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SOURCE ROCK FACIES CHARACTERIZATION FROM ORGANIC GEOCHEMISTRY IN THE CENTRAL SUMATRA BASIN, INDONESIA

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SOURCE ROCK FACIES CHARACTERIZATION FROM ORGANIC GEOCHEMISTRY IN THE CENTRAL SUMATRA BASIN, INDONESIA

A DISSERTATION APPROVED FOR THE
CONOCO PHILLIPS SCHOOL OF GEOLOGY AND GEOPHYSICS

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To Diego Ignacio

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Abstract

The geochemical composition of thirty two (32) oil samples in the Central Sumatra Basin (CSB) were determined by gas chromatography (GC), gas chromatography coupled with mass spectrometry (GC-MS) and gas chromatography isotope ratio mass spectrometry (GC IR-MS). The carefully selected sample set is representatively distributed among the oils producing grabens in the CSB: Aman, Balam, Tanjung Medan, Kiri and Bengkalis Troughs. The oils are derived from the lacustrine Brown Shale Formation of Eocene – Oligocene age.

The main objective of this study was to perform a detailed geochemical characterization of the sampled oils in order to understand the observed chemical variability within the CSB. Moreover, it aimed at interpreting changes in depositional environments within the source rock that generated these oils.

Combination of molecular and carbon isotopic composition revealed that five source rock facies developed in the studied grabens: (1) deep lacustrine, (2) shallow lacustrine, (3) saline lacustrine, (4) coal, and (5) mixed coal/lacustrine shale. The geographic distribution of the samples indicates that deep stratified lakes developed in the Aman and Bengkalis Troughs. Oils in the Kiri graben are predominantly derived from a shallow lacustrine facies while the oils south of the Aman and Kiri grabens display a more saline lacustrine facies. Coal derived oils and oils derived from a mixed coal/lacustrine shale facies seem to be restricted to the northern part of the Central Sumatra Basin.

A detailed look at the geochemical composition of the oils in the Aman Trough allowed identification of paleoproductivity and paleoclimatic changes that took place

during source rock deposition. Isotopic data indicate CO_2 limiting conditions prevailed during source rock deposition and that changes occured in paleoclimatic conditions, possibly associated with the Eocene-Oligocene paleoclimatic transition. These changes in depositional conditions had an effect on the geochemical composition of the source rocks in the Aman Trough.

A new sesquiterpane biomarker compound was identified in the oils from the Aman Trough and was tentatively identified as a C_{15} sesquiterpane.

Chapter I

Introduction

The Central Sumatra basin is considered the most prolific in Indonesia with estimated tens of billions of barrels of oil (Katz, 1995; Williams and Eubank, 1995) generated from organic rich lacustrine shales belonging to the Brown Shale Formation of the Pematang group (Williams et al., 1985; Katz and Mertani, 1989; Katz, 1995; Katz and Dawson, 1997; Huang et al., 2002).

This basin is one of a series of back-arc basins formed by north-south grabens and half-grabens developed as a result of transtensional stress during the Early Eocene. This extensional episode was associated with the early stages of back-arc basin evolution, as a result of subduction of the Indian Ocean Plate beneath the Southeast Asian Plate (Williams et al., 1985; Longley et al., 1990).

Stratigraphic variations within lacustrine systems have been attributed to several factors including productivity (Hollander et al., 1990; Curiale and Gibling, 1994), subsidence history, nutrient availability, water depth and chemistry, water column stability, basin hydrodynamics and climate (Katz, 1991 and 1995). All these factors could influence deposition of organic matter in different ways.

Climatic induced cycles are well developed within the mid-Pematang lacustrine sequence where deep lacustrine, shallow lacustrine and lake margin facies appear to cycle over relatively short stratigraphic intervals. These changes reflect variations in the hydrologic cycle, possibly introduced through Milankovitch forcing (Katz, 1991; Katz and Dawson, 1997). Subsidence and sedimentary history also play an important role in

the lithologic character of the source rock. For example, the greater balance between subsidence and sedimentation in the Kiri sub-basin lead to a coalier Pematang Group than the Aman sub-basin where deep lacustrine facies developed (Katz and Dawson, 1997).

Overall, these controlling factors affect each of the individual lakes (troughs) at different stages of source rock deposition and with different degrees of intensity, creating ideal conditions for both lateral and stratigraphic facies variations within a single source rock. This is evidenced in the variability of the organic chemistry of the oils found in the Central Sumatra Basin.

A simple model combining subsidence rate and terrigenous input has been successfully applied to explain the distribution of the bulk of hydrocarbon reserves (Williams et al., 1985); however this model does not explain the source of the smaller accumulations in the basin. Moreover, several oil families have been described (Seifert and Moldowan, 1981; Katz and Mertani, 1989), yet the specific depositional environments associated with each of the facies have not been established.

The main objective of this study was to perform a detailed geochemical characterization of thirty (32) oil samples from the Central Sumatra Basin in order to establish source rock facies variations from the oils.

Geochemical analyses focus on the molecular composition of the oils as well as compound specific isotopic compositions of the *n*-alkanes. The use of several source facies specific biomarkers and correlation techniques allow for the identification and differentiation of the depositional environments of the source rock associated with each of the sub-basins.

Such an approach will allow development of a depositional model for lacustrine source rocks in tropical clastic settings. Source rock depositional models have the potential to be used as a predictive tool for several important geochemical parameters associated with oil and gas exploration and production: Source rock type and quality (e.g. oil prone vs. gas prone); Hydrocarbon phase (e.g. oil vs. gas); Hydrocarbon quality (e.g. waxy vs. non-waxy). Additionally, they can also be used as depositional analogs for source rock intervals deposited under similar conditions during different geologic times and spaces. These applications go beyond simply identifying oils families that are basin specific and only applicable to the area for which they were developed.

Specific objectives for this study will include:

1. The characterization of suites of oils from several sub-basins.

2. Establish the number of oil families based on biomarker and isotope analyses and determine the organic facies of the corresponding source rock.

3. Confirm that the differences do not reflect biodegradation or any other secondary effects.

4. Establish a relationship between organic facies variations and changes in lacustrine depositional environments.

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Chapter II

Productivity and paleoclimatic controls on source rock character in the Aman Trough, North Central Sumatra, Indonesia.

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Abstract

The Central Sumatra Basin (CSB) is a prolific oil producing basin in Indonesia where a single source rock has been identified, the Brown Shale Formation of the Paleogene Pematang Group. Despite the presence of a single source rock, the oils in the Central Sumatra Basin and particularly in the Aman Trough, exhibit variable molecular and isotopic compositions, previously described as reflective of lateral facies variations within the source rock. Analyses by gas chromatography (GC), gas chromatography – mass spectrometry (GC-MS) and gas chromatography – isotope ratio mass spectrometry (GC-IRMS) of 15 oil samples from the Aman Trough allowed identification of vertical and lateral facies changes within the Brown Shale Formation as well as paleoproductivity and paleoclimatic changes that took place during deposition of this prolific source rock. The molecular and isotopic data indicate the source rock for these oils was deposited in a fresh to brackish water stratified lake in which CO_2 limiting conditions prevailed. Compound specific isotopic data also indicate that changes in paleoclimatic conditions, possibly associated with the Eocene-Oligocene paleoclimatic transition, had an effect on the geochemical composition of the source rock in the Aman Trough.

1. Introduction

The Central Sumatra Basin (CSB) is the most prolific oil producing basin in Indonesia (Fig. 1) with tens of billions of barrels of oil in place (Kelley et al., 1994; Katz, 1995; Williams and Eubank, 1995). The Pematang - Sihapas petroleum system is the only hydrocarbon producing system in the basin, with 12.8 BBOE estimated untapped reserves (Clure, 2005). The Brown Shale Formation of the Pematang Group has been identified as the source rock for the oils in the CSB (Williams et al., 1985; Katz and Mertani, 1989; Katz, 1995). The general depositional environment of the Brown Shale Formation has been interpreted as a freshwater lake system with anoxic bottom conditions (Williams et al., 1985; Katz and Mertani, 1989; Longley et al., 1990; Katz, 1995). This interpretation is supported by the presence of the remains of diagnostic freshwater organisms like *Pediastrum* sp., *Botryococcus* sp. and freshwater dinoflagellates cysts (Longley et al., 1990). Oils in the CSB have variable molecular and isotopic compositions, which in many cases could be interpreted as evidence for the presence of multiple source rocks. Instead, these differences have been interpreted as representing source rock facies variations within the Brown Shale Formation (Seifert and Moldowan, 1981; Katz and Mertani, 1989).

Facies variations within similar lacustrine systems have been attributed to several factors including: productivity levels (Hollander et al., 1990; Curiale and Gibling, 1994), subsidence history, nutrient availability, water depth and chemistry, water column stability, basin hydrodynamics and climate (Katz, 1995; 2001). Although several oil families have been identified in multiple troughs in the CSB, and several factors have been proposed to explain the geochemical variability in the oil samples, only few direct

relationships have been suggested between the specific geochemical characteristics and associated controlling factors (Seifert and Moldowan, 1981; Katz, 1995).

In this paper, we present molecular and isotopic data from selected oils samples in the Aman Trough of the CSB (Fig. 1). We seek to establish relationships between the molecular and isotopic composition of the oils and changes in productivity and paleoclimate conditions during source rock deposition. The oils from the CSB represent an ideal sample suite for such a study because: 1) they are known to be derived from a single source rock; 2) have exhibited largely vertical and limited short migration distances within the Aman Trough (Hwang et al., 2002); and 3) the samples appear to have similar levels of thermal maturity.

2. Geologic Setting

The Central Sumatra Basin is one of a series of back-arc basins formed as a result of transtensional stress. This extensional episode was associated with the early stages of back-arc basin evolution, as a result of subduction of the Indian Ocean Plate beneath the Southeast Asian Plate (Williams et al., 1985; Longley et al., 1990). The sedimentary section has been divided into four tectonostratigraphic sequences (Longley et al., 1990). These sequences and associated formations are shown in Fig. 2.

During the Late Eocene (?) - Early Oligocene a pattern of north-south oriented horsts and grabens resulted from back-arc extensional processes in the CSB (De Smet and Barber, 2005). The grabens include the Bengkalis (south-east of the study area, not shown), Balam, Kiri, Rangau and Aman sub-basins or troughs (Fig. 1). The Balam-Aman

Central Deep contains over 3000m of Tertiary sediments (Yarmanto et al., 1995) separated from the Bengkalis Trough by a region of structural highs (Clure, 2005).

Sedimentation was initiated with the Pematang Group during the initial rifting stage, which comprises alluvial fan, fluvial, paludal and lacustrine sediments deposited under humid tropical conditions (Katz and Mertani 1989; Katz, 1995). The Pematang Group is overlain by a sequence of sediments of the Sihapas Group comprising alluvial sandstones of the Menggala Formation, fluvial, deltaic and shallow marine sandstones of the Bekasap and Duri Formations and marine shales of the Telisa Formation. This sediment succession records a marine transgression during a time of tectonic quiescence (De Smet and Barber, 2005). The third sequence is comprised of marine shales of the Petani Formation and fluvio-deltaic sediments of the lower Minas Formation, both deposited during a phase of transpresional tectonism that generated the major structures in the basin. The fourth and final sequence consists of alluvial-estuarine sands, peats and mudstones that resulted from the cessation of tectonism from the Pleistocene to recent times (Williams et al., 1985; Williams and Eubank, 1995).

The lacustrine facies of the Pematang Group is known as the Brown Shale Formation, and is considered the main source of hydrocarbons in the Central Sumatra Basin (Williams et al., 1985; Katz, 1995). Other fine grained intervals, which include the Petani and Telisa formations, have proved to be too organic-lean, display only marginal hydrocarbon generation potential, or are thermally immature (Katz and Mertani, 1989). Significant portions of the Brown Shale Formation are organic-rich, have elevated generation potential, oil prone character and are thermally mature (Katz and Mertani, 1989; Katz and Dawson, 1997).

Within the Brown Shale Formation, at least two organic-rich facies have been described (Williams et al., 1985; Longley et al., 1990). The dominantly deep lacustrine facies consist of dark brown to black, well laminated, non calcareous shales, containing type I and type II kerogens with total organic carbon (TOC) values ranging from 1% to 14%. Planktonic lacustrine algae (*Pediastrum* sp.) are dominant with variable amounts of freshwater dinoflagellate cysts and *Botryococcus* sp. A terrigenous organic matter contribution is interpreted from plant derived material observed during visual kerogen analyses, high pristane/phytane ratios, high wax contents and presence of oleanane in bitumen extracts from the Bengkalis Trough (Longley et al., 1990).

The dominantly shallow lacustrine facies consists of red-brown laminated mixed carbonate and terrigenous mudstones with abundant organic material and occasional coal stringers. Algal derived organic matter predominates resulting in oil prone type I kerogen with average TOC values of 3.4% (Williams et al., 1985; Longley et al., 1990). Bitumen extracts from the shallow lacustrine facies show high wax content, intermediate Pr/Ph ratios and oleanane with minor occurrences of gammacerane indicating water stratification or salinity cycles within the lake system (Longley et al., 1990).

3. Samples and Methods

Fifteen crude oil samples from the Aman Trough were selected for this study and their locations are depicted in Fig. 1. Twenty milligrams of sample was placed in a centrifuge tube and asphaltenes were precipitated using an excess (40:1) of *n*-pentane. Ultrasonic agitation was used for 60 minutes to promote complete asphaltene precipitation. The resulting maltene fractions were diluted using a ratio of 2 mg of sample

per 50 µL hexane for compound class fractionation. Fractionation was accomplished through column chromatography using activated silica gel (100°C/24h). Aliphatic, aromatic and NSO (nitrogen, sulfur and oxygen containing fraction) fractions were separated using hexane, toluene/hexane (70/30; v/v) and dichloromethane, respectively.

The maltene fraction was analyzed by gas chromatography (GC) using an Agilent 6890 series GC system with a split/splitless capillary injection system equipped with a 35 m x 0.25 mm (i.d.) J&W scientific DB-5 Petro fused silica capillary column with a 0.5 µm film thickness. Samples were analyzed in splitless injection mode with a temperature program set to an initial temperature of 40°C with a 1.5 minutes holding time. Temperature was increased to 300°C at 4°C/min rate and then isothermal for 31 min. Detector temperature was 310°C. Helium was used as the carrier gas with a flow rate of 1.4 ml/min.

Samples were also analyzed by gas chromatography-mass spectrometry (GC-MS) using an Agilent 7890 GC coupled with a 5975C MSD running on splitless injection mode. The GC used a 60 m x 0.25 mm J&W scientific DB-5 fused silica capillary column coated with a 0.25 µm liquid film. Selected ions were chosen for biomarker analyses using single ion monitoring (SIM) on all samples. In addition, full scan GC-MS analyses were completed on the saturate fraction of selected samples. The temperature program for the analyses started at 40°C with 1.5 minutes hold time. Oven temperature was increased to 300°C at 4°C/min rate and held isothermal for 54 minutes for a total run time of 123 minutes. Helium was used as the carrier gas with a flow rate of 1.4 ml/min.

Isotopic compositions of the individual compounds in the saturate fraction were determined by gas chromatography-isotope ratio mass spectrometry (GC-IRMS) using a

Varian 3400 gas chromatograph coupled through a combustion reactor with a Finnigan MAT 253 isotope ratio-mass spectrometer. The GC was equipped with a 65 m x 0.25 mm J&W scientific fused silica DB-1 Petro capillary column with a 0.5 μm film thickness. The GC oven program consisted of an initial temperature of 40°C held constant for 1.5 min. Oven temperature was then increased to 300°C at a rate of 4°C/min and then held constant for 24 minutes for a total run time of 90 minutes. The reported molecular ratios were calculated from peak areas on the gas chromatograms and the SIM mass chromatograms, as indicated.

4. Results and Discussion

4.1. Biomarker analysis

Table 1 summarizes the GC ratios used in the discussion. Gas chromatograms of the maltene fraction for selected samples representative of the variability observed in the sample set are presented in Fig. 3.

The chromatograms of all but the Duri oils are dominated by a series of *n*-alkanes ranging from C_{10}-C_{34}, and the isoprenoid hydrocarbons pristane, phytane and botryococcane. The chromatograms of the Duri oils are dominated by a series of partially degraded *n*-alkanes ranging from *n*C_{15}-*n*C_{33}, and the isoprenoids pristane, phytane and botryococcane (Fig. 3). The two oils from the Duri field show evidence of partial *n*-alkane removal, however alkylcyclohexanes and isoprenoids are still present in the samples, indicating they have been biodegraded to stage two on the Peters and Moldowan biodegradation scale (Peters and Moldowan, 1993).

The *n*-alkanes in non-biodegraded samples maximize between nC$_{14}$-nC$_{17}$ indicating a major input from algal organic matter (Gelpi et al., 1970; Tissot and Welte, 1984). Additional contributions from waxy hydrocarbons (C_{22}+), with considerable proportions of C_{27}, C_{28} and C_{29} *n*-alkanes with slight odd-over-even carbon predominance (Marzi et al., 1993) could indicate contributions from terrigenous organic matter (Eglinton, 1967; Simoneit, 1977; Pancost et al., 2002). Botryococcane was also identified in all but one of the samples, namely Pematang Bow. Botryococcane is derived from the green algae *Botryococcus braunii*, which is typically found in fresh to brackish water lacustrine environments (Metzger et al., 1985; Seifert and Moldowan, 1981). *n*-Alkanes in the C_{23}-C_{30} range can also be derived from *B. braunii* (Gelpi et al., 1970, Moldowan et al., 1985), however the presence of small quantities of 18α(H) oleanane and 4β-eudesmane in most samples support the interpretation of at least some contribution of terrigenous organic matter to these oils (Alexander et al., 1984; Moldowan et al., 1994).

Three distinct races of *B. braunii* (A, B, and L) have been recognized according to their hydrocarbon composition. Race A exclusively produces straight chain alkadienes and trienes (Metzger et al., 1985; Derenne et al., 1988), while race L yields only the C_{40} isoprenoid hydrocarbon lycopadiene (Metzger et al., 1991). Only race B is capable of generating C_{30} to C_{37} isoprenoid hydrocarbons named botryococcenes, the only known precursors of the biomarker botryococcane (Metzger et al., 1985 and 1991). The absence of botryococcane in the Pematang Bow sample could indicate changes in the paleodepositional conditions of the source rock facies that generated this oil. Smittenberg et al. (2005) suggested that lake eutrophication can lead to *B. braunii* extinction under

conditions of increased nutrient availability. Alternatively, race B of *B. braunii* was absent during deposition of the source rock interval for this particular sample.

Pristane/phytane (Pr/Ph) ratios in oils from the Aman Trough range from 1.8-3.1. Such values indicate oxic/sub-oxic depositional conditions (Didyk et al., 1978). The relationship between Pr/nC$_{17}$ and Ph/nC$_{18}$ (Fig. 4) has been used to infer oxicity and organic matter type in the source rock depositional environment as well as thermal maturity and biodegradation of oils (Hunt, 1996; Peters et al., 1999). The samples from the Aman Trough plot relatively close together near the boundary between non-marine and mixed organic matter potentially reflecting a dual source of organic matter for these oils. It also indicates the samples represent a limited range of thermal maturity. The two biodegraded samples are clearly distinguished from the main group of oil samples. This distinction results from the selective removal of *n*-alkanes during the biodegradation process that causes the Pr/nC$_{17}$ and Ph/nC$_{18}$ ratios to increase with increasing biodegradation level (Peters et al., 1999). The low level of biodegradation in these oils allows the use of terpane and hopane biomarkers in the interpretation of their thermal maturity and source rock depositional environment.

Selected GC-MS derived biomarker ratios are presented in Table 2 and discussed below. Interpretations of source rock depositional environments from oils through biomarker analysis are usually hindered by differing maturity levels between the studied samples (Curiale, 2008). Two biomarker ratios Ts/(Ts+Tm) and H_{32} S/(S+R), that are considered largely reflective of thermal maturity of the source rock at the time of expulsion (Peters and Moldowan, 1993) are presented in Table 2. These ratios indicate

the oils in this study were generated at similar maturity levels, therefore, minimizing the effect of maturity on source rock facies interpretations.

Relatively high values of the C_{26}/C_{25} tricyclic terpane ratios ($C_{26}/C_{25}>1$; Zumberge, 1987) combined with low values of the $C_{31}R/C_{30}$ hopane ratios ($C_{31}R/C_{30}<0.40$; Peters et al., 2005) indicate the oils in the Aman Trough were generated by a lacustrine source rock (Fig. 5a). These biomarker ratios support the interpretation derived from the presence of botryococcane in all but one of the oils. High C_{22}/C_{21} and low C_{24}/C_{23} tricyclic terpanes ratios are usually indicative of carbonate source rocks (Peters et al., 2005). The opposite is observed in the samples from the Aman Trough. The C_{22}/C_{21} tricyclic terpane ratios are lower than 0.31 while the C_{24}/C_{23} tricyclic terpane ratios are greater than 0.59 (Fig. 5b) indicating a clastic character for the oil's source. This interpretation is supported by ratios of 30-norhopane/hopane (C_{29}/H) which are consistently lower than 1 (Table 2). C_{29}/H ratios are typically greater than 1.0 in anoxic carbonate or marl source rocks (Peters et al., 2005).

Gammacerane was identified in all non-biodegraded samples from the Aman Trough and the relationship between the gammacerane index (Ga/C_{31}R) and the Pr/Ph ratio is shown in Fig. 5c. Gammacerane commonly indicates water column stratification in marine and non-marine depositional environments (ten Haven et al., 1988; Sinninghe Damste et al., 1995; Peters et al., 2005). The presence of gammacerane is usually accompanied by Pr/Ph lower than 1.0 and is typically interpreted as showing water column stratification due to hypersalinity. In the Aman Trough, however, the presence of gammacerane is accompanied by Pr/Ph values greater than 1.8 shedding doubt on hypersalinity as the cause for water column stratification. Stratified water columns can

easily develop from temperature gradients in warm, humid climate regimes with minimal seasonal contrasts (Talbot, 1988). In the case of the Aman Trough, the presence of gammacerane is interpreted as indicative of the development of a stratified water column due to a lack of seasonal temperature changes.

Oleanane was recognized in all oil samples in the Aman Trough, with oleanane index values raging from 0.07 to 0.26 (Table 2). Oleanane is frequently used as a marker for source rock input and age. It is derived from organic compounds present in angiosperms (flowering plants, ten Haven and Rullkotter, 1988), which became prominent in the Late Cretaceous and younger times (Gensel and Andrews, 1987). The presence of oleanane in the Aman Trough samples, therefore, indicates terrigenous contribution to the organic matter in the source rock, as well as a Late Cretaceous or younger age. This interpretation agrees with the hypothesis of the Eocene-Oligocene Brown Shale Formation as the main source rock for the oils in the Aman Trough.

Higher relative values of extended tricyclic terpanes from C_{28}-C_{30} were identified in the Pematang Bow sample (Fig. 5d). These compounds are also present in oil samples from the Pudu (Katz, 2001) and Pinggir (Katz, Personal communication) fields in the Aman Trough, located west and south of the Pematang Bow field, respectively. The occurrence of extended tricyclic terpanes in petroleum was first reported by Moldowan et al. (1983) and has been reported in source rocks and oils of lacustrine and marine origin (Kruge et al., 1990; de Grande et al., 1993). Kruge et al. (1990) reported the presence of extended tricyclic terpanes in samples from a black shale interval in a lacustrine sequence in the Hartford Basin in the U.S.A., deposited in a thermally stratified lake characterized by alkaline water conditions, rich in dissolved bicarbonate, calcium, magnesium, sodium

and sulfate. Furthermore, de Grande et al. (1993) suggested precursors for these compounds are suppressed by hypersalinity and freshwater conditions. In this study, high values of extended tricyclic terpanes are only present in the Pematang Bow sample, which is also the only sample in which botryococcane is absent. The gammacerane ratio value in the Pematang Bow sample is similar to other samples in this study that do contain botryococcane (Fig. 5c), suggesting fresh to brackish water conditions prevailed during source rock deposition. Conversely, the ratio of the sum of C_{28}+C_{29}+C_{30} extended tricyclic terpanes relative to hopane (C_{28}+C_{29}+C_{30}/H) is significantly higher in the Pematang Bow sample (Fig. 5d). Higher relative amounts of extended tricyclic terpanes, therefore, could indicate an increase in lake water alkalinity during source rock deposition for the Pematang Bow and other samples in the Aman Trough containing these compounds. Increased lake water alkalinity is a common result from increased water productivity due to CO_2 removal during the photosynthetic process (Lerman and Stumm, 1989). The absence of botryococcane in the Pematang Bow sample could have resulted from the total or partial extinction of *B. braunii* race B due to eutrophication which ultimately resulted in increased water alkalinity (Lerman and Stumm, 1989).

A suite of C_{14} to C_{16} sesquiterpane hydrocarbons were identified in the Aman Trough samples by monitoring the m/z 123 fragment ion. Eudesmane, drimane, homodrimane and compound A from Nytoft et al. (2009) (also identified as compound A in this study) were identified as well as other bicyclic terpanes (Fig. 6, Table 3).

The sesquiterpane eudesmane has been linked to higher plant terpanes (Alexander et al., 1984; Peters et al., 2005), while compound A is thought to be derived from degradation of oleanoids (Nytoft et al., 2009) and is also considered a marker for higher

plant input. The presence of these compounds supports the hypothesis of terrigenous organic matter contribution to the source rock of the oils.

Eudesmane is absent from the two biodegraded samples from the Duri field. According to the Peters and Moldowan (1993) biodegradation scale, *n*-alkanes, alkylcyclohexanes and isoprenoids are more prone to biodegradation than the C_{14}-C_{16} bicyclic terpanes. However, the two samples contain the isoprenoids pristane, phytane and botryococcane, and part of the *n*-alkane series (nC_{14}-nC_{33}). This seems to indicate successive episodes of biodegradation and recharge have taken place at the Duri field.

A new bicyclic terpane (Compound Z, Fig. 6) was identified in the oil samples from the Aman Trough. In an attempt to identify compound Z, its mass spectrum (Fig. 7) was compared with several previously published sesquiterpane spectra (Alexander et al., 1983; Noble, 1986; Roderick et al., 1989; Nytoft et al., 2009). The molecular ion at m/z 208 and relative retention time indicated that this compound was in all probability a C_{15} sesquiterpane. Comparison with the spectra of 4α(H) and 4β(H) eudesmane showed very similar mass spectral fragmentation patterns, specifically the ions at m/z 165 (loss of isopropyl fragment) and m/z 109 (A ring fragment with monomethyl substituent at C_4). However, the relative intensity of the ion at m/z 165 relative to m/z 193 plus difference in retention times suggested that this compound was not either of the eudesmane isomers. Furthermore, the ion at m/z 137 that is evident in the eudesmanes is not present in this spectrum. Therefore while the similarity in the fragmentation patterns suggests a structure that is similar to the eudesmane it would appear that in all probability this is a previously unidentified sesquiterpane. (Personal communication with Peter Nytoft indicated that

based on a search of a personal collection of C_{15} sesquiterpanes, this compound had not been previously identified in crude oils or source rock extracts.)

4.2. Isotopic analysis

Carbon isotope values of individual *n*-alkanes are listed in Table 4 and plotted in Fig. 8. $\delta^{13}C$ values are expressed in ‰ relative to the Vienna Pee Dee Belemnite (VPDB) standard. The carbon isotopic composition of the samples varies between -27.2 and -24.7 ‰ for the lower carbon number compounds, and becomes lighter with increasing carbon number. The greatest difference in isotopic composition between samples occurs at carbon number 29 where isotopes values range from -33.4 to -26.2 ‰. Three populations are identified based on isotopic composition and the *n*-alkane isotope profiles (Fig. 8). The first group (Fig. 8A) represents samples with the lightest isotopic values, although still with a wide range of isotope values. This group displays the greatest difference between the isotope values of the lowest (C_{15}) and highest (C_{34}) carbon number *n*-alkanes studied for a single sample (e.g. from -27.7 to -33.5 ‰). The second group of samples (Fig. 8b) is represented by heavier average $\delta^{13}C$ values and the lowest isotopic difference between the low and the high carbon number compounds. The third group corresponds to the Pematang Bow oil (Fig. 8C) which is the sample with the heaviest average isotope value, in which botryococcane is absent and also contains higher relative values of extended tricyclic terpanes. The squares (Fig. 8C) represent one of the two biodegraded samples analyzed in this study. The Duri 1 oil did not contain sufficient *n*-alkanes for compound specific isotope analyses.

The main difference between groups 1 and 2 is the trend observed in the isotopic composition of the oils. Oils within group 1 have lighter $\delta^{13}C$ values in the C_{27}-C_{34} carbon range compared to $\delta^{13}C$ values in the C_{15}-C_{26} carbon range, and an overall isotopically lighter composition compared to samples in group 2. Samples in group 2 have more constant $\delta^{13}C$ values, and an overall heavier isotopic composition compared to samples in group 1. The Pematang Bow sample has the heaviest $\delta^{13}C$ values in the dataset.

Despite the wide range of $\delta^{13}C$ values observed within and among the three oil groups, the molecular data do not suggest significant differences in depositional environment, with the exception of the Pematang Bow sample. We believe that the observed variations in the isotopic composition are reflecting changes in paleoproductivity and paleoclimatic conditions that are not readily reflected in the molecular composition of the oils. Curiale and Gibling (1994) introduced the concept of CO_2 limiting conditions on carbon isotope composition during source rock deposition in lacustrine settings. CO_2 limiting conditions develop when productivity blooms sequester CO_2 in the upper part of the water column, resulting in the isotopic enrichment of the remaining CO_2 available for photosynthesis in the water column. This process ultimately results in a positive correlation between productivity and the $\delta^{13}C$ of the preserved organic matter.

$\delta^{13}C$ values of the samples in group 1 show a progressively heavier isotopic composition which we believe is evidence of the development of CO_2 limiting conditions during deposition of the source rock (or source rock intervals). Development of a stratified water column is evident from the presence of gammacerane in the samples.

Additional support for this hypothesis is apparent in published data from Katz and Mertani (1989) where a positive correlation is observed between $\delta^{13}C$ and the hydrogen to carbon ratio (H/C) of isolated kerogen from the Brown Shale Formation in the Balam Trough (Fig. 9), northwest of the study area (Fig. 1).

Mixed algal and terrigenous organic matter contribution to these samples is evident through the assessment of the molecular data and is reflected in the *n*-alkane carbon isotopic profile of the samples.

A pronounced shift in the isotopic composition of the higher molecular weight *n*-alkanes is observed from the lighter to the heaviest samples in group 1, and from samples in group 1 compared to samples in groups 2 and 3.

Average isotope values for the odd long-chain n-alkanes nC_{29} and nC_{31} for samples in group 1 are -31.6 and -29.7 ‰ respectively (Table 5). These values are within the range of $\delta^{13}C$ values characteristic for C_3 plants (Collister et al., 1994). $\delta^{13}C$ values for the odd long-chain n-alkanes nC_{29} and nC_{31} for samples in group 2 show an average 2-4 ‰ enrichment compared to samples in group 1. The Pematang Bow sample shows an additional average 2 ‰ enrichment compared to average values from samples in group 2 (Table 5). Decreased terrigenous organic matter contribution to the source rock could have resulted in the observed carbon isotopic enrichment of long-chain *n*-alkanes. Decreased contribution from C_3 plants would result in an increase in the relative contribution of *B. braunii* derived long-chain *n*-alkanes to the organic matter as race A of *Botryococcus braunii* mimics terrestrial plant input with an odd over even predominance (Lichtfouse et al., 1994). Interestingly, samples in groups 2 and 3 only show a subdued odd over even predominance and botryococcane is absent from the Pematang Bow oil,

the isotopically heaviest sample in the dataset. Alternatively, we suggest that the observed shift in $\delta^{13}C$ values from group 1 to groups 2 and 3 could be the consequence of a shift from C_3 plants to a combination of C_3 and C_4 plants derived organic matter contribution to the source rock. Carbon isotopic composition of C_4 terrestrial plants (e.g. grasses and sedges) is approximately 10 ‰ heavier than C_3 terrestrial plants (e.g. tobacco, soybeans and most trees; Meyers, 1994). Plants following the C_4 pathway have been identified as early as in the Early Oligocene (Urban et al., 2010), and are tolerant to high temperatures and aridity and tend to thrive under conditions of low pCO_2 (Sharpe, 2007). This interpretation is independent from the presence/absence of botryococcane in the Aman Trough paleo-lake and is in agreement with global paleoclimatic changes that took place during the Eocene-Oligocene transition. The Eocene-Oligocene transition has been described as a time of profound climate change characterized by substantial ice growth and global decline in atmospheric CO_2 (Lear et al., 2008; Miller et al., 2009; Liu et al., 2009). Atmospheric pCO_2estimates indicate a reduction from ~1,100 ppmv to ~760 ppmv during the initial phase of the Eocene-Oligocene transition (Pearson et al., 2009). As atmospheric CO_2 decreased and warm temperatures prevailed in the tropical paleolakes of Central Sumatra, CO_2 limiting conditions were progressively enhanced which combined with changes in terrigenous organic matter contribution to the source rock resulted in the observed variations in carbon isotopic composition in the studied oils.

5. Summary and Conclusions

Analysis of the molecular and isotopic composition of oils from the Aman Trough in the Central Sumatra Basin indicate the source rock for these oils was deposited in a

fresh to brackish water stratified lake, with a mixture of algal and terrigenous organic matter contributions, in which CO_2 limiting conditions prevailed. The oil samples in this study are considered representative of three source rock settings or facies within the Brown Shale Formation. These three facies reflect progressive changes in productivity, organic matter sources and paleoclimate during source rock deposition.

One source rock facies is represented by the isotopically lighter samples in group 1. During this time, source rock accumulation occurred in a fresh to brackish water stratified lake in which CO_2 limiting conditions developed due to high productivity associated with high nutrient availability. The second facies is represented by the isotopically heavier samples in group 2. A shift in terrigenous organic matter contribution is interpreted from the carbon isotopic composition of the long chain n-alkanes in the oils, associated with paleoclimatic changes during the Eocene-Oligocene transition. Continued high productivity as well as CO_2 limiting conditions resulted in lake eutrophication and later increase in water alkalinity reflected by the isotopically heaviest sample (Pematang Bow oil).

A new sesquiterpane biomarker compound was identified in the oils from the Aman Trough. The new compound has tentatively been identified as a C_{15} sesquiterpane based on mass spectra, however, more analyses are needed in order to establish its molecular structure.

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Table 1. Biomarker ratios calculated from gas chromatograms of the maltene fraction.

Sample name	***Pr/Ph***	***Pr/nC_{17}***	***Ph/nC_{18}***	***CPI2 (Marzi et al., 1993)***
Ami	2.2	0.35	0.17	1.02
Kakap	2.4	0.32	0.15	1.05
Libo	2.5	0.62	0.28	1.05
Minas 3	2.5	0.35	0.16	1.05
Minas 7	2.7	0.35	0.15	1.01
Pematang	3.0	0.45	0.17	1.06
Pungut	2.8	0.28	0.12	1.04
Ubi	3.1	0.50	0.17	1.05
Mindal	2.6	0.26	0.13	1.08
Libo SE	2.6	0.22	0.10	1.04
Minas 6	2.5	0.34	0.15	1.06
Pematang Bow	2.3	0.30	0.14	1.04
Petani	2.2	0.38	0.18	1.07
Duri 1	1.8	4.50	3.24	1.19
Duri 2	2.2	3.96	2.30	1.41

Table 2. Biomarker ratios ratio calculated from m/z 191 fragmentograms in SIM, GC-MS analysis

Sample name	***C_{22}/C_{21}***	***C_{26}/C_{25}***	***C_{24}/C_{23}***	***$Ga/C_{31}R$***	***Ol/H***	***C_{29}/H***	***$C_{28}+C_{29}+C_{30}/H$***	***Ts/Ts+Tm***	***H_{32} S/(S+R)***	***$C_{31}R/H$***
Ami	0.27	1.47	0.85	0.17	0.15	0.39	0.57	0.82	0.53	0.34
Kakap	0.19	1.65	0.94	0.10	0.14	0.88	0.34	0.80	0.55	0.23
Libo	0.29	1.43	1.06	0.12	0.22	0.48	0.31	0.75	0.52	0.28
Minas 3	0.24	1.65	0.93	0.16	0.13	0.37	0.29	0.84	0.55	0.24
Minas 7	0.25	1.64	0.91	0.13	0.10	0.43	0.31	0.85	0.54	0.26
Pematang	0.20	1.59	0.91	0.10	0.13	0.84	0.26	0.83	0.56	0.20
Pungut	0.21	5.02	0.88	0.14	0.12	0.56	0.33	0.83	0.52	0.25
Ubi	0.23	1.30	0.77	0.13	0.20	0.84	0.50	0.78	0.53	0.29
Mindal	0.31	1.44	0.93	0.37	0.16	0.38	0.46	0.86	0.53	0.25
Libo SE	0.18	1.54	0.59	0.09	0.23	0.47	0.57	0.79	0.50	0.30
Pematang Bow	0.22	1.15	0.97	0.18	0.26	0.38	1.48	0.77	0.55	0.31
Petani	0.23	1.45	1.01	0.09	0.12	0.42	0.31	0.82	0.55	0.26
Duri 1	0.18	1.35	0.92	0.11	0.08	0.81	0.11	0.83	0.56	0.22
Duri 2	0.18	1.55	0.90	0.00	0.07	0.81	0.10	0.84	0.56	0.24

C_{22}/C_{21} is the ratio of the C_{22} tricyclic terpane to the C_{21} tricyclic terpane. C_{26}/C_{25} is the ratio of C_{26} tricyclic terpane to C_{25} tricyclic terpane. C_{24}/C_{23} is the ratio of C_{24} tricyclic terpane to C_{23} tricyclic terpane. $Ga/C_{31}R$ is the ratio of Gammacerane to the C_{31} 22R homohopane. Ol/H is the ratio of Oleanane to C_{30} 17α-hopane. C_{29}/H is the ratio of C_{29} 17α-norhopane to C_{30} 17α-hopane. $C_{28}+C_{29}+C_{30}/H$ is the sum of $C_{28}+C_{29}+C_{30}$ tricyclic terpanes relative to C_{30} 17α-hopane. Ts/Ts+Tm is the ratio of the sum of C_{27} 18α-trisnorhopane (Ts) and C_{27} 17α-trisnorhopane (Tm) relative to C_{30} 17α-hopane. H_{32} S/(S+R) is the homohopane isomerization ratio of C_{32} 22S homohopane relative to the sum of C_{32} 22S homohopane+C_{32} 22R homohopane. C31/H is the ratio of C_{31} 22R homohopane relative to C_{30} 17α-hopane.

Table 3. Peak identification of bicyclic alkanes in the m/z 123 chromatogram in Figure 6.

Label	***Compound***
X	C_{14} Sesquiterpane
Y	C_{14} Sesquiterpane
Z	C_{15} Sesquiterpane
A	C_{15} Sesquiterpane (Probably compound A from Nytoft et al., 2009/Oleanane derived)
L	4β (H) - Eudesmane
B	C_{15} Sesquiterpane
C	8β (H) - Drimane
D	C_{15} Sesquiterpane
E	C_{16} Sesquiterpane
F	C_{16} Sesquiterpane
G	C_{16} Sesquiterpane
H	8β (H) - Homodrimane

Table 4. $\delta^{13}C$ values for *n*-alkanes of the oils in the Aman Trough. $\delta^{13}C$ values expressed in ‰ relative to the Vienna Peedee belemnite (VPDB) standard.

Sample name	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	C_{33}	C_{34}
Ami	-27.3	-27.6	-28.2	-28.6	-28.8	-29.1	-29.4	-29.6	-30.1	-29.8	-30.3	-30.3	-30.6	-30.2	-30.8	-31.7	-30.8	-31.2		
Kakap	-26.5	-26.8	-26.2	-27.3	-27.7	-27.9	-28.2	-28.4	-28.5	-28.4	-28.6	-28.8	-29.4	-29.7	-32.4	-31.9	-31.4	-32.1	-31.7	-30.3
Libo	-26.7	-27.2	-27.3	-27.9	-28.7	-29.0	-28.8	-29.7	-29.8	-29.6	-29.8	-30.5	-30.4	-29.7	-30.7	-31.3	-29.3	-30.2	-30.0	
Minas 3	-26.6	-26.7	-27.3	-27.6	-28.5	-28.0	-28.5	-28.5	-28.6	-28.6	-28.5	-29.1	-29.0	-28.9	-29.8	-29.7	-30.1	-28.6	-28.6	
Minas 7	-26.9	-27.1	-27.7	-27.9	-28.6	-28.8	-30.2	-29.2	-29.6	-29.7	-29.7	-29.9	-29.8	-29.6	-32.2	-30.4	-29.4	-29.9		
Pematang	-25.4	-25.6	-26.5	-26.9	-27.2	-27.2	-27.5	-27.8	-28.2	-28.2	-28.5	-27.8	-28.0	-28.0	-30.7	-28.2	-27.9	-28.2	-27.5	
Pungut	-27.0	-27.3	-28.4	-29.1	-29.3	-29.6	-30.1	-30.2	-30.3	-30.4	-31.1	-31.1	-31.0	-30.8	-33.5	-32.4	-30.6			
Ubi	-25.1	-25.2	-25.8	-26.3	-26.6	-27.0	-27.4	-27.5	-27.9	-27.9	-27.9	-28.4	-28.8	-28.0	-32.7	-28.9	-28.2	-29.9	-27.1	
Mindal	-26.1	-26.4	-26.0	-26.8	-27.3	-27.4	-27.8	-28.1	-28.4	-28.1	-28.0	-27.8	-27.9	-28.4	-28.2	-28.0				
Libo SE	-25.8	-26.1	-26.9	-26.8	-27.1	-27.1	-27.6	-27.6	-27.8	-27.7	-27.6	-28.4	-28.2	-28.1	-28.6	-28.7	-28.5			
Minas 6	-26.1	-26.2	-25.9	-26.9	-27.3	-27.7	-27.8	-28.1	-28.2	-28.0	-28.0	-27.8	-28.1	-28.0	-27.7	-27.5	-27.9	-28.5		
Pematang Bow	-24.7	-24.2	-24.6	-24.7	-25.3	-25.1	-25.5	-25.1	-25.0	-25.1	-25.0	-24.9	-25.1	-25.4	-26.2	-26.8	-25.4	-25.5		
Petani	-24.7	-25.0	-24.9	-25.4	-26.0	-25.9	-26.1	-26.4	-26.7	-26.5	-26.6	-26.6	-26.7	-26.6	-26.6	-26.5	-26.3	-26.5		
Duri 2	-25.8	-25.4	-24.1	-25.4	-26.3	-26.3	-26.1	-26.7	-26.0	-27.5	-26.5	-29.7	-28.1							

Table 5. Average $\delta^{13}C$ values for long-chain *n*-alkanes (nC_{29} and nC_{31}) of the three groups of oils in the Aman Trough. $\delta^{13}C$ values expressed in ‰ relative to the Vienna Peedee belemnite (VPDB) standard.

Group	***Avg. nC_{29}***	***Avg. nC_{31}***
Group 1	-31.6	-29.7
Group 2	-27.8	-27.6
Pematang Bow	-26.2	-25.4

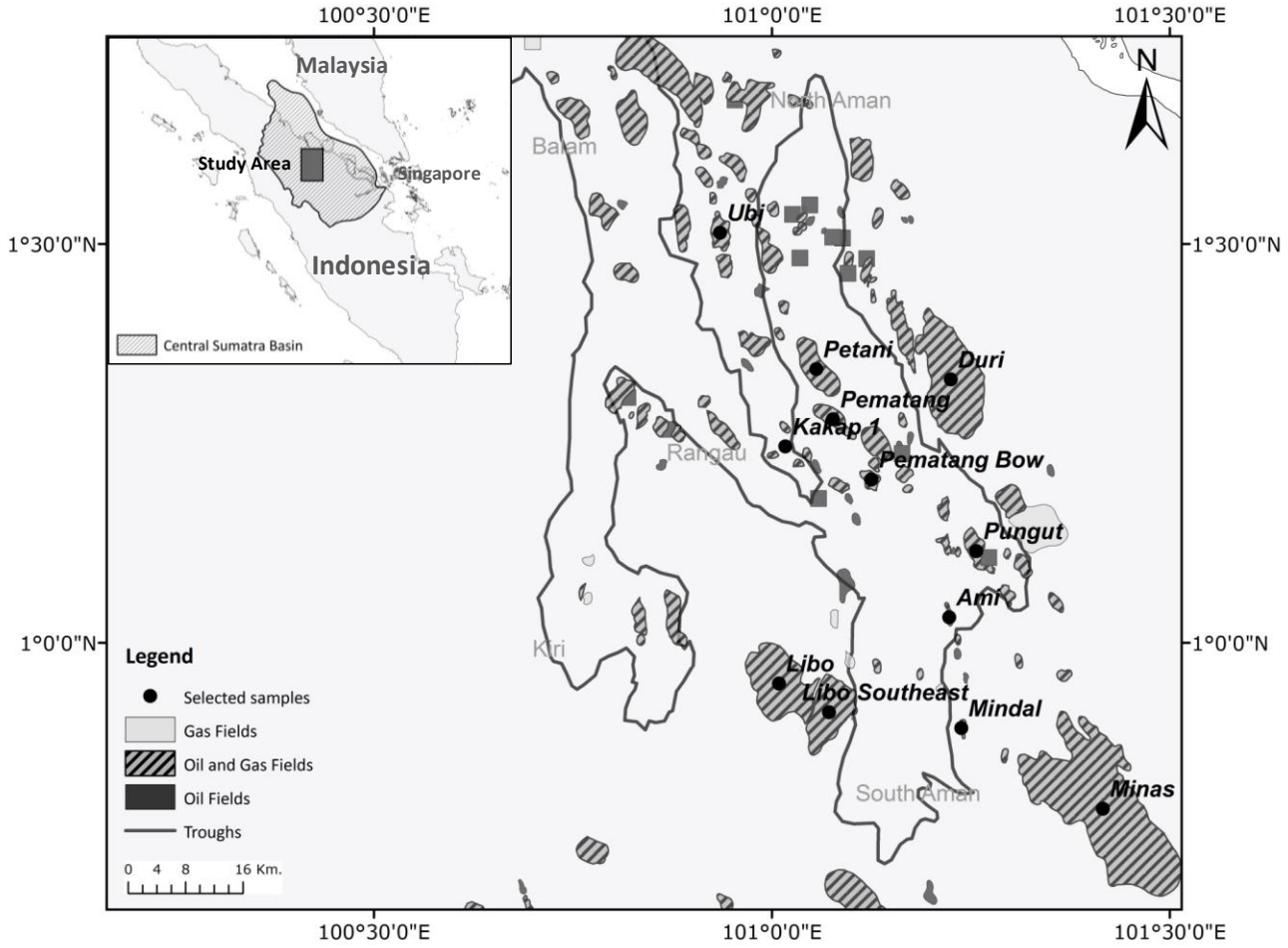
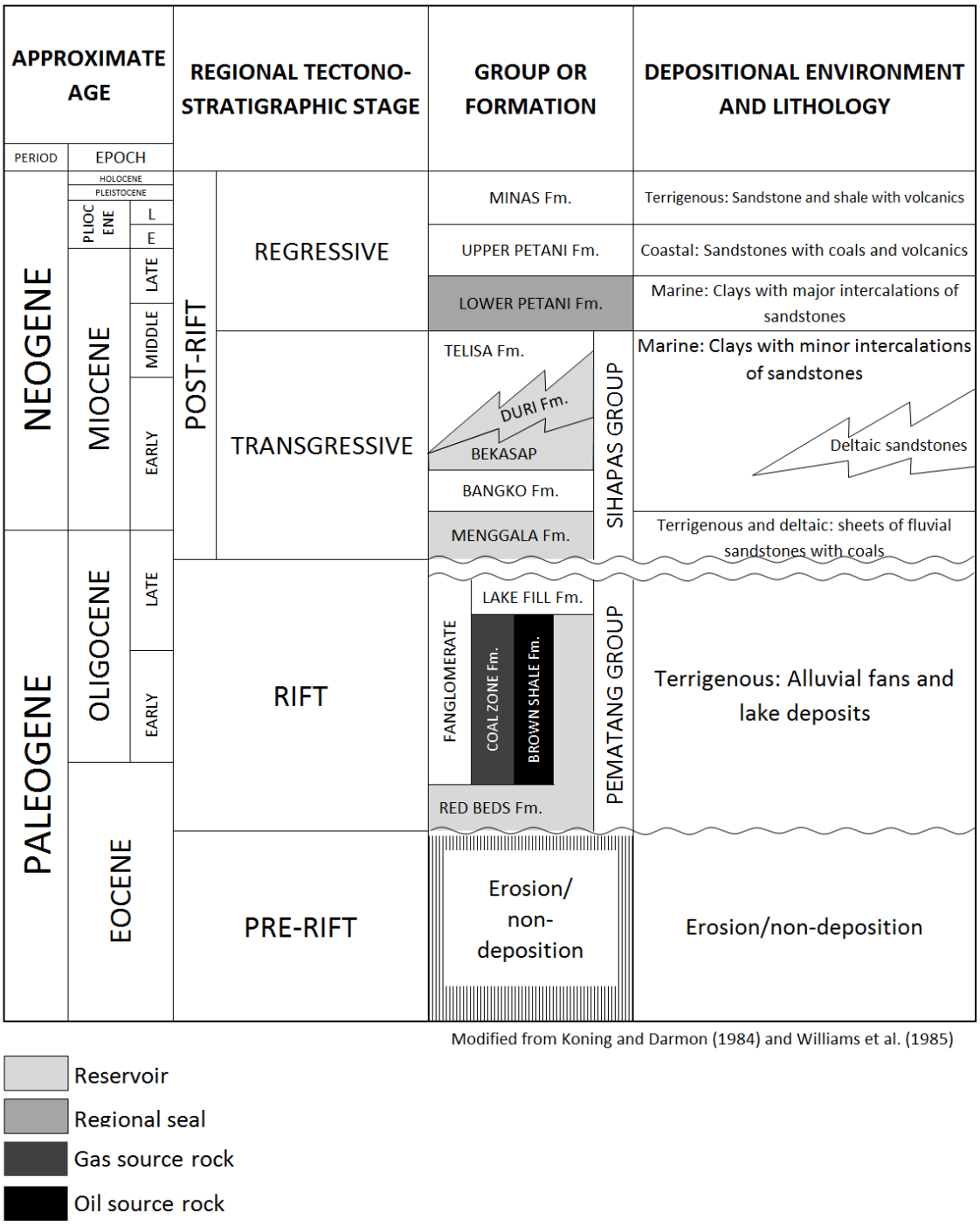


Figure 1. Map showing the location of fields and samples analyzed in this study. The Central Sumatra Basin is outlined by the hatched area on the inset map. The study area is indicated as a gray square within the hatched area.



Modified from Koning and Darmon (1984) and Williams et al. (1985)

Figure 2. Stratigraphic chart of the Central Sumatra Basin showing the main tectono-stratigraphic stages and depositional environments associated with them. Definition of regional seal, reservoirs and source rock from Katz and Mertani (1989).

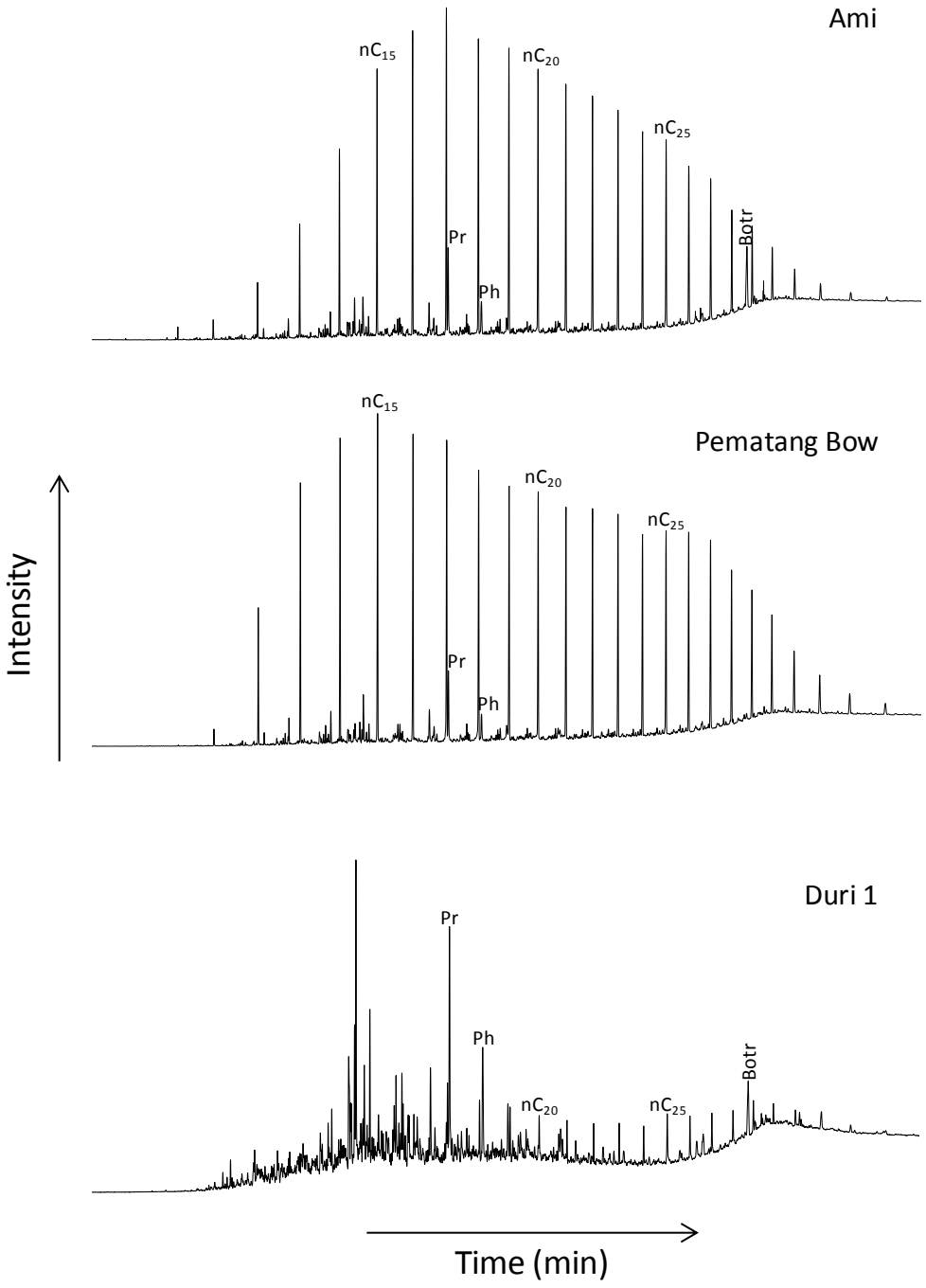


Figure 3. Gas chromatograms of selected samples in the Aman Trough.

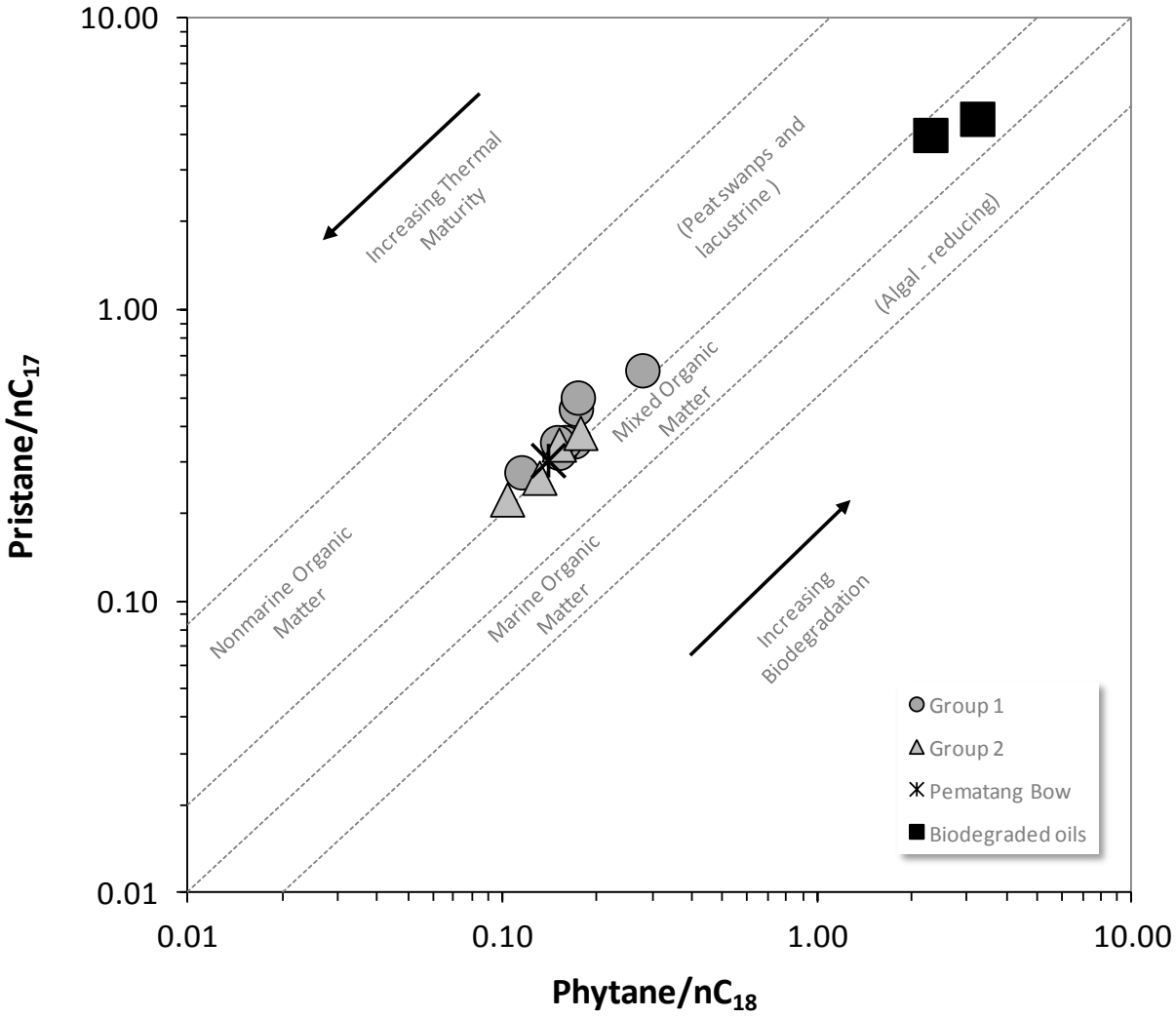


Figure 4. Pristane/nC_{17} ratio vs. phytane/nC_{18} ratio calculated from gas chromatograms of the maltene fraction.

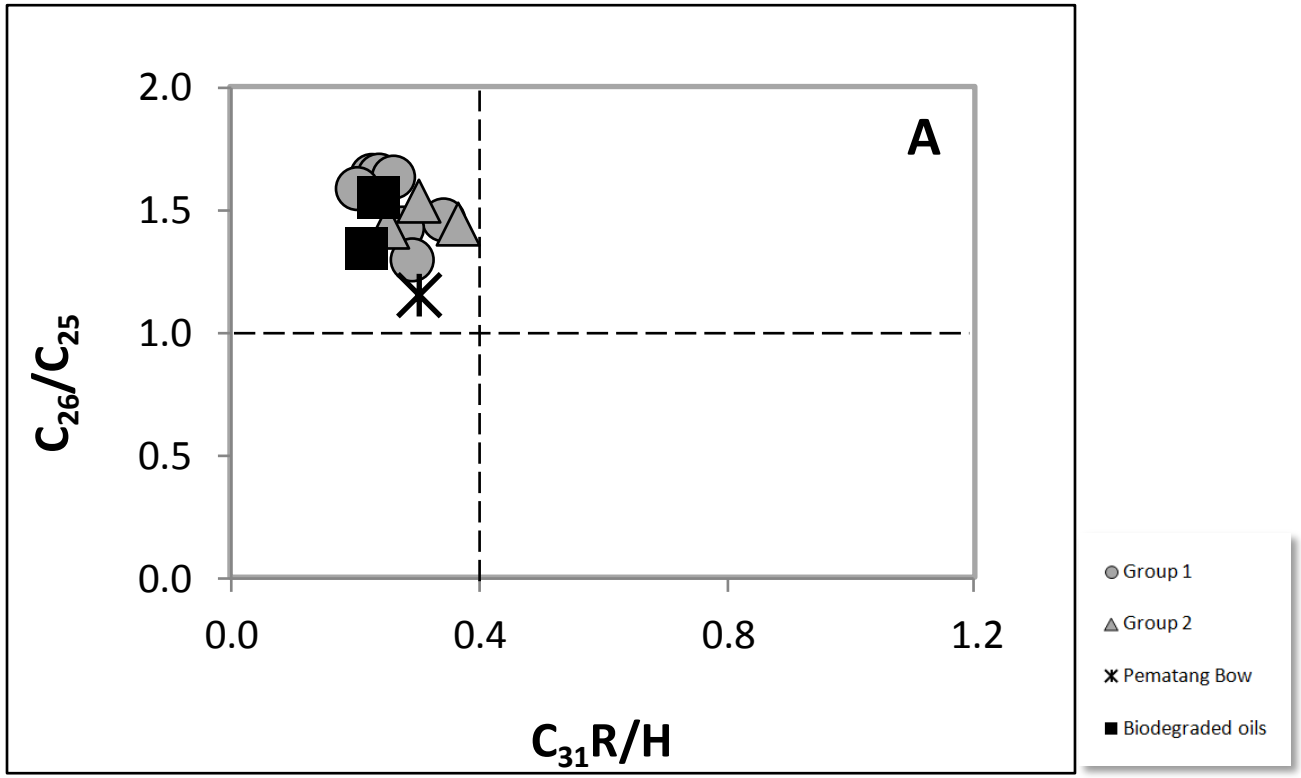


Figure 5a. $C_{31}R/H$ vs. C_{26}/C_{25} ratio calculated from m/z 191 fragmentogram in SIM, GC-MS analysis

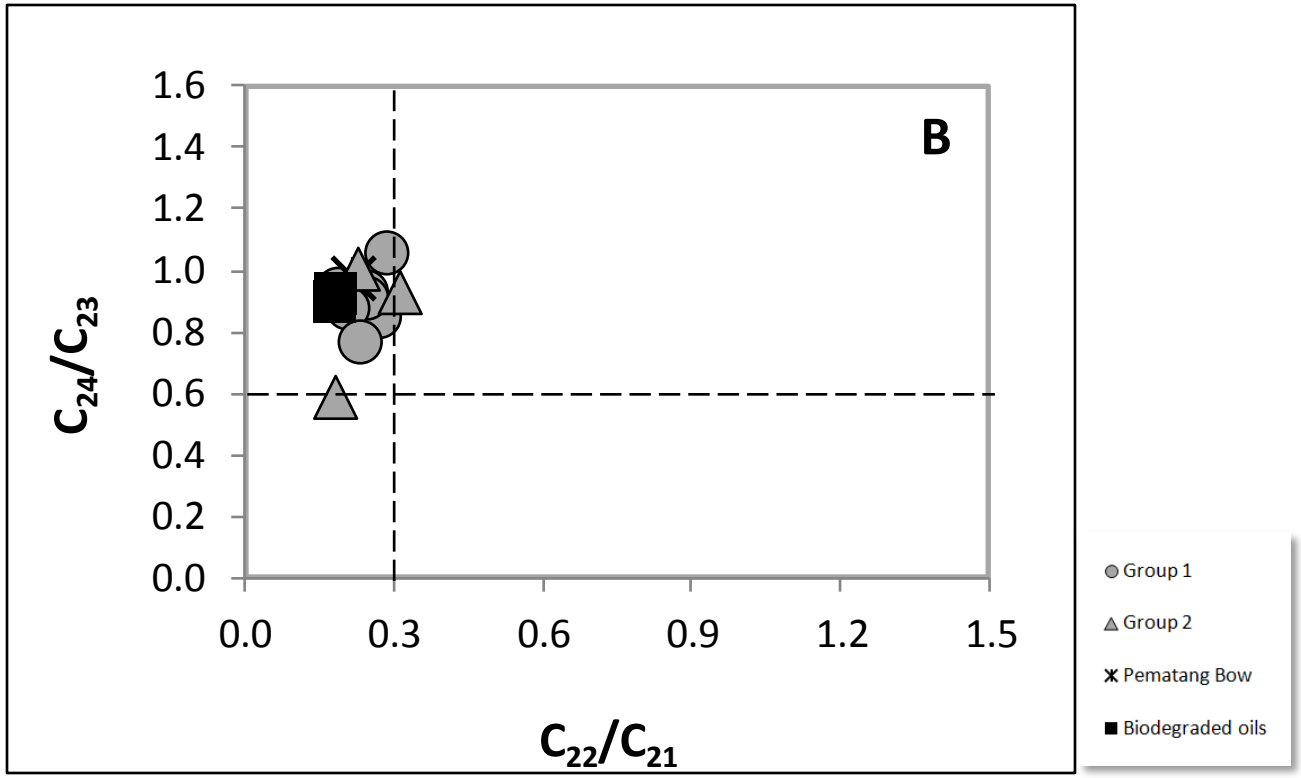


Figure 5b. C_{22}/C_{21} vs. C_{24}/C_{23} ratio calculated from m/z 191 fragmentogram in SIM, GC-MS analysis..

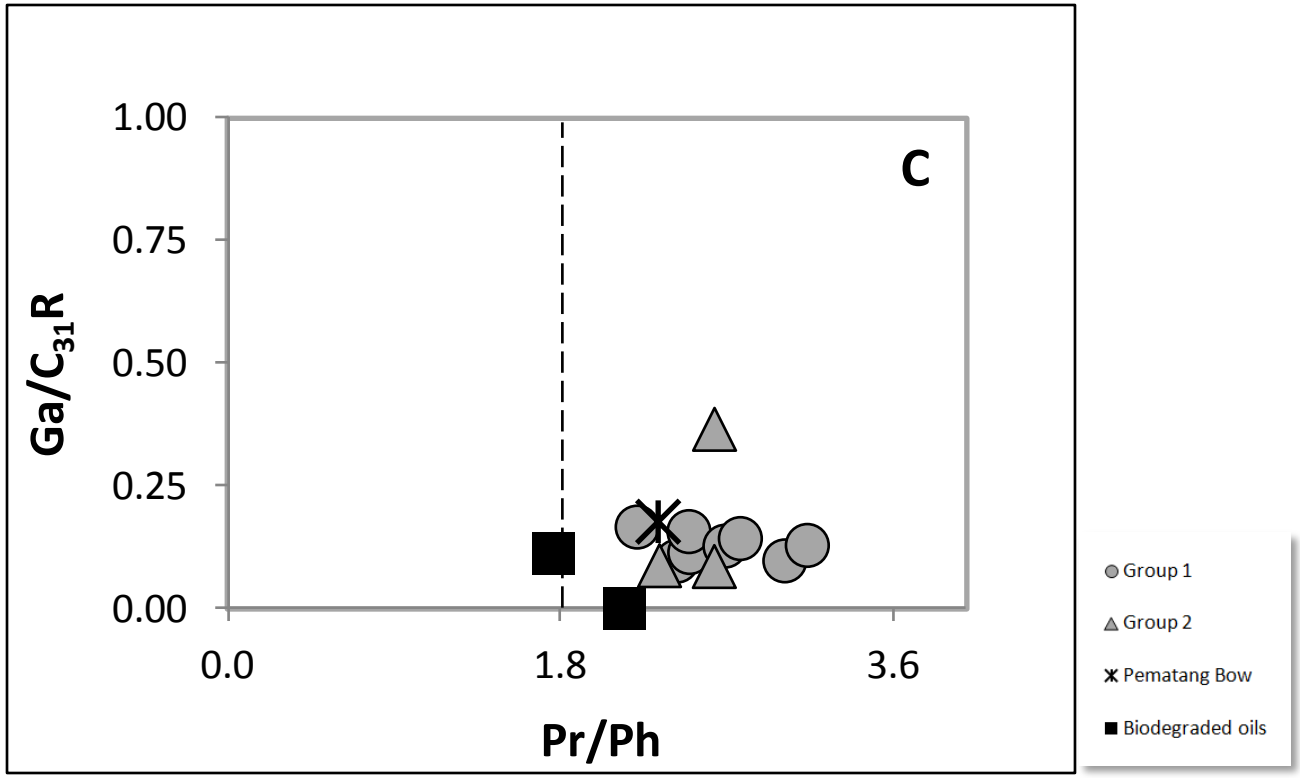


Figure 5c. Pr/Ph vs. $Ga/C_{31}R$ ratio calculated from m/z 191 fragmentogram in SIM, GC-MS analysis.

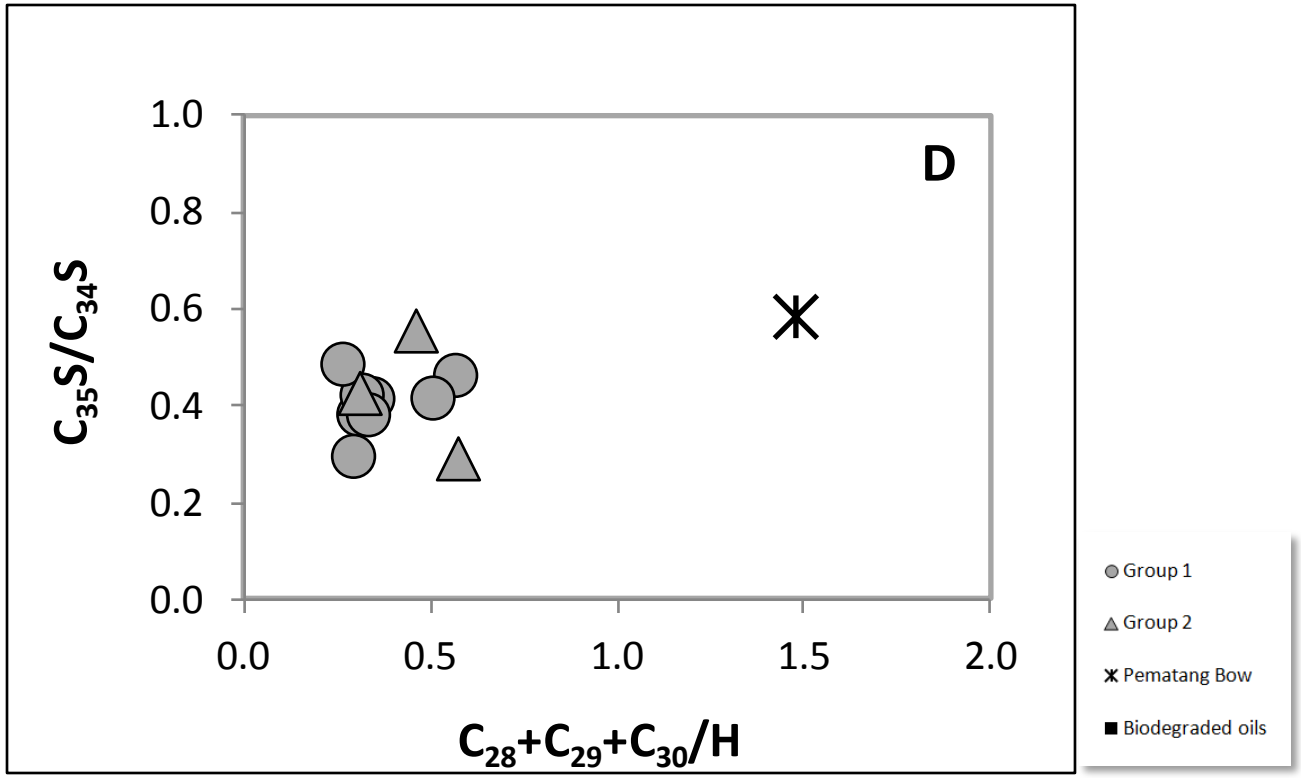


Figure 5d. $C_{28}+C_{29}+C_{30}/H$ vs $C_{35}S/C_{34}S$ ratio calculated from m/z 191 fragmentogram in SIM, GC-MS analysis.

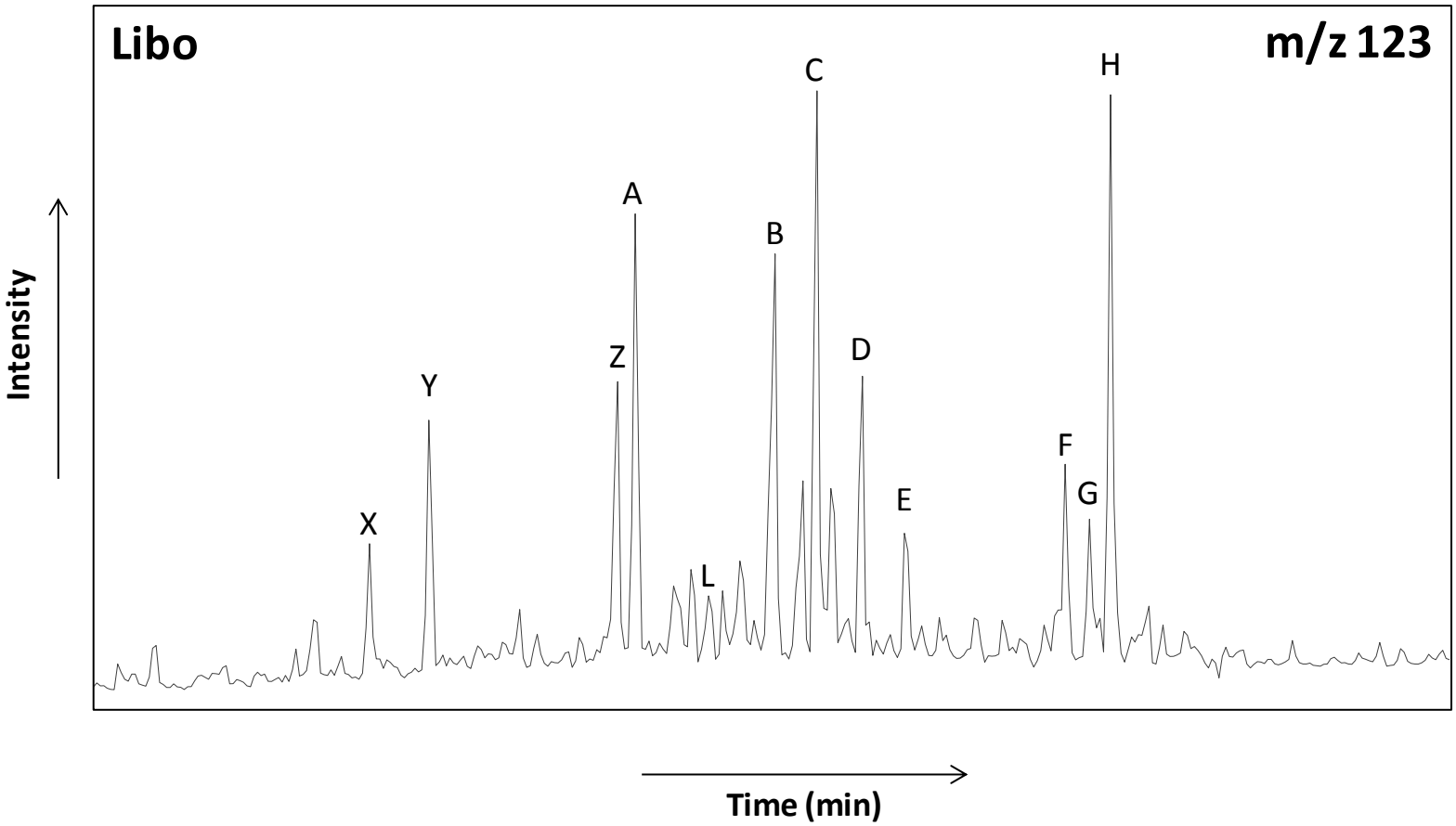


Figure 6. Typical m/z 123 fragmentogram for sesquiterpanes in the Aman Trough (Peak definitions included in Table 3).

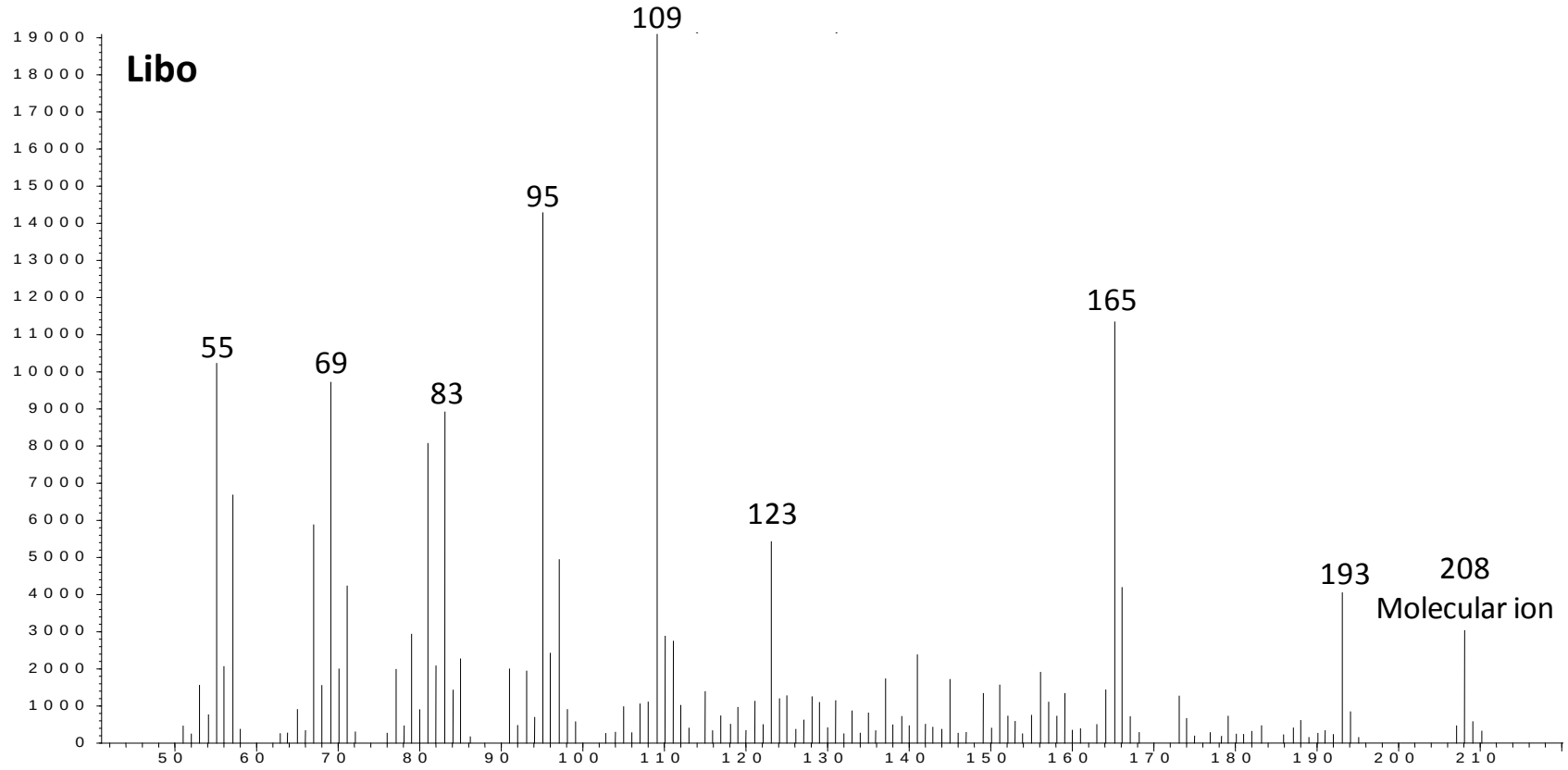


Figure 7. Mass spectra for sesquiterpane compound Z.

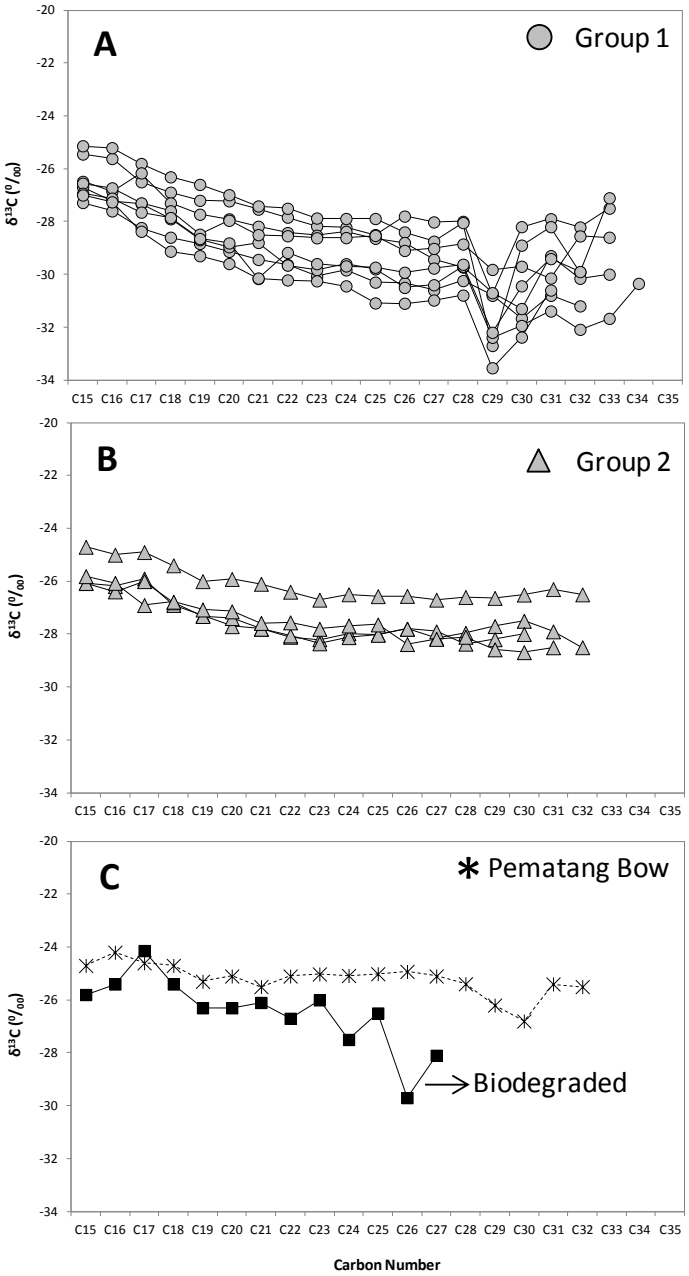


Figure 8. n-alkane isotope profiles of oils in the Aman Trough. Solid lines represent samples that contain the biomarker botryococcane while dashed lines represent samples with no botryococcane present. Top graph contains samples in group 1, middle graph samples in group 2 and bottom graph shows the isotope profile of the Duri 1 biodegraded sample (squares) and the Pematang Bow sample (stars).

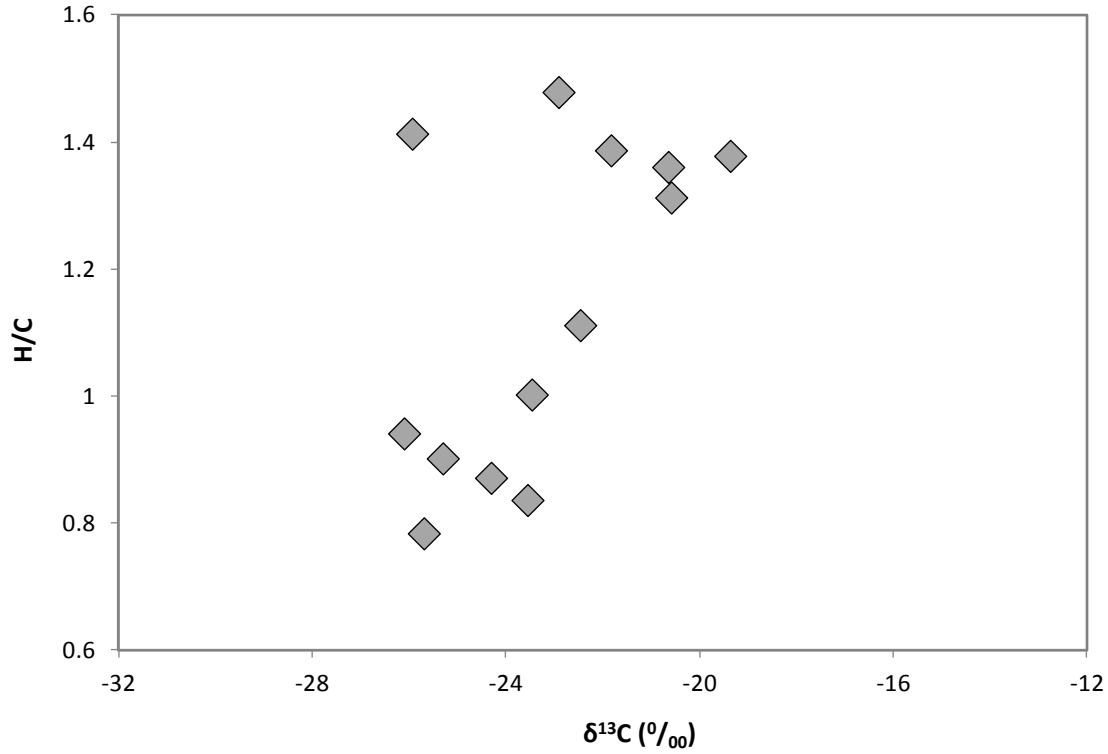


Figure 9. $\delta^{13}C$ vs H/C ratio. After Katz and Mertani, 1989.

Chapter III

Source rock facies distribution predicted from oil geochemistry in the Central Sumatra Basin, Indonesia.

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Abstract

We measured the molecular composition and compound specific isotopic composition of the *n*-alkanes in thirty (30) oil samples from the Central Sumatra Basin, with the purpose of determining facies variations of the source rock in this basin. The oil samples were generated by the Eocene-Oligocene lacustrine Brown Shale Formation. Biomarkers in the oil samples indicate varying contributions from algal and terrigenous organic matter, primarily under oxic/sub-oxic depositional conditions. Five source rock facies were identified based on the relative concentrations of *n*-alkanes, isoprenoids, tricyclic terpanes and steranes, and also distinguished by the compound specific isotopic composition of the *n*-alkanes. Source rock depositional environments vary from deep lacustrine, shallow lacustrine and lacustrine saline to coal and mixed coal/lacustrine shale. Deep lacustrine facies predominate in the Aman and Bengkalis Troughs while saline and shallow lacustrine facies predominate in the South Aman and Kiri Troughs respectively. Oils derived from coal and mixed coal/lacustrine shale facies predominate in the northen part of the Central Sumatra Basin, in the Tanjung Medan and north of the Balam grabens.

1. Introduction

The Central Sumatra Basin is a back-arc rift basin that developed during the Paleogene (Eocene-Oligocene) as a result of subduction of the Indian Ocean plate beneath the South East Asian plate (Eubank and Makki, 1981; Williams et al., 1985). The basin encompasses a series of parallel half graben structures that formed along pre-Paleogene structural trends following a general N-S to NNW-SSE orientation (Katz and Dawson, 1997; Doust and Noble, 2008) containing a sedimentary fill in excess of 3 Km (Eubank and Makki, 1981) composed of two main stratigraphic sequences: a syn-rift lacustrine sequence and a post-rift marine sequence (Katz and Dawson, 1997). The synrift lacustrine section hosts the main source rock in the basin, the Brown Shale Formation, while reservoir intervals are mainly present in the post-rift marine sequence with some minor reservoir occurrences in the synrift section (Williams and Eubank, 1985; Katz and Dawson, 1997). Oil producing areas include the Aman, Balam, Kiri, Tanjung Medan and Bengkalis Troughs, however the greatest reserves in the basin are associated with the Aman graben (Katz and Dawson, 1997; Fig. 1).

Hydrocarbons derived from lacustrine source rocks account for more than 20% of the worldwide hydrocarbon production (Bohacs et al., 2000). The Brown Shale Formation has been largely recognized as the main oil source rock in the Central Sumatra Basin, the most prolific oil producing basin in Indonesia (Katz and Mertani, 1989; Longley et al., 1990; Katz, 1994; Camell et al., 1998; Huang et al., 2002). Lateral and vertical stratigraphic variability within lacustrine sequences in rift basins have been widely recognized (Talbot, 1988; Katz, 1995; Lambiase and Morley, 1999; Bohacs et al., 2000). Several depositional environments can coexist within lacustrine settings and can

include deep lacustrine, shallow lacustrine, fluvial-deltaic, alluvial and paludal stratigraphic sequences (Lambiase and Morley, 1999; Bohacs et al., 2000). In the case of the Brown Shale Formation, two main sedimentary facies have been described: deep lacustrine and shallow lacustrine facies (Longley et al., 1990). The dominantly deep lacustrine facies consist of non calcareous shales, with primarily type I and II kerogens and total organic carbon (TOC) values ranging from 1% to 14%. The dominantly shallow lacustrine facies consists of red-brown laminated mixed carbonate and terrigenous mudstones with abundant organic material, occasional coal stringers, mainly type I kerogen and average TOC values of 3.4% (Longley et al., 1990). An additional marsh/bog facies, laterally equivalent to the Brown Shale Fm., has been described primarily within the Kiri graben. This facies consists mainly of coals, coaly shales and black shales usually interbedded with the shallow lacustrine facies (Williams and Eubank, 1995).

Organic geochemical and compound specific isotopic compositions of oils have been commonly used for the purpose of oil-oil and oil-source rock correlations (e.g. Sun et al., 2000; Huang et al., 2003) and to predict source rock depositional environments (e.g. Seifert and Moldowan, 1981; Moldowan et al., 1985; Mello and Maxwell, 1990; Curiale et al., 2005). These approaches have allowed characterization of prolific source rocks in producing basins where rock samples are not readily available for geochemical analyses.

In this study we aim to use a similar methodology to understand changes in source rock depositional environments amongst each of the oil producing grabens of the Central Sumatra Basin. This approach is based on the assumption that changes in source rock

depositional environments will result in organic influx variations that will be reflected in the molecular and isotopic composition of the studied oils. Here we present and discuss the molecular and compound specific isotopic composition of a representative set of 30 oils from the Central Sumatra Basin with the purpose of unraveling the number and character of organic facies responsible for these fluids.

This work represents an expansion of the work presented by Rodriguez and Philp (2012). In their study, they identified source rock facies variation within the Aman Trough (Fig. 1) by analyzing the molecular and compound specific isotopic composition of 15 oil samples from this sub-basin. In this study, we add 15 oils samples to the dataset, representative of 5 additional troughs in the Basin. This addition allowed us to compare and contrast different depositional environments associated with each of the grabens, as well as unravel source rock depositional environments distribution in the Central Sumatra Basin.

2. Geologic Setting

Several authors have published detailed descriptions of the structural and stratigraphic evolution of Central Sumatra. Here we provide a general summary of the most important aspects relevant to the main petroleum systems of the basin. The reader is referred to the original citations for more detailed information (Longley et al., 1990; Williams and Eubank, 1995; Katz and Dawson, 1997; Barber and Crow, 2005; Clure, 2005; De Smet and Barber, 2005).

A generalized stratigraphic chart of the area is presented in Fig. 2. The stratigraphic sequence in the Central Sumatra Basin includes a syn-rift lacustrine

sequence and a post-rift marine sequence (Katz and Dawson, 1997). The syn-rift lacustrine sequence is of Eocene (?)-Oligocene age and was accumulated within syntectonic grabens that developed in response to transtensional stress in a back-arc setting (Longley et al., 1990). The Pematang Group encompasses the Lower Red Beds Fm., Brown Shale Fm., Coal Zone Fm. Lake Fill Fm. and Fanglomerate Fm. (Williams and Eubank, 1995). Depositional environments inferred from the Pematang Group include alluvial fans and fluvial systems that grade laterally into lacustrine environments (Barber and Crow, 2005). Alluvial and fluvial sediments are sedimentologically immature and relatively thin while lacustrine sediments can reach thicknesses of several kilometers, often displaying anoxic bottom conditions (De Smet and Barber, 2005).

The post-rift marine sequence is Miocene-Pleistocene in age and records successive transgressive and regressive cycles within the Central Sumatra Basin (De Smet and Barber, 2005). During the late Oligocene, a change in tectonic regime caused regional subsidence that resulted in a post-rift sag phase. Transgressive sediments of the Sihapas Group accumulated during this stage. The lower part of the Sihapas Group (Menggala Formation) consists of thick fluvial sandstones with subordinate shales. The upper part of the Sihapas Group is dominated by marine shales of the Telisa Formation, which marks the maximum transgression in the basin (Clure, 2005; De Smet and Barber, 2005). Sandstones within the Sihapas group form the primary reservoirs in this basin. Secondary reservoirs are found in the Upper Red Bed Formation of the Pematang Group (Clure, 2005). From the Middle Miocene to the Present, a regressive stage predominates, marked by the uplift of the Barisan Mountains, west of the study area. Uplift and erosion increased during the Late Pliocene coeval with a time of intense volcanism. Increased

clastic input resulted in a shift in depositional environments from the marine shales of the Petani Formation to the alluvial and deltaic deposits the Minas Formation (Barber and Crow, 2005). Present day oil bearing structures were mainly developed during this stage of increased tectonic activity (De Smet and Barber, 2005).

3. Sample distribution and experimental methods

Thirty (30) produced crude oil samples from the Central Sumatra Basin were selected for this study and their locations are depicted in Fig. 1. Twenty nine (29) samples are representatively distributed among the main producing grabens in the basin: Aman, Balam, Tanjung Medan, Kiri and Bengkalis Troughs (Fig. 1). One additional sample Nene-1 is outside the main producing areas, close to the Tonga-1 field. The data presented here was generated entirely at the petroleum geochemistry laboratories of the University of Oklahoma in Norman, Oklahoma.

3.1. Sample preparation

Twenty milligrams of sample were placed in a centrifuge tube for asphaltene precipitation using an excess (40:1) of *n*-pentane. Complete asphaltene precipitation was promoted using ultrasonic agitation during 60 minutes. Resulting maltene fractions were diluted using a ratio of 2 mg of sample per 50 μL hexane for compound class fractionation. The samples were fractionated through column chromatography using activated silica gel (100°C/24h). Aliphatic, aromatic and NSO (nitrogen, sulfur and oxygen containing fraction) fractions were separated using hexane, toluene/hexane

(70/30; v/v) and dichloromethane, respectively. All data presented here were generated through analyses of the saturate fraction without removal of the *n*-alkanes.

3.2. Gas Chromatography

Maltene fractions were analyzed by gas chromatography (GC) using an Agilent 6890 series GC system with a split/splitless capillary injection system equipped with a 35 m x 0.25 mm (i.d.) J&W scientific DB-5 Petro fused silica capillary column with a 0.5 µm film thickness. Samples were analyzed in splitless injection mode using a temperature program set to initial temperature of 40°C with a 1.5 minutes holding time, continuing with a temperature ramp of 4°C/min to 300°C and then isothermal for 31 min. Detector temperature was 310°C. Helium was used as the carrier gas with a flow rate of 1.4 ml/min.

3.3. Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) was carried out using an Agilent 7890 GC coupled with a 5975C MSD running on splitless injection mode. The GC used a 60 m x 0.25 mm J&W scientific DB-5 fused silica capillary column coated with a 0.25 µm liquid film. Selected ions were chosen for biomarker analyses using single ion monitoring (SIM). The samples were analyzed using a temperature program set to initial temperature of 40°C with a 1.5 minutes holding time, continued by a temperature ramp of 4°C/min to 300°C and then isothermal for using a temperature program set to initial temperature of 40°C with a 1.5 minutes holding time, continuing with a temperature ramp of 4°C/min to 300°C and then isothermal for 54 minutes for a

total run time of 123 minutes. Helium was used as the carrier gas with a flow rate of 1.4 ml/min.

3.4. Gas Chromatography-Isotope Ratio Mass Spectrometry

Compound specific isotopes of individual compounds in the saturate fraction were determined by gas chromatography-isotope ratio mass spectrometry (GC-IRMS) using a Varian 3400 gas chromatograph coupled through a combustion reactor with a Finnigan MAT 253 isotope ratio-mass spectrometer. The GC was equipped with a 65 m x 0.25 mm J&W scientific fused silica DB-1 Petro capillary column with a 0.5 μm film thickness. The GC oven was set to an initial temperature of 40°C held constant for 1.5 min. Oven temperature was then increased to 300°C at a rate of 4°C/min and held constant for 24 minutes for a total run time of 90 minutes.

4. Results and Discussion

4.1 Molecular Composition

Detailed geochemical characterization of the samples from the Aman Trough has been described elsewhere (Rodriguez and Philp, 2012). In summary, oil samples in the Aman Trough were generated by a source rock deposited in a fresh to brackish lacustrine environment. Compound specific isotopes of the *n*-alkanes indicated that CO_2 limiting conditions prevailed during source rock deposition in a stratified lacustrine system with anoxic bottom waters. Mixed contributions from algae and terrigenous organic matter are evidenced from the presence of botryococcane, sesquiterpanes biomarkers, and oleanane in the oil samples. Additional evidence for a significant contribution from algal organic

matter is provided by *n*-alkane distributions maximizing between nC$_{15}$-nC$_{17}$, albeit with some contributions from terrigenous organic matter as indicated by long chain *n*-alkanes in the nC$_{27}$-nC$_{31}$ range.

GC molecular ratios of oil samples from the Central Sumatra Basin are listed in Table 1 and discussed below. Fig. 3 illustrates GC traces representative of the variability observed in the studied samples. Three main patterns are observed in the *n*-alkane distribution of the oil samples: (1) Oils displaying a marked bimodal *n*-alkane distribution, with modes around nC$_{15}$ and nC$_{27}$, respectively. Such a distribution would indicate a mixed algal/terrigenous organic matter contribution to the oil's source (Lijmbach, 1975; Hunt, 1979). Samples exhibiting biomodal *n*-alkane distributions are widespread throughout the basin and observed in the Tanjung Medan (Fig. 3A), Balam and Bengkalis (Fig. 3B) Troughs, and the Kasikan (Fig. 3C), Petapahan and Kotabatak samples, south of the Aman Trough. (2) Oils samples with a unimodal *n*-alkane distribution with a predominance of relatively low carbon number *n*-alkanes (nC$_{15}$-nC$_{17}$) are mainly restricted to the Aman (Fig. 3D) and Kiri (Fig. 3E) Troughs. This distribution would indicate a predominance of algal organic matter with limited contribution from terrigenous input (Hunt, 1979; Tissot and Welte, 1984). (3) Unimodal distributions with predominance of long chain *n*-alkanes (nC$_{27}$-nC$_{29}$) are only observed in the Damar (Fig. 3F) and Nene samples, north and west of the study area, respectively (Fig. 1). This predominance of long-chain *n*-alkanes is also observed numerically in the nC$_{27}$/nC$_{17}$ ratio which displays the highest values in the dataset for these two samples (Table 1). This pattern strongly suggests a significant contribution of terrigenous organic matter to the oil's source rock organic matter (Eglinton, 1967; Simoneit, 1977; Pancost et al., 2002).

A similar grouping of oil samples is inferred from the pristane/phytane (Pr/Ph) ratio of the oils. Pristane and phytane are primarily formed during diagenesis of the phytyl side of chlorophyll and are thought to reflect redox conditions during the early stages of chlorophyll degradation (Brooks et al., 1969). Pristane is typically formed by decarboxylation of phytanic acid, while phytane usually results from dehydration and hydrogenation of the phytol chain (Brooks et al., 1969). Preferential formation of phytanic acid predominates in oxidizing environments (Powell and Mckirdy, 1973). In the Central Sumatra Basin, Pr/Ph ratios vary from 1.8 to 11.9 indicating sub-oxic to oxic depositional conditions (Didyk et al., 1978; Table 1). Two samples are exceptional (i.e. Damar and Nene) in that they exhibit relatively higher Pr/Ph ratios (9.6-11.9) compared to other samples in the dataset. These relatively higher Pr/Ph values in the Damar and Nene samples would indicate oxidizing conditions prevailed during deposition of the source rock interval that generated these oils.

Coincidentally, the same samples are the only two characterized by an *n*-alkane distribution dominated by n-alkanes in the nC_{27}-nC_{29} range. Samples with bimodal distributions show average Pr/Ph values of 2.79, while samples with unimodal *n*-alkane distributions dominated by algal derived *n*-alkanes show comparatively lower Pr/Ph values with average values of 2.65.

The relationship between the isoprenoids pristane and phytane and their adjacent *n*-alkanes has been used to predict source rock depositional environments (Shanmugan, 1985; Hunt, 1996; Peters et al., 1999). A diagram of Ph/$n C_{18}$ versus Pr/$n C_{17}$ is depicted in Fig. 4. The studied samples plot within the region of non-marine organic matter consistent with a lacustrine origin for the source rock of the oils. Furthermore, the Damar

and Nene samples are again outliers from the main groups of samples in this dataset. Two additional oils (Buaya and Tanjung Medan) are distinguished from the main group of oils and also from the Damar and Nene oils. These two samples display a bimodal *n*-alkane distribution and Pr/Ph ratios at the upper end compared to other samples with bimodal *n*-alkanes distributions. Pr/Ph ratios for the Buaya and Tanjung Mendan samples are 3.6 and 3.7, respectively (Table 1) compared to average Pr/Ph values of 2.79 for samples with bimodal *n*-alkanes distributions. Moreover, these two samples are restricted to the Tanjung Medan Trough.

Selected GC-MS derived biomarker ratios from tricyclic terpanes, hopanes and sterane compounds are included in Table 2. Curiale (2008) have shown that depositional environment inversions from oil geochemistry can be affected by the choice of inappropriate samples with differing thermal maturity levels. Two biomarker ratios, Ts/(Ts+Tm) and H_{32} 22S/(22S+22R), largely indicative of thermal maturity of the source rock at the time of expulsion, have been used to evaluate the thermal maturity of the oils in this study. C_{27} 17α-trisnorhopane (Tm) is thermally less stable than C_{27} 18α-trisnorhopane (Ts) (Seifert and Moldowan, 1978), therefore the Ts/(Ts+Tm) ratio will increase as maturity increases. Similarly, the ratio of 17α-homohopane isomerization can be used to predict oil generation maturity (Peters et al., 2005). Typically, biologically produced hopanes carry a 22R configuration, and as maturity increases, that configuration is gradually converted to a mixture of 22R and 22S diastereomers (Seifert and Moldowan, 1981).

Similar values for these two ratios indicate the samples were generated at similar maturity levels, therefore minimizing the effects of thermal maturity on source rock

depositional environment interpretations. Only the Damar sample shows relatively lower Ts/(Ts+Tm) ratio compared to other samples in the basin, indicating a lower maturity level at the time of expulsion. Nevertheless, the H_{32} S/(S+R) ratio is in agreement with samples within the Balam graben, and other samples throughout the basin.

Despite differing maturity levels, maturity alone could not account for the molecular and isotopic (see discussion below) differences observed between the Damar and Nene samples and other samples in the Central Sumatra Basin, therefore, these are considered truly representative of a unique depositional environment within the basin.

Huang and Meinchein (1979) proposed that phytoplankton are the dominant source of C_{27} sterols while the dominant source of C_{29} sterols is related to higher plants. Consequently, the distribution of C_{27}, C_{28} and C_{29} steranes on a ternary diagram could be used to define ecological systems. This approach has been successfully applied to distinguish oils and source rocks from differing depositional environments (e.g. Peters et al., 1999; Sun et al., 2000).

Similar to the observations from *n*-alkane distributions and isoprenoid biomarkers, the distribution of steranes according to carbon number (Table 2) also distinguishes three populations (Fig. 5). The first population consists of samples located in the Aman Trough containing relatively greater amounts of C_{27} steranes compared to C_{28} and C_{29} steranes. The second population is represented by samples with significantly higher proportions (>55%) of C_{29} steranes than its sterol homologs. Finally, the third population is represented by samples with a sterane distribution in between the two end members described above.

4.2 Source rock facies

Mixed algal/terrigenous organic matter input has been interpreted for the oil samples in the Aman Trough (Rodriguez and Philp, 2012). Moreover, the same general interpretation is true for all studied samples from the Central Sumatra Basin. However, additional inspection of the molecular composition of the oils, has allowed further qualitative discrimination based on the relative proportions of algal versus terrigenous organic matter input and the relationship between this distribution and the geographic location of the samples. Oil samples from the Aman Trough primarily show a predominance of algal organic matter contribution with some input from terrigenous organic matter. These oils are characterized by presence of botryococcane (Rodriguez and Philp, 2012), unimodal *n*-alkane distributions with a predominance of short chain *n*-alkanes, relatively lower Pr/Ph ratios and sterane distributions dominated by C_{27} steranes. This molecular composition indicates a fresh to brackish water, suboxic to oxic depositional environment for the source rock with mixed organic matter contribution, albeit with predominant contribution from algal organic matter.

Oils from the Kiri graben also display unimodal *n*-alkane distributions with slightly higher values of gammacerane (0.24-0.27, Table 2) relative to other oils. No botryococcane was identified in these samples. Longley et al., (1990) described extracts from the shallow lacustrine facies of the Brown Shale as high wax, with intermediate Pr/Ph ratios, presence of oleanane and minor occurrences of gammacerane. The molecular composition of the oils from the Kiri graben have a similar composition and therefore seem to correlate with the shallow lacustrine facies as described by Longley et al., (1990)

The oils Damar and Nene show the most distinct molecular composition in the basin in that they have a marked unimodal distribution of *n*-alkanes skewed towards the higher carbon number *n*-alkanes, coupled with the highest Pr/Ph values in the basin and a predominance of C_{29} steranes in their sterol distribution. This molecular composition would indicate these oils were generated by a source rock with significant contributions from terrigenous organic matter, in an oxic depositional environment. This interpretation is also supported by the C_{19}/C_{23} tricyclic terpane ratio (Table 2).

The C_{19}/C_{23} tricyclic terpane ratio has been widely used as indicative of terrigenous organic matter contribution (e.g. Preston and Edwards, 2000; Volk et al., 2005; Hao et al., 2009). The Damar and Nene samples display significantly greater C_{19}/C_{23} values , again supporting considerably higher contributions of terrigenous organic matter to these samples compared to other oils in the study area.

Comparison of the molecular composition of the Damar and Nene oils with similar published geochemical data (e.g. Philp, 1994; Sun et al., 2000) seems to indicate these two samples were generated either by coal or by an organic-rich shale with significant dispersed coaly type material. In the Central Sumatra Basin, coals and coal type organic matter is found within the synrift section as part of the Brown Shale lateral equivalent, the Coal Zone Formation. Coals from the Coal Zone Formation have been described in Kiri graben (Longley et al., 1990) and the Ombilin Basin, southwest of the Central Sumatra Basin (Suwarna et al., 2007; Fig. 1). These coals are mainly humic organic matter with up to 95% vitrinite content, average TOC of 54% and potential yields of 244-300 mgHC/gr. rock (Suwarna et al., 2007).

Significant controversy exists about the capability of coal seams to expel significant accumulations of liquid hydrocarbons (Katz, 1994; Wilkins and George, 2002 and references therein). Moreover, the question still remains as to what set of geochemical parameters will allow unequivocal distinction between coal derived oils from oils simply derived from shales containing coal type dispersed organic matter or shales interbedded with coal seams. Although our dataset is not sufficient to answer this question (lack of source rock material prevented proper oil-source rock correlations), it does show that the molecular composition of these two samples clearly differs from the molecular composition of other samples in the basin and the possibility exist that they were generated by a coaly lateral equivalent of the Brown Shale.

Samples with an intermediate composition between the end-members described above are characterized by a biomodal *n*-alkane distribution, Pr/Ph ratios between 1.8 and 3.8 and sterane distributions with a slight predominance of C_{29} steranes over C_{27} and C_{28} steranes (Fig. 5). The two oils from the Tanjung Medan graben, display slightly higher Pr/*n*C_{17} and Ph/*n*C_{18} ratios than the oils in this group. An intermediate composition between lacustrine shale derived oils and "coal" derived oils could indicate a mixed contribution from these end-members. This interpretation is further supported by compound specific isotopic compositions of *n*-alkanes (see discussion below).

Further distinctions based on molecular composition can be made for the three oils located south of the Aman Trough: Kasikan, Petapahan, and Kotabatak. Inspection of the m/z 125 chromatogram indicated these oils contain β-carotane (Fig. 6). β-carotane was not identified in other oils in the study area. β-carotane is derived from halotolerant algae and was first identified in the Green River Formation by Murphy et al., (1967). Its

presence is associated primarily with anoxic, saline lacustrine or highly restricted marine depositional settings (Peters et al., 2005 and references therein). Organic-rich marine mature source rocks have not been identified in the Central Sumatra basin, therefore the presence of β-carotane in these samples is interpreted as indicative a lacustrine saline source rock facies. Interestingly, these samples display very low (<0.1) gammacerane ratios ($Ga/C_{31}R$), suggesting that increased salinity is not always associated with lake water stratification.

4.2. Isotopic evidence for source rock facies interpretations

Carbon isotope values of individual *n*-alkanes and the isoprenoids pristane and phytane are listed in Table 3. Rodriguez and Philp (2012) identified the occurrence of CO_2 limiting conditions in the isotopic composition of the oils from the Aman Trough. This phenomenon is expressed in a progressive enrichment in isotopic composition. A similar enrichment in isotopic composition is observed in oil samples from the Bengkalis Trough (Fig. 7). CO_2 limiting conditions develop when productivity blooms sequester CO_2 in the upper part of the water column, resulting in the isotopic enrichment of the remaining CO_2 available for photosynthesis in the water column. This process typically takes place in lacustrine settings with a well developed stratified water column (Curiale and Gibling, 1994). Stratified water columns are easily developed under tropical climatic conditions and enhanced in deep water lakes (Katz, 1994). According to Longley et al., (1990) deep lakes only developed in the Aman and Bengkalis grabens, albeit the Aman graben is the deepest graben in the basin. An outlier sample, Pulai South, displays lighter

isotope values which seem to have a similar isotopic composition as the mixed "coal"/shale derived oils (Fig.8).

Compound specific isotopic compositions support the source rock facies identified through analysis of the molecular composition of the oils. The shallow lacustrine oils from the Kiri Trough, Hitam and Waduk, display the heaviest isotopic composition of the entire dataset. This is probably due to sourcing from mainly algal organic matter in a shallow restricted basin. The oils from the Tanjung Medan graben have an intermediate isotopic composition between the shale and "coal"-derived oils, supporting an interpretation of mixed shale/"coal" sourcing for these oils. The oils from the saline lacustrine facies and coal derived display the lightest isotopic compositions in the entire dataset.

Oil isotopic compositions are a direct reflection of the original isotopic composition of the source rock that generated them. Isotopic composition of individual *n*-alkanes is a powerful correlation tool, however the data presented here is a clear example that adds the most value when combined with other geochemical parameters (e.g. bulk composition, biomarker, metals, etc). Carbon isotopic values alone would have indicated a single family for the lacustrine saline oils and the Damar and Nene oils, however biomarker composition indicate these oils were derived by very different facies of the Pematang Brown Shale.

4.3. Importance of source rock facies interpretations from oil geochemistry

The carbonaceous Coal Zone Formation has been primarily described in the Kiri Graben, although it is also present in the Balam, Aman, and Rangau grabens, as part of

the basal section of the Brown Shale Formation (Williams and Eubank, 1985). Interestingly, the oils from the Kiri graben show primarily a shallow lacustrine signature (Longley et al., 1990). On the other hand, some of the best lacustrine facies are present in the Balam Trough (Katz, personal communication) yet the oils in the northern part of the basin display a coaly or mixed coaly/lacustrine shale facies signature.

It is possible that different types of coals (e.g. liptinite vs. vitrinite rich) were deposited in the Kiri and Balam grabens. Liptinite-rich coals generally have a higher generation potential than vitrinite-rich coals, although coals rich in perhydrous vitrinite can also generate hydrocarbons (Wilkins and George, 2002). Alternatively, in the Balam graben, only the basal section of the Brown Shale is thermally mature to generate and expel hydrocarbons. This would explain why, even though typical lacustrine shale facies have been described in the Balam graben, oils displaying the coal and mixed coal/lacustrine shale facies predominate.

The inconsistencies between source rock facies described from available rock data and facies derived from oil geochemistry highlight the importance of incorporating source rock facies interpretations from oil geochemistry in the evaluation of source rock presence and facies distribution in oil producing basins.

Without this type of analyses, source rock variations that could impact fluid character (e.g. paraffinic vs. waxy), hydrocarbon phase (e.g. oil vs. gas), etc, could be easily overlooked, resulting in erroneous predictions of hydrocarbon properties during oil and gas exploration and appraisal phases.

The source rock depositional environments interpretations from this study indicate that additional source rock facies are present in these grabens, that were not

previously described or taken into account as possible contributors to charge the oil accumulations observed in the Central Sumatra Basin. The dataset presented here indicate that a shallow lacustrine facies is present and generating hydrocarbons in the Kiri Trough. Similarly, coaly or mixed coaly/lacustrine shale facies developed and generated hydrocarbons in the Balam and Tanjung Mendan grabens.

5. Summary and Conclusions

The molecular and isotopic composition of 30 oils from the Central Sumatra Basin has allowed identification of 5 source rock facies within the Pematang Brown Shale. Additionally, it appears that coals or shale containing coal type dispersed organic matter, probably associated with the Coal Zone Formation generated two of the oils analyzed in this study. Table 4 summarizes the molecular and isotopic composition of the 5 source rock facies identified in this study.

The geographic distribution of the samples indicates deep stratified lakes developed in the Aman and Bengkalis grabens. Deep stratified grabens allowed development of CO_2 limiting conditions that are readily expressed in the compound specific isotopic composition of the oils. Oils in the Kiri graben are predominantly derived from a shallow lacustrine facies. Oils south of the Aman and Kiri grabens are characterized by the presence of β-carotane, indicating a saline lacustrine facies developed in this part of the basin. This saline lacustrine facies is probably associated with the shallow lacustrine facies that developed in the Kiri graben rather than the deep lacustrine facies predominant in the Aman Trough. The absence of botryococcane in the Kasikan, Petapahan and Kotabatak samples supports this interpretation. Finally, coal

derived oils and oils with a mixed shale/coal derived facies seem to be restricted to the northern part of the Central Sumatra Basin, particularly the Balam and Tanjung Medan Grabens. This would indicate oxidizing conditions and increased contributions from terrigenous organic matter prevailed in the northern part of the basin. In contrast, deep sub-oxic (Aman, Bengkalis), shallow sub-oxic (Kiri), and anoxic (South Aman) prevailed in the southern part of the Central Sumatra Basin.

Source rock facies described in this work, are in agreement with the oils groupings established by Seifert and Moldowan (1981). Type I oils correspond to the coaly facies, type IIa, IIb and IV oils correspond to the deep lacustrine facies, type IIc correspond to the shallow lacustrine facies and type III oils correspond to the saline lacustrine facies.

However, source rock depositional environments described here, as well as the summary of geochemical properties compiled in Table 4, present a more comprehensive analysis of source rock distributions in the Central Sumatra Basin, associated with the different source rock prone depositional environments that could have developed in lacustrine environments.

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Table 1. *n*-alkane and isoprenoid biomarker ratios. *from (Rodriguez and Philp, 2012)

Field	***Pr/Ph***	***Pr/nC$_{17}$***	***Ph/nC$_{18}$***	***nC$_{27}$/nC$_{17}$***
Ami*	2.2	0.4	0.2	0.5
Hitam*	3.6	0.5	0.2	0.6
Kakap *	2.4	0.3	0.2	0.4
Libo*	2.5	0.6	0.3	0.6
Libo Southeast*	2.6	0.2	0.1	0.4
Menggala South	2.9	0.5	0.2	0.7
Minas 3*	2.5	0.3	0.2	0.5
Minas 7*	2.7	0.3	0.1	0.6
Mindal*	2.6	0.3	0.1	0.2
Pematang*	3.0	0.5	0.2	0.5
Pematang Bow*	2.3	0.3	0.1	0.7
Petani*	2.2	0.4	0.2	0.4
Pungut*	2.8	0.3	0.1	0.5
Ubi*	3.1	0.5	0.2	0.6
Waduk	3.5	0.5	0.2	0.6
Buaya	3.6	1.9	0.6	0.9
Kasikan	2.3	0.5	0.2	0.8
Katobatak	2.5	0.8	0.3	0.9
Kayuara	2.8	0.4	0.1	0.7
Lirik	2.3	0.6	0.2	1.1
Mengkapan	1.8	0.2	0.1	0.5
Pekan	2.9	0.5	0.2	0.8
Petapahan	2.4	0.5	0.2	1.0
Pinang	3.4	0.8	0.3	0.8
Pulai South	3.8	0.9	0.3	1.1
Pusaka	2.1	0.3	0.1	1.3
Tanjung Medan	3.7	1.5	0.5	1.2
Zamrud	2.7	0.6	0.2	0.6
Damar	9.6	3.0	0.3	1.9
Nene	11.9	8.9	0.7	2.7

Table 2. Terpane and sterane biomarker ratios. * from (Rodriguez and Philp, 2012)

	Terpanes and Hopanes (m/z 191)					***Steranes (m/z 218)***		
Field	C_{19}/C_{23}	$Ga/C_{31}R$	*Ol/H*	*Ts/Ts+Tm*	H_{32} *S/(S+R)*	$\%C_{27}$	$\%C_{28}$	$\%C_{29}$
Ami*	0.6	0.17	0.15	0.8	0.5	39	23	38
Hitam*	0.5	0.27	0.24	0.9	0.5	36	22	42
Kakap *	0.5	0.10	0.14	0.8	0.5	42	21	37
Libo*	0.6	0.12	0.22	0.7	0.5	40	24	36
Libo Southeast*	0.0	0.09	0.23	0.8	0.5	40	23	36
Menggala South	0.4	0.14	0.10	0.8	0.5	39	24	37
Minas 3*	0.6	0.16	0.13	0.8	0.5	48	20	33
Minas 7*	0.6	0.13	0.10	0.9	0.5	42	23	35
Mindal*	0.7	0.37	0.16	0.9	0.5	49	21	30
Pematang*	0.5	0.10	0.13	0.8	0.6	45	21	34
Pematang Bow*	0.3	0.18	0.26	0.8	0.6	47	22	32
Petani*	0.5	0.09	0.12	0.8	0.5	44	21	35
Pungut*	0.0	0.14	0.12	0.8	0.5	38	23	38
Ubi*	0.0	0.13	0.20	0.8	0.5	44	22	35
Waduk	0.4	0.24	0.21	0.8	0.5	34	26	40
Buaya	0.2	0.07	0.07	0.9	0.6	27	26	47
Kasikan	0.1	0.07	0.13	0.8	0.5	26	28	46
Katobatak	0.2	0.06	0.19	0.8	0.5	33	24	43
Kayuara	0.4	0.13	0.12	0.8	0.5	37	23	40
Lirik	0.1	0.09	0.10	0.7	0.5	nd	nd	nd
Mengkapan	0.5	0.13	0.38	0.7	0.6	35	24	41
Pekan	0.1	0.00	0.25	0.7	0.5	nd	nd	nd
Petapahan	0.1	0.06	0.17	0.8	0.5	32	26	43
Pinang	0.2	0.09	0.08	0.8	0.5	38	18	44
Pulai South	0.3	0.06	0.09	0.8	0.5	19	25	56
Pusaka	0.3	0.15	0.61	0.8	0.5	32	28	40
Tanjung Medan	0.4	0.13	0.12	0.8	0.5	29	25	46
Zamrud	0.2	0.09	0.10	0.8	0.5	27	21	52
Damar	13.5	0.05	0.21	0.2	0.6	17	25	57
Nene	4.1	0.02	0.03	0.8	0.6	16	22	62

Table 3. Compound specific isotopes of n-alkanes. * from (Rodriguez and Philp, 2012)

Field	*Sub-basin*	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	C_{33}	C_{34}
Ami*	Aman	-27.3	-27.6	-28.2	-28.6	-28.8	-29.1	-29.4	-29.6	-30.08	-29.8	-30.3	-30.3	-30.6	-30.24	-30.8	-31.7	-30.8	-31.2		
Kakap *	Aman	-26.5	-26.8	-26.2	-27.3	-27.7	-27.9	-28.2	-28.4	-28.53	-28.4	-28.6	-28.8	-29.4	-29.73	-32.4	-31.9	-31.4	-32.1	-31.67	-30.3
Libo*	Aman	-26.7	-27.2	-27.3	-27.9	-28.7	-29.0	-28.8	-29.7	-29.83	-29.6	-29.8	-30.5	-30.4	-29.7	-30.7	-31.3	-29.3	-30.2	-30	
Libo Southeast*	Aman	-25.8	-26.1	-26.9	-26.78	-27.1	-27.1	-27.6	-27.6	-27.8	-27.7	-27.6	-28.4	-28.2	-28.11	-28.6	-28.7	-28.5			
Menggala South*	Aman	-24.4	-24.3	-24.7	-25	-25.7	-25.3	-25.5	-25.5	-25.7	-25.6	-25.5	-25.8	-25.3	-22.6						
Minas 3*	Aman	-26.6	-26.7	-27.3	-27.6	-28.5	-28.0	-28.5	-28.5	-28.62	-28.6	-28.5	-29.1	-29.0	-28.86	-29.8	-29.7	-30.1	-28.6	-28.6	
Minas 7*	Aman	-26.9	-27.1	-27.7	-27.86	-28.6	-28.8	-30.2	-29.2	-29.6	-29.7	-29.7	-29.9	-29.8	-29.62	-32.2	-30.4	-29.4	-29.9		
Mindal*	Aman	-26.1	-26.4	-26.0	-26.8	-27.3	-27.4	-27.8	-28.1	-28.35	-28.1	-28.0	-27.8	-27.9	-28.37	-28.2	-28.0				
Pematang*	Aman	-25.4	-25.6	-26.5	-26.89	-27.2	-27.2	-27.5	-27.8	-28.18	-28.2	-28.5	-27.8	-28.0	-28	-30.7	-28.2	-27.9	-28.2	-27.5	
Pematang Bow*	Aman	-24.7	-24.2	-24.6	-24.7	-25.3	-25.1	-25.5	-25.1	-25.02	-25.1	-25.0	-24.9	-25.1	-25.39	-26.2	-26.8	-25.4	-25.5		
Petani*	Aman	-24.7	-25.0	-24.9	-25.4	-26.0	-25.9	-26.1	-26.4	-26.7	-26.5	-26.6	-26.6	-26.7	-26.6	-26.6	-26.5	-26.3	-26.5		
Pungut*	Aman	-27.0	-27.3	-28.4	-29.13	-29.3	-29.6	-30.1	-30.2	-30.25	-30.4	-31.1	-31.1	-31.0	-30.79	-33.5	-32.4	-30.6			
Ubi*	Aman	-25.1	-25.2	-25.8	-26.31	-26.6	-27.0	-27.4	-27.5	-27.87	-27.9	-27.9	-28.4	-28.8	-28.05	-32.7	-28.9	-28.2	-29.9	-27.11	
Damar	Balam	-29.4	-29.4	-29.6	-29.8	-29.7	-29.7	-29.9	-30.0	-30.28	-30.2	-30.4	-30.5	-30.7	-30.74	-30.7	-30.2	-30.7	-31.5		
Pinang	Balam	-26.9	-26.1	-26.9	-26.99	-27.0	-27.3	-27.4	-27.1	-27.36	-27.5	-27.5	-27.5	-27.5	-27.23	-27.9	-27.8	-27.9	-26.9	-27.54	
Pulai South	Bengkalis	-28.2	-28.2	-28.3	-28.52	-28.5	-28.4	-28.8	-28.8	-29.11	-28.7	-28.8	-29.4	-29.5	-29.9	-30.8	-30.4				
Kayuara	Bengkalis	-24.2	-24.1	-24.6	-23.83	-24.2	-24.1	-24.4	-24.2	-24.5	-24.4	-24.5	-25.4	-24.5	-24.59	-27.9	-25.4	-26.7	-27.0		
Pekan	Bengkalis		-24.7	-25.0	-25.3	-25.2	-25.2	-25.6	-25.5	-25.58	-25.4	-25.4	-25.7	-25.8	-25.84	-26.4	-26.1	-26.3	-25.6	-25.14	
Lirik	Bengkalis			-25.5	-25.6	-26.2	-26.1	-26.6	-26.5	-26.5	-26.4	-26.5	-26.7	-26.9	-26.5	-26.8	-26.7	-26.3	-27.0		
Mengkapan	Bengkalis	-25.0	-24.7	-25.1	-25.08	-25.5	-25.2	-25.6	-25.8	-25.86	-25.9	-25.7	-25.6	-25.8	-25.39	-25.6	-26.1	-25.1	-25.1	-25.2	

Table 3. Compound specific isotopes of n-alkanes. * from (Rodriguez and Philp, 2012)

Field	*Sub-basin*	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	C_{33}	C_{34}
Pusaka	Bengkalis	-25.2	-25.0	-25.7	-25.7	-26.2	-26.5	-26.8	-26.6	-26.5	-26.5	-26.4	-26.7	-26.3	-26.09	-26.6	-26.4	-26.8	-25.8		
Zamrud	Bengkalis	-25.5	-25.0	-25.6	-25.81	-26.0	-26.1	-26.1	-26.3	-26.4	-26.3	-26.4	-26.6	-26.8	-26.67	-26.8	-26.7	-26.6			
Hitam	Kiri	-22.5	-22.1	-22.2	-22.3	-22.1	-21.8	-22.4	-22.4	-22.3	-22.2	-22.3	-22.3	-22.2	-22.2	-22.5	-22.3	-22.4	-22.3		
Waduk	Kiri	-22.8	-22.5	-22.1	-21.9	-22.3	-22.3	-22.2	-22.5	-22.49	-22.1	-22.4	-22.2	-22.0	-22.3	-22.5	-22.5	-22.3	-22.5		
Nene	Nene		-29.3	-29.5	-29.73	-29.8	-29.9	-30.2	-30.2	-30.53	-30.6	-30.6	-30.7	-30.6	-30.77	-31.3	-31.5	-31.6	-30.9	-32	
Kasikan	South Aman			-29.6	-30.34	-30.2	-30.6	-31.0	-31.0	-31.13	-31.3	-30.9	-31.3	-31.1	-30.4	-32.7					
Katobatak	South Aman		-29.3	-29.6	-30.02	-30.2	-30.4	-30.8	-30.7	-30.61	-30.5	-30.2	-30.2	-29.9	-28.94	-29.1	-28.4	-28.4	-27.6	-27.6	-26.9
Petapahan	South Aman			-28.9	-29.3	-29.9	-29.6	-30.3	-30.1	-30.46	-30.1	-30.0	-30.1	-30.0	-30	-31.3					
Buaya	Tanjung Medan	-30.8		-25.7	-26.3	-28.7	-27.1	-27.6	-27.9	-28.08	-27.5	-27.7	-27.9	-27.7	-27.1	-27.5	-27.4	-27.9	-28.0		
Tanjung Medan	Tanjung Medan	-25.5	-25.9	-26.1	-26.7	-26.5	-27.3	-27.8	-28.3	-28.1	-27.9	-28.1	-28.1	-27.5							

Table 4. Summary of geochemical characteristics for each source rock facies.

Geochemical property	***Deep lacustrine***	***Sallow Lacustrine***	***Saline lacustrine***	***Coal***	***Mixed coal/lacustrine shale***
n-alkane distribution	Unimodal/slightly bimodal	Unimodal	Bimodal	Unimodal	Bimodal
Carbon length preference	Short	Short	Bimodal	Long	Bimodal
Pr/Ph	1.8-3.1	3.50	2.40	9.6-11.9	3.6-3.8
nC_{27}/nC_{17}	0.1-1.3	0.60	0.8-1	1.9-2.7	0.9-1.2
C_{19}/C_{23}	0.1-0.7	0.45	0.20	4.1-13.5	0.30
$Ga/C_{31}R$	0.1-0.37	0.26	0.06	0.04	0.06-0.13
Betacarotane	No	No	Yes	No	No
Sterane distribution	Strong C_{27} Pref.	No	Slight C_{29} Pref.	Strong C_{29} Pref.	Strong C_{29} Pref.
$\delta^{13}C$ range	-30 to -24	-22	-30 to -29	-30	-29 to -27

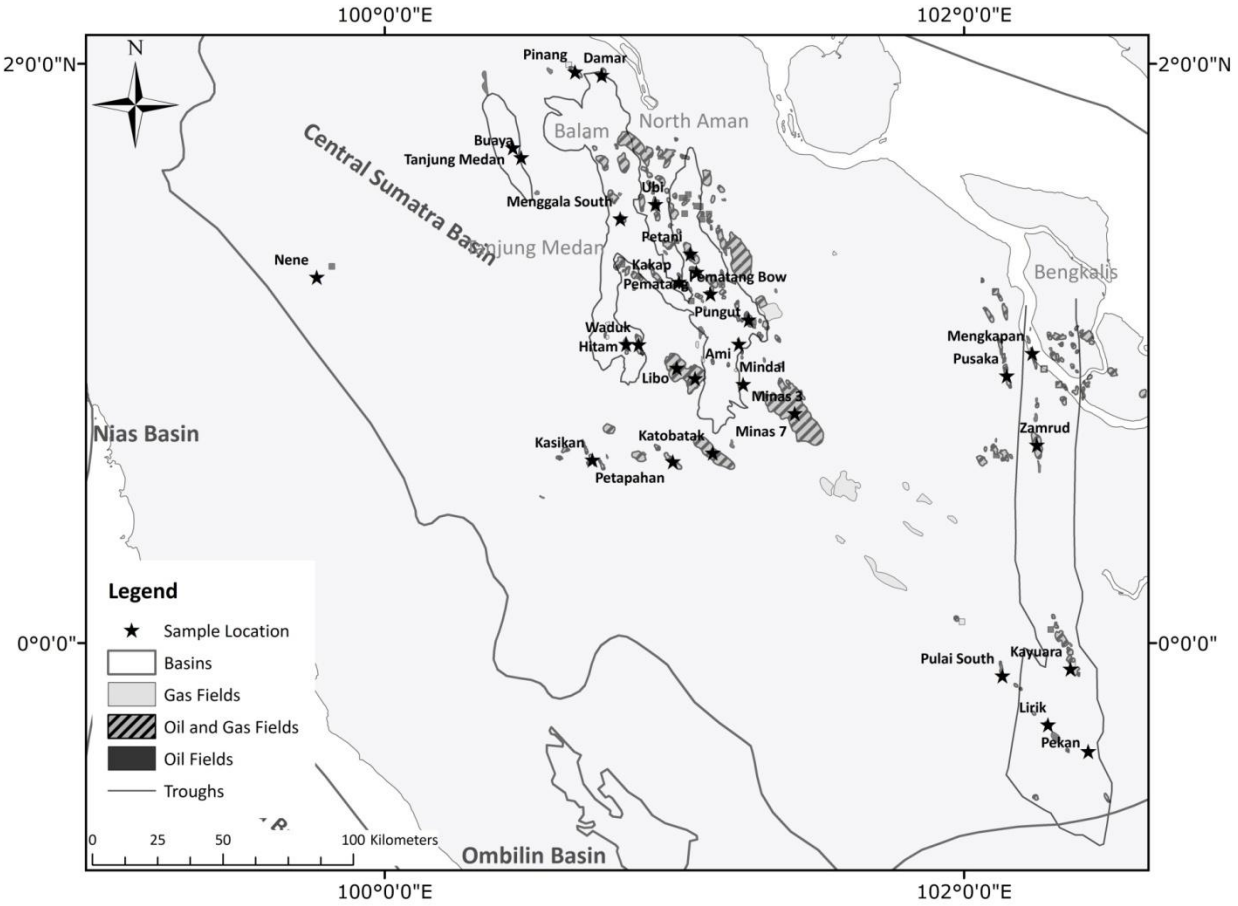


Figure 1. Map showing the relative location of samples analyzed in the Central Sumatra Basin.

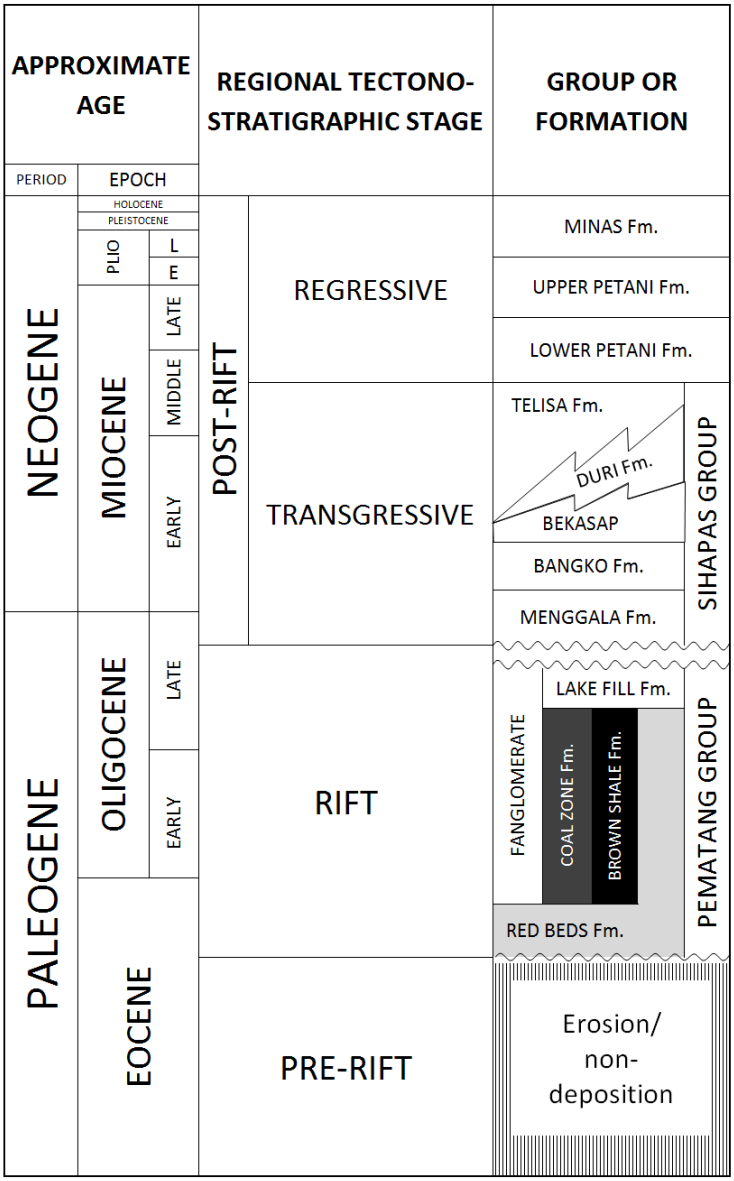


Figure 2. Generalized stratigraphic chart of the Central Sumatra Basin. Modified from Koning and Darmon (1984) and Williams et al., (1985)

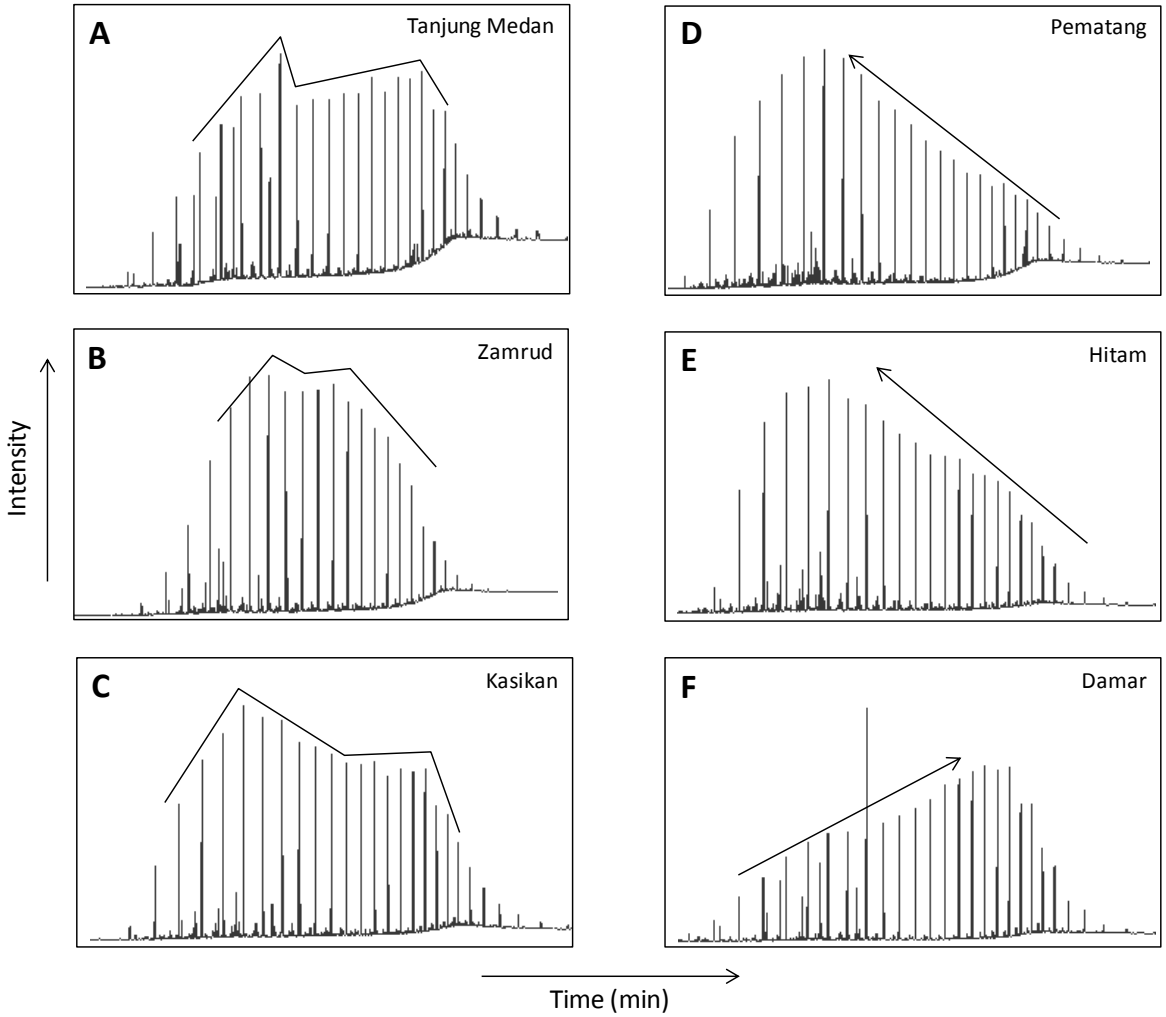


Figure 3. Representative GC chromatograms for the main grabens in the Central Sumatra Basin. Arrows indicate unimodal versus bimodal *n*-alkane distributions and carbon number preference.

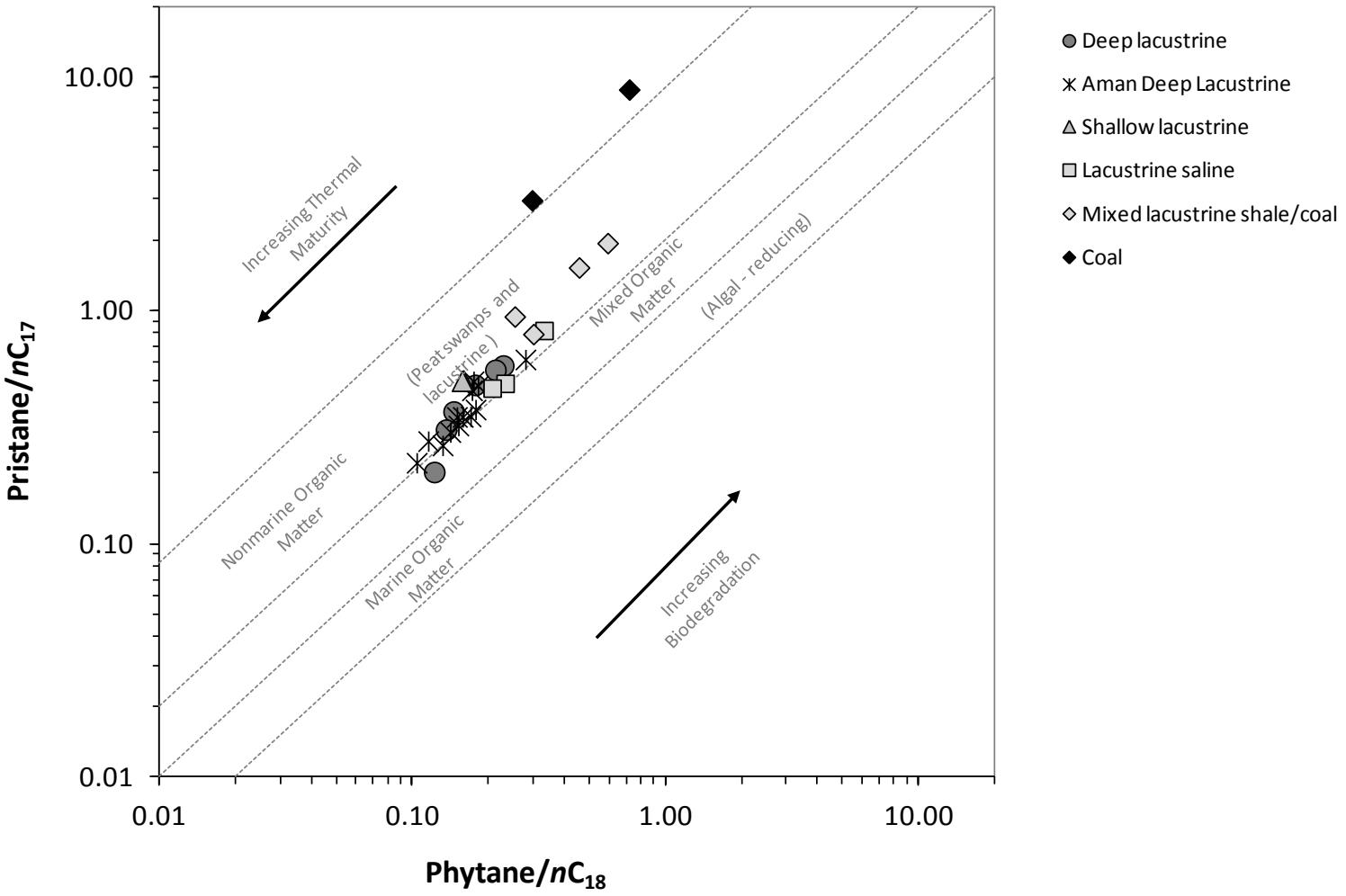


Figure 4. Pristane/nC_{17} ratio vs. phytane/nC_{18} ratio calculated from gas chromatograms of the maltene fraction.

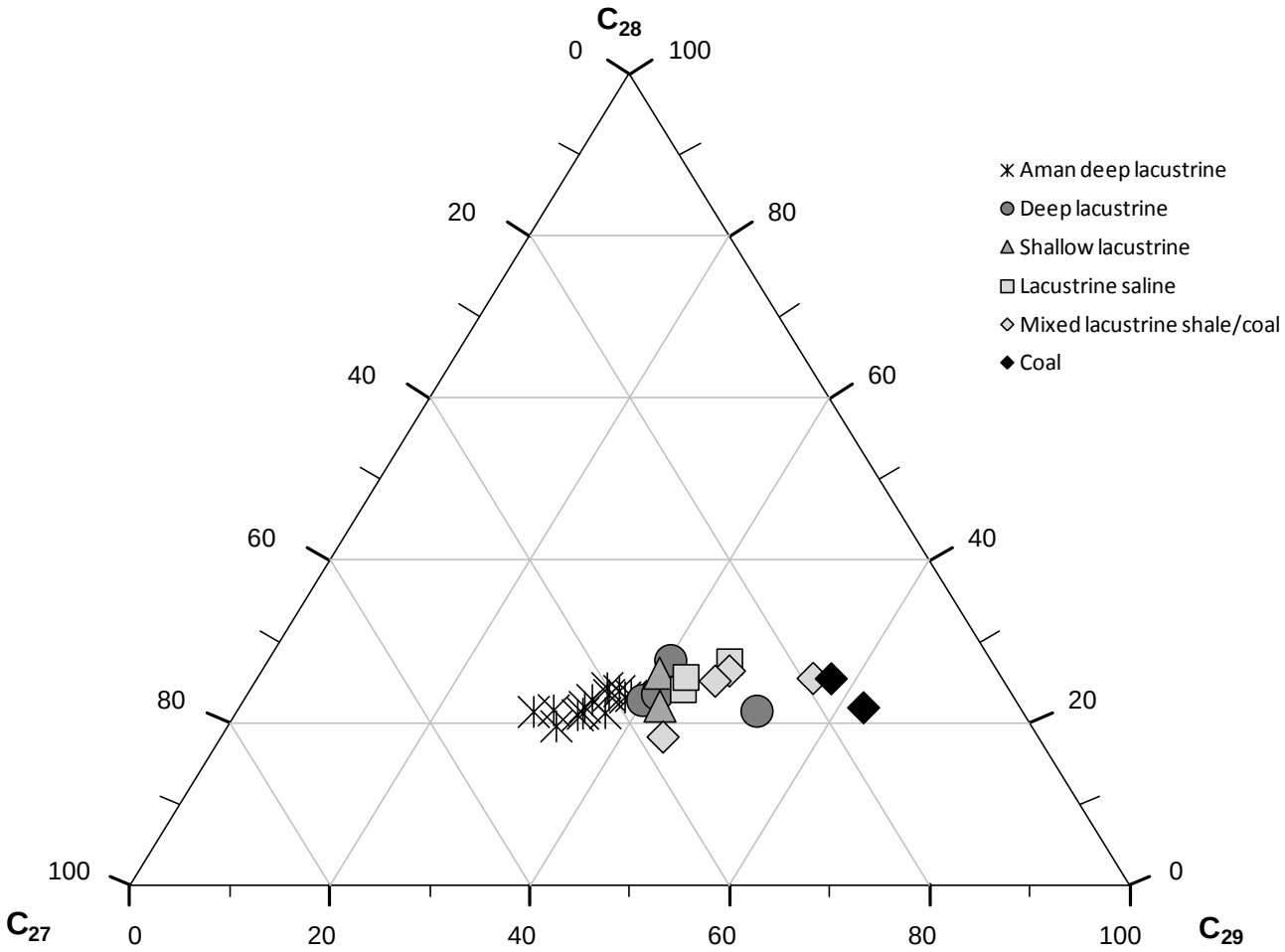


Figure 5. Ternary diagrams for the sterane carbon distributions of C_{27}, C_{28} and C_{29} (αββ). Data are derived from GC-MS m/z 218.

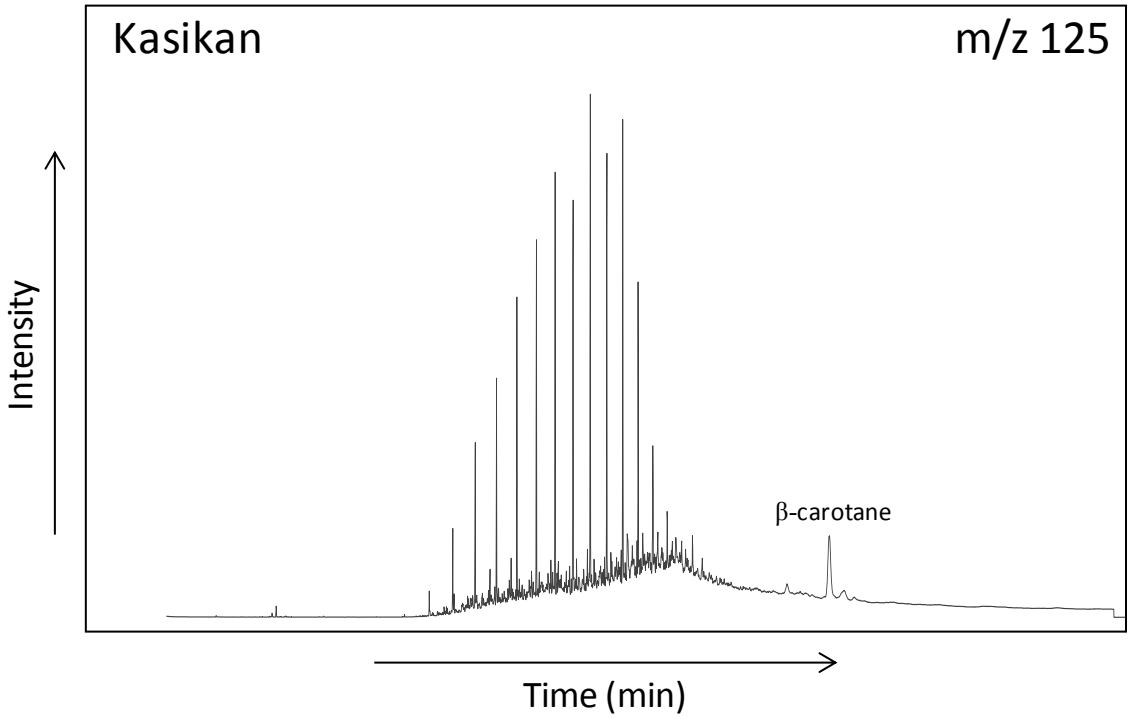


Figure 6. Typical m/z 125 fragmentogram for oils containing the biomarker β-carotane.

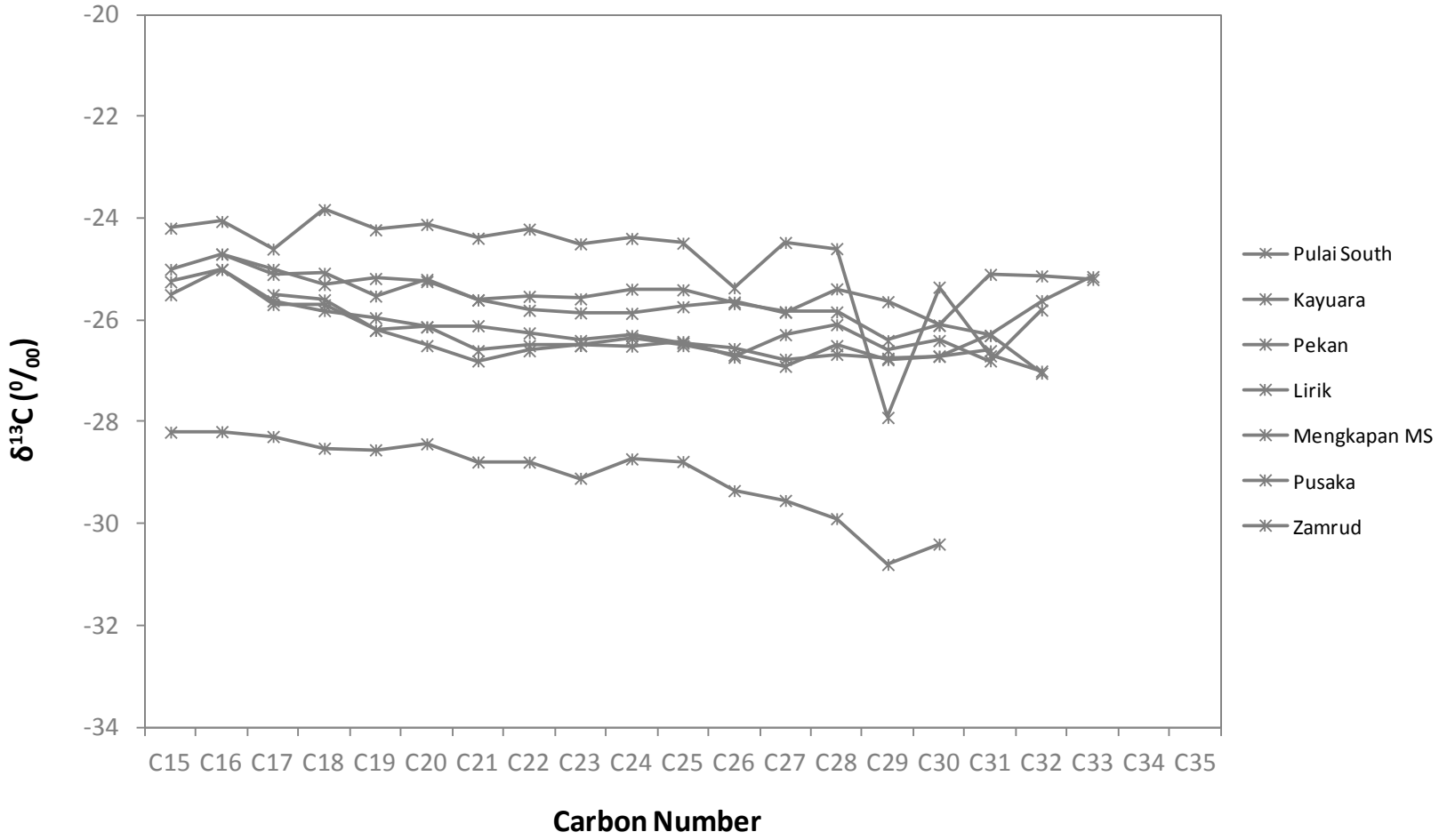


Fig. 7. Compound specific carbon isotopic composition of oils in the Benkgalis Trough.

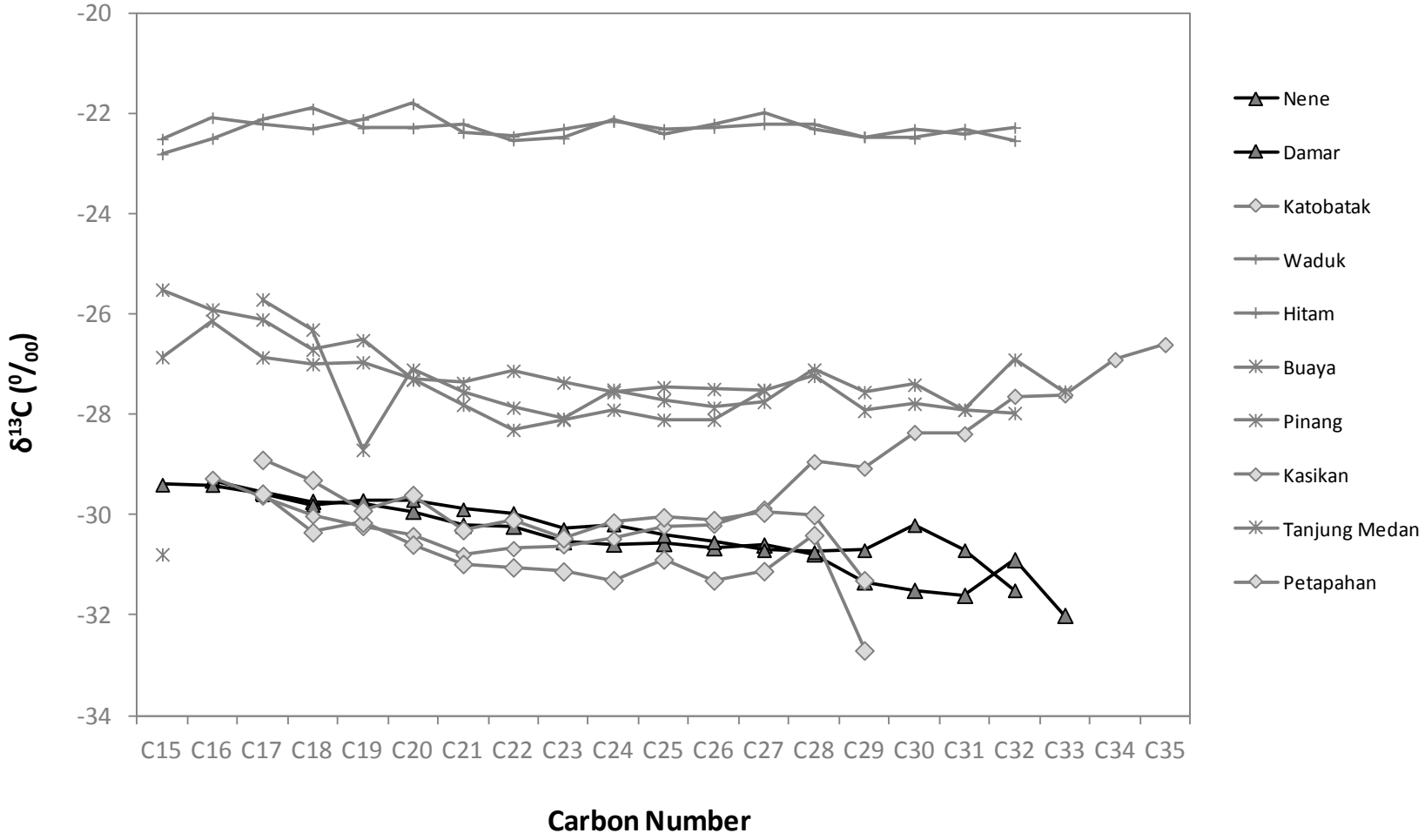


Fig. 8. Compound specific carbon isotopic composition of oils in the Kiri, Balam, South Aman Troughs and Nene oil.

Chapter IV

Summary and Outlook

This study was inspired by the need to understand the observed geochemical variability of the oils produced in the Central Sumatra Basin of Indonesia. The main objective was to characterize the depositional conditions that prevailed during deposition of the oil's source rock, not only by grouping the oils in geochemical families, but linking those families to specific depositional environments or facies.

A representative sample set was carefully chosen to cover all oil producing grabens in the basin. The molecular and compound specific isotopic composition of oil samples from the Aman, Balam, Tanjung Medan and Bengkalis grabens were analyzed using a series of chromatographic techniques including gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) and gas chromatography isotope ratio-mass spectrometry (GC IR-MS).

Combination of molecular and carbon isotopic composition allowed identification of 5 facies that developed in the studied grabens of the Central Sumatra Basin. The geographic distribution of the samples indicates that deep stratified lakes developed in the Aman and Bengkalis Troughs. Although both the Aman and Bengkalis developed similar deep lacustrine organic facies, the majority of the oils in the Aman Trough are characterized by the presence of botryococcane and the same biomarker is absent in the oils in the Bengkalis Trough.

A detailed look at the geochemical composition of the oils in the Aman Trough allowed identification of productivity and paleoclimatic controls on the source rock

character of the Brown Shale Formation. Deep stratified lakes developed CO_2 limiting conditions and these are readily expressed in the carbon compound specific isotopic composition of the oils. Absence of botryococcane from oil samples derived from the deep lacustrine facies is probably associated with changes in lake water chemistry, most likely associated with lake euthrophication.

Oils in the Kiri graben are predominantly derived from a shallow lacustrine facies while the oils south of the Aman and Kiri graben display a more saline lacustrine facies as indicated by the presence of β-carotane. This difference between the oils south of the Aman and Kiri basin and other oils in the basin probably indicates these oils are being sourced by an isolated graben where lacustrine saline conditions developed.

"Coal" derived oils and oils derived from a mixed coal/lacustrine shale facies seem to be restricted to the northern part of the Central Sumatra Basin.

Differences between the source rock depositional environments described in this study and source rock facies described in the literature for each of the grabens, highlight the importance of incorporating source rock facies interpretations from oil geochemistry in the evaluation of source rock presence and facies distribution in oil producing basins. Changes in rock facies that can impact fluid character (e.g. paraffinic vs. waxy), hydrocarbon phase (e.g. oil vs. gas), etc, could be easily overlooked, resulting in erroneous predictions of hydrocarbon properties during petroleum exploration and appraisal phases. This is particularly important in areas where little or no source rock samples are available for source rock facies characterization.

A new sesquiterpane biomarker compound was identified in the oils from the Aman Trough. The new compound has tentatively been identified as a C_{15} sesquiterpane

based on mass spectra, however, more analyses are needed in order to establish its molecular structure.

Recommended future work

Combination of data derived from gas chromatography-mass spectrometry with compound specific isotopic analysis has proven very valuable in identifying source rock facies variation in lacustrine environments. Although significant improvements in the understanding of source rock facies distributions in the Central Sumatra Basin were accomplished, a better source rock depositional model could be accomplished by incorporating source rock samples and performing oil-source rock correlations in each of the grabens.

Recent development of advanced (two dimensional) chromatographic techniques (e.g. GCxGC-TOFMS and GCxGC-FID) could provide an additional level of information to characterize source rock depositional environments. These techniques would be particularly useful in the analysis of biodegraded samples, in which peak resolution using traditional chromatographic techniques is rather limited. At this time, only a limited number of laboratories can generate two dimensional chromatographic data, although the greatest limitation in the application of these techniques comes with the analysis of the vast datasets generated due to the increased peak resolution capacity.

Finally, additional experiments should be carried out to determine the molecular structure of the new C_{15} sesquiterpane biomarker identified in this study. More importantly, its origin and possible application as a diagnostic biomarker ought to be investigated.