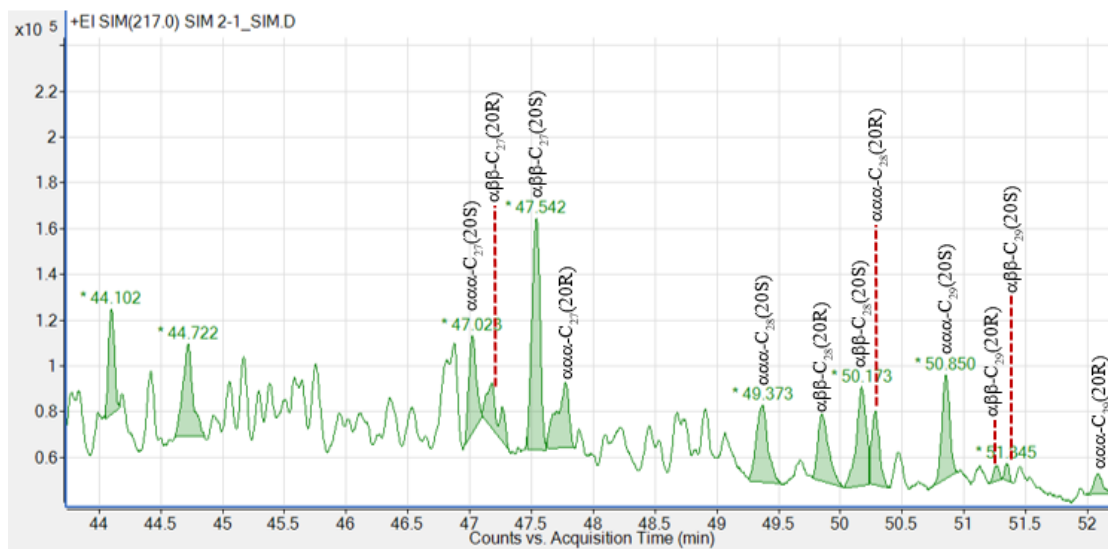
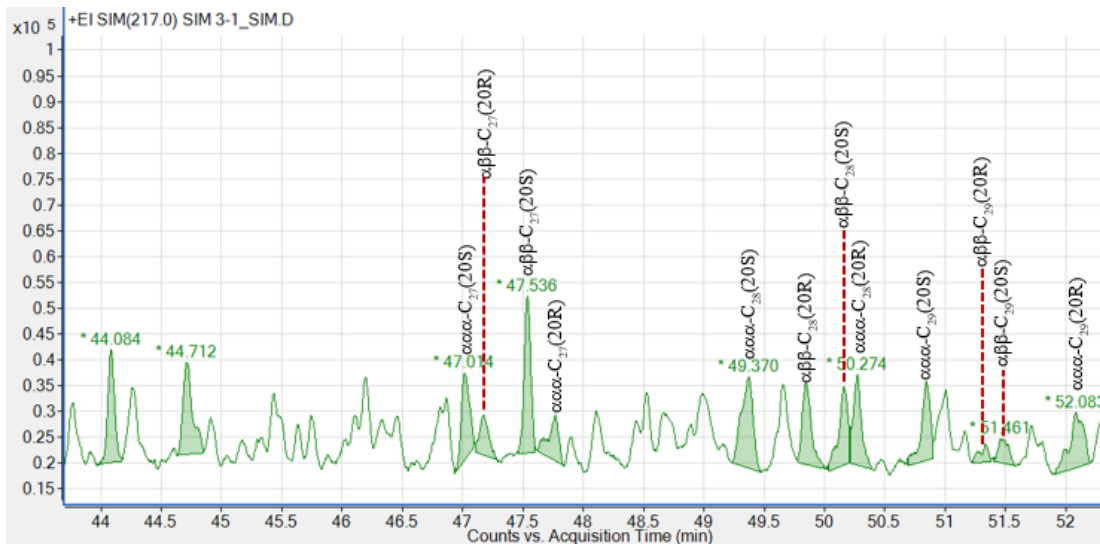Sample ID: BP2-4/1

Sample ID: BP2-4/2

Location: Chon Daen section (Phu Pra That temple), Phetchabun Province
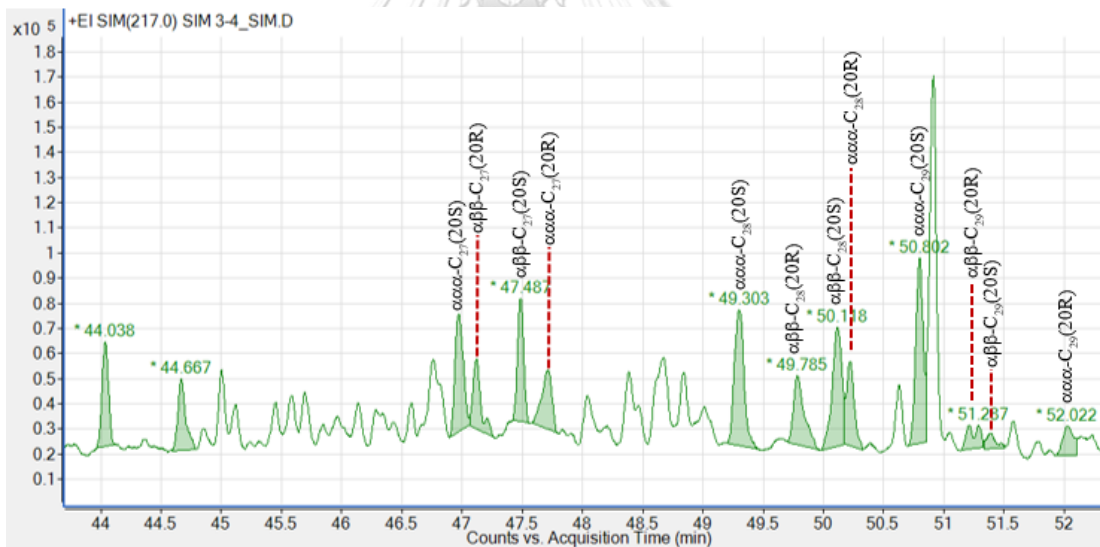
Sample ID: CD-2/1

Location: Nong Phai section, Phetchabun Province
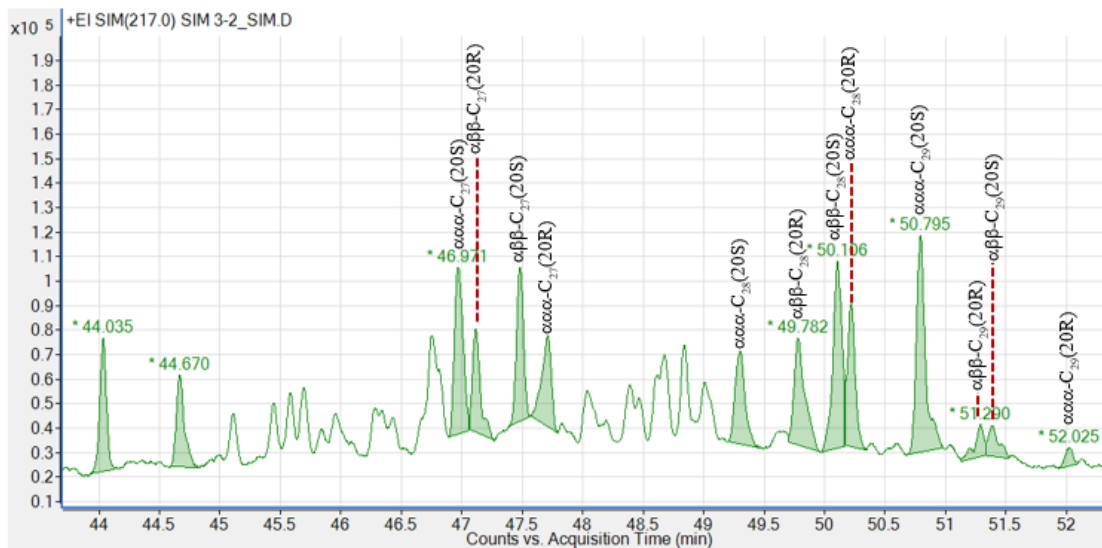
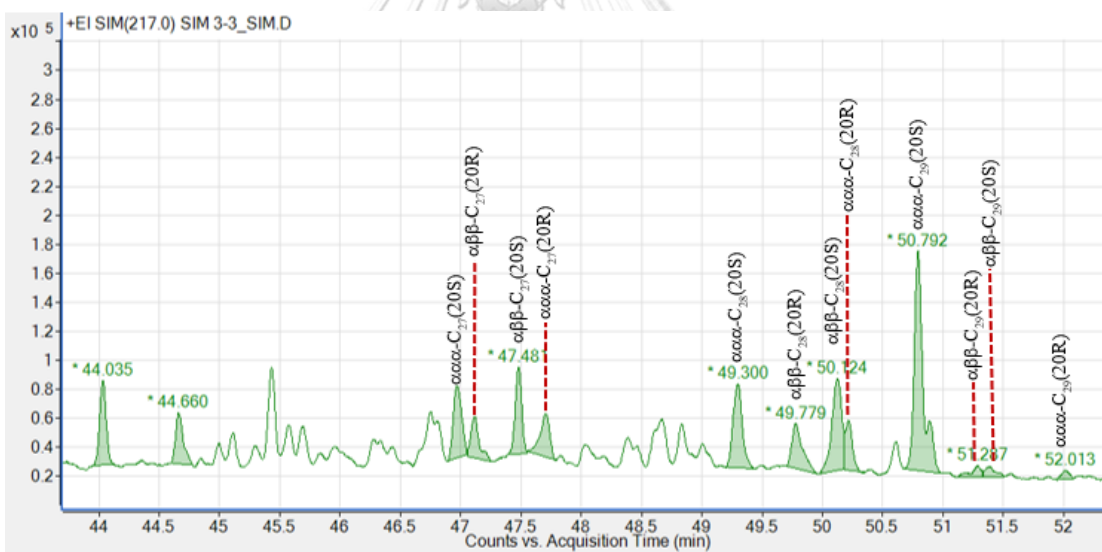Sample ID: NP-3/1

Sample ID: NP-3/4

Location: Nong Phai section, Phetchabun Province

Sample ID: NP-3/2

Sample ID: NP-3/3

VITA

Mr.Supawich Fuengfu was born in Bangkok since 1993. He studied at Wat Rajadhiwas School in Bangkok from 2006-2012. He graduated in bachelor's degree of science of chemistry from Srinakharinwirot University in 2016. After graduated, he has been started in master's degree of science in earth sciences program at Department of Geology, Faculty of Science, Chulalongkorn University since 2016.

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