



# Reconstruction of floral changes during deposition of the Miocene Embalut coal from Kutai Basin, Mahakam Delta, East Kalimantan, Indonesia by use of aromatic hydrocarbon composition and stable carbon isotope ratios of organic matter

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## ABSTRACT

The distribution of aromatic hydrocarbons and stable carbon isotope ratios of organic matter in a series of nine Miocene Embalut coal samples obtained from nine coal seams of Kutai Basin, East Kalimantan, Indonesia were studied. The rank of the Embalut coals ranged from lignites to low rank sub-bituminous coals (0.36–0.50% Rr), based on measurements of huminite reflectance. The aromatic hydrocarbon fractions of all coal samples were dominated by cadalene in the lower boiling point range and picene derivatives in the higher boiling point range of the gas chromatograms. Cadalene can be attributed to the contribution of *Dipterocarpaceae* and various hydrated picenes to the contribution of additional angiosperms to the coal forming vegetation. The picenes originate from alpha- and beta-amyrin. However, in some coal samples minor amounts of simonellite and retene were also detected which argues for an additional contribution of gymnosperms (conifers) to coal forming vegetation preferentially in the Middle Miocene and at the beginning of the Late Miocene. The results of stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) in most of the coal samples are consistent with their origin from angiosperms ( $\delta^{13}\text{C}$  between  $-27.0\text{‰}$  and  $-28.0\text{‰}$ ). During the Miocene the climate of Mahakam Delta was not uniformly moist and cooler than the present day climate. This would have been favourable for the growth of conifers, especially in the montane forests. The contribution of conifers to the Embalut coals might be a result of the cool Middle/Late Miocene climate during peat accumulation in the Kutai Basin.

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## 1. Introduction

The study of biomarkers in coals can provide valuable information about the biological materials contributing to the former coal swamp depositional environments and early transformation processes during the first stages of diagenesis. Biomarker analyses have been applied to study many coals and lignites from different areas and ages (Dzou et al., 1995; Casareo et al., 1996; Hasiah and Abolins, 1998; Lie et al., 2001; Bechtel et al., 2002a, 2002b, 2003, 2004, 2007a, 2007b; Stefanova et al., 2002, 2005; Sun et al., 2002). Biomarkers have also been investigated in recent peat deposits that may act as analogues for ancient coal forming mires (e.g., Pillon et al., 1986a, 1986b; Dehmer, 1993, 1995; Dellwig et al., 1998; Ficken et al., 1998; van Aarssen et al., 2000; Xie et al., 2000; Tareq et al., 2004).

In previous biomarker studies of coals, shales and crude oils from the Mahakam Delta, Kalimantan, Indonesia abundant pentacyclic triterpenoid alkanes, alkenes, and ketones with the carbon

skeleton of  $\alpha$ - and  $\beta$ -amyrin were identified (Hoffmann et al., 1984). van Aarssen et al. (1990) investigated fossil resin from a Miocene outcrop in Lumapas, Brunai (Kalimantan), southeast Asia and extant dammar resin obtained from the family *Dipterocarpaceae* by use of pyrolysis GC–MS. The pyrolysis products from both the fossil and extant resinites were characterized by a high abundance of compounds with the cadinane skeleton ( $\text{C}_{15}$ ) and bicadinane skeleton ( $\text{C}_{30}$ ) associated with amyrin derived triterpenoids. Later, van Aarssen et al. (1992) found bicadinanes, cadinane, and aromatized compounds such as cadalene and aromatic seco-bicadinanes also in crude oils from southeast Asia and suggested that the co-occurrence of cadinanes and bicadinanes is a strong argument for an origin of the compounds from *Dipterocarpaceae*.

Anggayana (1996) investigated the organic geochemistry of some Tertiary coals from Ombilin and Tanjung Enim (Sumatra) and Tanito Harum (East Kalimantan), Indonesia. Coals of low rank were dominated by sesquiterpenoids and picene derivatives indicating a dominating origin from angiosperms. Stankiewicz et al. (1996) investigated macerals from a Miocene lignite and an Eocene bituminous coal in Indonesia by use of pyrolysis GC–MS and found

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cadalene and 1,6-dimethylnaphthalene in high abundance in resinites. This was interpreted as a dammar-related origin of the resinites. Also, in Late Miocene/Early Pliocene Lower Suban coals from the South Sumatra Basin, Indonesia pentacyclic aromatic hydrocarbons related to  $\alpha$ - and  $\beta$ -amyrin were dominating by far and tricyclic saturated and aromatic hydrocarbons of undefined structure from gymnosperms were only detected in trace concentrations in the background of the chromatograms from some samples (Amijaya et al., 2006).

Results from palynological investigations of Miocene coals from Kalimantan are rare. Anderson and Muller (1975) isolated and determined 76 different pollen grains in a Holocene peat and a Miocene coal deposits from northwest Kalimantan. Most pollen in this area is related to angiosperms. Conifer (gymnosperms) pollen grains (*Dacrydium* and *Podocarpus*) were not detectable in the Miocene coals but only in low amounts in the Holocene peat. This is consistent with findings of Morley (1981), who studied the development and vegetation dynamics of lowland ombrogenous Holocene peat swamp in the Palangkaraya, central Kalimantan, Indonesia by means of palynological methods using material from sediment cores. The deeper peat was built up from a forest dominated by *Dacrydium* sp. (gymnosperm) and *Combretocarpus rotundatus* (angiosperm). In the latter phase of peat development, the area was influenced by the widespread invasion of *Calophyllum retusum* (angiosperm).

According to these results, the plant biomass of the Tertiary coal deposits in Kalimantan was exclusively composed of angiosperms. Indications for the presence of gymnosperms in peat and coal from Indonesia are so far restricted to the Late Miocene/Early Pliocene of the South Sumatra Basin (Amijaya et al., 2006) and to Holocene of Kalimantan (Morley, 1981). The recent vegetation of the forests in East Kalimantan is preferentially composed of angiosperms with a strong dominance of *Dipterocarpaceae* (Appanah and Turnbull, 1998; Hashimoto et al., 2000; Phillips et al., 2002).

The present study provides an organic geochemical characterisation of coals from the Kutai Basin, Kalimantan (Indonesia) ranging from Middle Miocene to Late Miocene age. The aim of the study is to reconstruct floral changes in the basin during this time period and clarify whether gymnosperms contributed to the flora at that time reflecting temperature changes during the Miocene in south-east Asia.

## 2. Geological setting

The Embalut coal mine is located in the vicinity of the Mahakam River, Kutai Basin, East Kalimantan Province (Fig. 1) and is situated  $00^{\circ}33'34.9''/117^{\circ}12'15.5''$ . Coal seams in the Embalut coal mine are present within the following formations: Pulau Balang of Middle Miocene age and Balikpapan of Late Miocene age. The Kutai Basin covers an area of approximately 165,000 km<sup>2</sup>. It is the largest Tertiary basin and well known as an area of major resources of oil, gas and coal in Indonesia (Syarifuddin and Busono, 1999). This basin was generated by Tertiary extension of a basement of mixed continental/oceanic affinity. The underlying sediments are of Jurassic and Cretaceous age and are composed of ophiolitic units overlain by a younger Cretaceous turbidite fan, sourced from Indochina. The Kutai Basin can be divided into two sub-basins; a western Inner or Upper Kutai Basin, and an eastern Outer or Lower Kutai Basin (Fig. 1). Today the Upper Kutai Basin is an area of major tectonic uplift as a result of Lower Miocene inversion of Paleogene depocenters and the effects of subsequent erosion (Moss and Chambers, 1999).

A nearly complete Tertiary sedimentary section from Eocene to Recent is present within the Kutai Basin, most of it being exposed at the surface due to the Miocene and younger tectonic processes. The basin was formed during the Middle Eocene in conjunction with rifting and likely sea floor spreading in the Makassar Strait. This produced a series of discrete fault bounded depocenters in some parts of the basin, followed by the sag phase sedimentation in response to

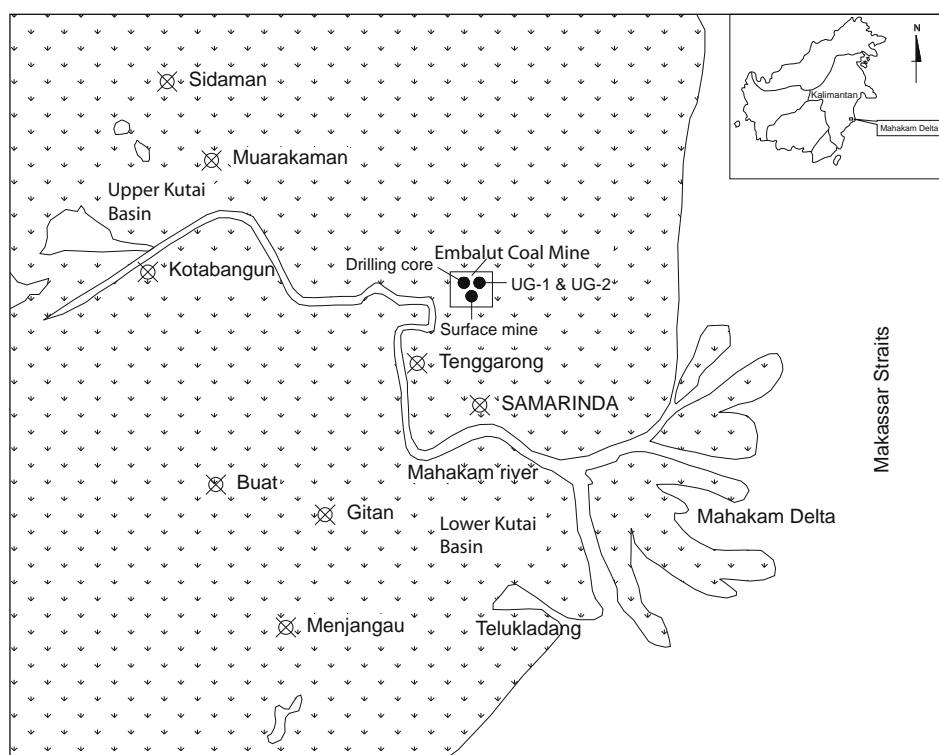


Fig. 1. Location of drilling core, surface mine and underground mines 1 and 2 (UG-1 and UG-2) of the Embalut coal mine in Kutai Basin, Mahakam Delta, East Kalimantan (Indonesia).

thermal relaxation. Tectonic uplift documented along the southern and northern basin margins and related subsidence of the Lower Kutai Basin occurred during the Late Oligocene. This subsidence was associated with significant intrusion of high level andesitic–dacitic material and associated volcanic rocks. Volcanism and uplift of the basin margin resulted in the supply of considerable volumes of material eastwards. During the Miocene, basin fill continued, with an overall regressive style of sedimentation, interrupted by periods of tectonic inversion throughout the Miocene to Pliocene (Moss and Chambers, 1999). Coal samples in the present study originate from the Embalut coal mine in the Lower Kutai Basin.

### 3. Samples and methods

Coal samples from the Embalut coal mine were collected from two active underground coal mines (nos. 1 and 2), one active surface mine (Bondowoso) and two drilling cores from Embalut coal mine. The coal samples consist of seven coal samples from Balikpapan Formation (seams 22, 21, 18, 17, 12, 10, and 9) and two coal samples from Pulau Balang Formation (seams 8 and 7). Location of the Embalut coal mine is shown in Fig. 1.

#### 3.1. Coal rank (huminite reflectance measurements)

Mean random huminite reflectance measurements were performed on the surface of huminite particles under oil immersion on a Leica MPV microscope. Calibration of the instrument has to be carried out before and after the measurement of every sample by use of an Yttrium Aluminium Garnet (YAG) reflectance standard (0.899%). The examination was conducted using a 50× magnification Epiplan objective lens and 12.5× magnification ocular lens under oil immersion ( $n_e = 1.518$  at 23 °C). Fifty points of huminite reflectance were taken on each sample at a wave length of 546 nm. From these 50 data points mean random huminite reflectance was calculated. Reflectance was measured on phlobaphinite and ulminite macerals that have a visible and homogeneous structural form. The mean random huminite reflectance values were then calculated using the Microsoft Excel program.

#### 3.2. Soxhlet extraction

Fifty grams of each coal sample were finely ground and sieved to obtain only particle size <0.2 mm. This fraction was extracted for 24 h in a Soxhlet apparatus using 200 ml DCM as solvent. The total hydrocarbon extract obtained was separated into different fractions by means of column chromatography.

#### 3.3. Organic carbon

Organic carbon contents (wt%) were measured using an LECO CS-344 carbon/sulfur analyzer. Prior to the analysis pulverized coal samples were treated with diluted (10%) hydrochloric acid to remove carbonates from the samples. Samples were washed three times with distilled water and dried for 1 h at 105 °C. For elemental analysis coal samples were mixed with iron chips and a tungsten accelerator and were combusted in an oxygen atmosphere at 1370 °C. The moisture and dust were removed from the combustion product and the CO<sub>2</sub> gas has been measured using a solid state infrared detector. Organic carbon contents were used for the determination of the extract yields (mg extract/g TOC).

#### 3.4. Column chromatography

The total extracts were separated using column chromatography (1.5 cm diameter) over activated silica gel (14 g) and eluted

sequentially into four fractions using 40 ml *n*-hexane (fraction 1) for the saturated hydrocarbon fraction, 100 ml *n*-hexane/DCM (90/10 v/v, fraction 2) for the aromatic hydrocarbon fraction, 40 ml DCM (fraction 3) for esters/ketones, and 40 ml methanol (fraction 4) for the more polar compounds (NSO compounds). The amount of asphaltenes was calculated as the difference between the total SOM and the sum of the four fractions obtained from column chromatography. A nitrogen pressure of 0.5 bar was used to accelerate the chromatography (flash chromatography). In this study, only the aromatic fractions were further analyzed.

#### 3.5. Gas chromatography–mass spectrometry (GC–MS)

The aromatic hydrocarbon fractions were analysed by gas chromatography–mass spectrometry (GC–MS). GC–MS analyses were carried out on a Thermo Quest GC 8000 series coupled to a Thermo Quest MD 800 mass spectrometer. Separation of the compounds was achieved using a fused silica SGE forte GC capillary column coated with BPX5 (30 m × 0.25 mm ID × 0.25 μm film thickness). The oven temperature was programmed from 60 to 300 °C at a rate of 4 °C/min, with a 20 min isothermal period at 300 °C. The samples were injected in the split less mode with the injector temperature at 280 °C. Helium was used as carrier gas. The mass spectrometer was operated in the electron impact mode (EI) at 70 eV ionization energy. Mass spectra were obtained by scanning from 45 to 700 Da at a cycle time of 1 s. For data processing, the Masslab software (FISONS Instruments) was used. Identification of compounds was made via comparison of mass spectra with those published in literature and based on GC retention behaviour.

#### 3.6. Stable carbon isotope analysis

The carbon isotope measurements were performed with a Flash Elemental Analyser – 1112 linked to a Thermo-Finnigan Mat 253 spectrometer. For isotopic analyses, the carbonate was removed with hydrochloric acid (10%) aliquots, rinsed with distilled water until neutral and finally loaded into tin capsules. The system was calibrated using USGS-24 pure graphite standard with a δ<sup>13</sup>C value of –15.99‰ on the Pee Dee Belemnite (PDB) scale. The results are reported relative to the PDB standard.

## 4. Results and discussion

#### 4.1. Huminite reflectance of the coals

Results from the determination of huminite reflectance R<sub>r</sub> (%) of Embalut coals are described in Table 1 and Fig. 2. Coal samples from Embalut provided mean random huminite reflectance values ranging from 0.36 to 0.50 R<sub>r</sub> (%). The data indicate a tendency of increasing mean random huminite reflectance with increasing depth of the coal seam (see profile in Fig. 2). The observed rank variations can be explained by differences in the temperature and pressure influences on the coals. The measured mean random huminite reflectance is equivalent to the lignite rank in the upper part of the profile (samples from seams 22 and 21 of Balikpapan Formation) and low rank sub-bituminous coal rank in the deeper section (classification after Teichmüller, 1982). Two exceptions are the coal samples from seams 22 and 21 (Balikpapan Formation) at the top of the profile which are classified as lignites (random reflectance values are 0.37 and 0.36 R<sub>r</sub> (%), respectively; see Table 1).

#### 4.2. Variations of soluble organic matter (SOM) yield of the coals

The amount of soluble organic matter (SOM) normalized to the organic carbon content (mg/g TOC) obtained from the coal samples

**Table 1**  
Coal samples, formations, coal seams, huminite reflectance Rr (%), carbon isotopic composition of organic matter TOC (‰), total organic carbon (wt%, daf), soluble organic matter (SOM) related to the organic carbon content (mg/g TOC), as well as relative proportions of saturated hydrocarbons (wt%), aromatic hydrocarbons (wt%), esters/ketones (wt%), NSO compounds (wt%), and asphaltenes (wt%).

Samples	Formation	Coal seams	Rank Rr (%)	$\delta_{13}C_{org}$ TOC (‰)	TOC (wt%, daf)	SOM yield (mg/g TOC)	Saturated HC (wt%)	Aromatic HC (wt%)	Esters/Ketones (wt%)	NSO (wt%)	Asphaltenes (wt%)
KTD-41	Balikpapan	22	0.37	-28.0	47.4	38.06	9.2	7.5	12.2	19.1	52.0
KTD-42	Balikpapan	21	0.36	-27.9	68.8	20.55	4.1	8.2	22.9	31.1	33.7
KTD-36	Balikpapan	18	0.48	-28.0	71.3	13.99	5.2	10.2	20.6	28.2	35.8
KTD-35	Balikpapan	17	0.43	-27.6	70.1	35.79	4.4	11.3	13.1	24.9	46.4
KTD-43	Balikpapan	12	0.43	-27.3	75.9	25.58	9.7	8.4	12.2	29.7	40.1
KTD-40	Balikpapan	10	0.47	-27.4	74.5	19.87	2.3	6.1	10.8	12.3	68.5
KTD-39	Balikpapan	9	0.42	-27.5	78.5	45.80	6.6	8.6	19.4	24.8	40.1
KTD-38	Pulau Balang	8	0.47	-27.9	70.2	46.64	6.4	11.2	9.4	14.0	59.0
KTD-37	Pulau Balang	7	0.50	-27.0	78.2	28.07	4.7	13.8	10.2	19.3	51.9

by Soxhlet extraction with DCM is listed in Table 1 and the vertical profile variations are shown in Fig. 2 together with the relative proportions of saturated hydrocarbons, aromatic hydrocarbons, ester/ketones, hetero compounds (NSO) and asphaltenes obtained from hydrocarbon group separation of the SOM by column chromatography. The variation of the SOM yield along the stratigraphic column varies irregularly and shows no trend with increasing rank of the coals. The SOM yields in coal samples vary from 13.99 to 46.64 mg/g TOC. The highest yield has been obtained from the coal sample of seam 8 (Pulau Balang Formation).

The proportions of saturated hydrocarbon fractions vary from 2.3 to 9.7% and the aromatic hydrocarbon fractions between 6.1 and 13.8%. In general, the aromatic hydrocarbon fractions predominate over saturated hydrocarbon fractions with two exceptions; in sample KTD-41 from coal seams 22 and in sample KTD-43 from coal seam 12 the proportion of saturated hydrocarbons predominates over the proportion of aromatic hydrocarbons. The sum of saturated and aromatic hydrocarbons does not exceed 13.8% for all coal samples which is in accordance with the low rank of the samples.

In most of the samples from Embalut, Kutai Basin, East Kalimantan the proportion of aromatic hydrocarbons predominates over the proportion of saturated hydrocarbons. The opposite is observed in almost all lignites from Central Europe investigated previously (Bechtel et al., 2001, 2002a, b). However, organic geochemical investigations on peat samples from Palangkaraya (Central Kalimantan) also revealed a predominance of aromatic hydrocarbon fractions over saturated hydrocarbon fractions (Dehmer, 1993). The dominance of aromatic hydrocarbons over saturated hydrocarbons in the peat samples has been explained by the relative high abundance of sclerotinite (inertinite) and fungal hyphae (plectenchym) (Dehmer, 1993). Another set of coal samples from the Kutai Basin (Anugerah Bara Kaltim) was also enriched in aromatic hydrocarbons and at the same time in inertinite. The high inertinite content of the coals argues for dry periods during peat accumulation resulting in lower proportions of saturated hydrocarbons relative to aromatic hydrocarbons. Moreover, the dominance of *Dipterocarpaceae* in the coal forming vegetation might result in increasing proportions of aromatic hydrocarbons in solvent extracts.

#### 4.3. Composition of the aromatic hydrocarbon fractions in the coal extracts

Two representative examples of total ion current chromatograms (GC-MS) of aromatic hydrocarbon fractions from samples KTD-43 (seam 12) and KTD-35 (seam 17) are shown in Fig. 3. In Table 2 peak assignments for unambiguously identified biomarkers (I–XVIII) in the aromatic hydrocarbon fractions of the coal samples are listed. In the chromatograms three groups of compounds are identified: one group represents derivatives of naphthalene including some sesquiterpenoids, one group are phenanthrene derivatives (diterpenoids) and the third group are pentacyclic compounds with the carbon skeleton of picene (triterpenoids).

Within the group of naphthalene derivatives including sesquiterpenoids the following compounds have been identified (Fig. 3): 2,2,7,8-tetramethyl-1,2,3,4-tetrahydronaphthalene (I), 1,1,5,6-tetramethyl-1,2,3,4-tetrahydronaphthalene (II), 1,2,7-trimethylnaphthalene (III), 1,2,5-trimethylnaphthalene (IV), 5,6,7,8-tetrahydrocadalene (V), norcadalene (VI), calamenene (VII), and cadalene (VIII) based on mass spectral data and retention times published previously (Anders et al., 1973; Simoneit and Mazurek (1982); Püttmann and Villar, 1987; Killips, 1991; Singh et al., 1994). Within the group of phenanthrene derivatives, simonellite (IX) and retene (X) were identified in some of the coal samples based on mass spectral data and GC retention behaviour provided by Bendoraitis (1974), Simoneit and Mazurek (1982) and Philp (1985).

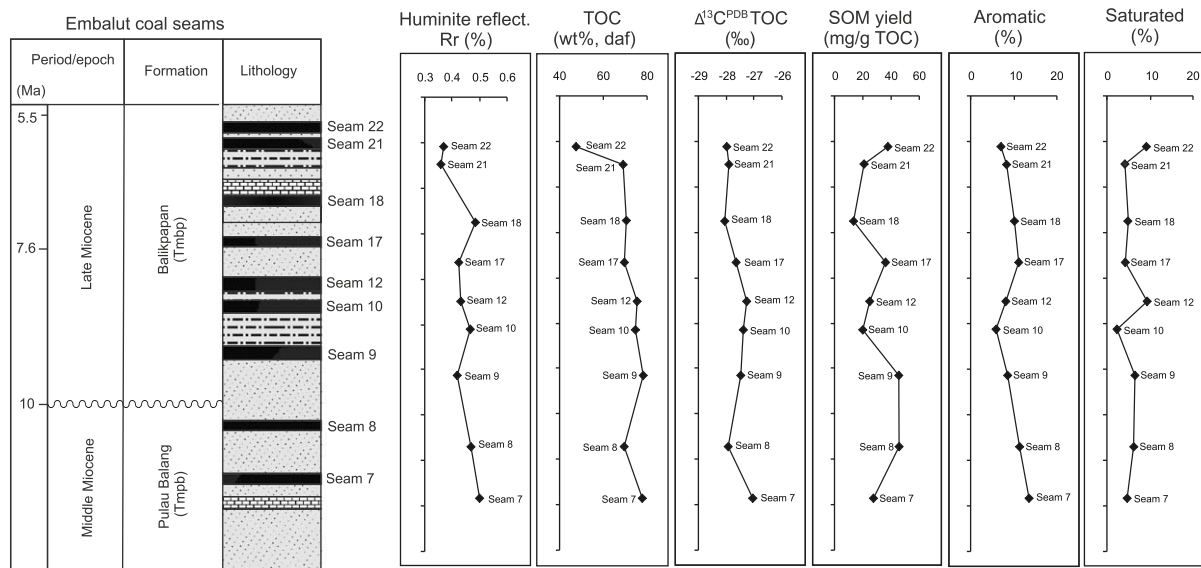


Fig. 2. Lithological profile of Embalut coal seams succession and vertical variation of huminite reflectance, total organic carbon (wt%, daf), stable carbon isotope (‰), SOM yields (mg/g TOC), aromatic hydrocarbon (%) and saturated hydrocarbon (%) (Fig. is not to scale).

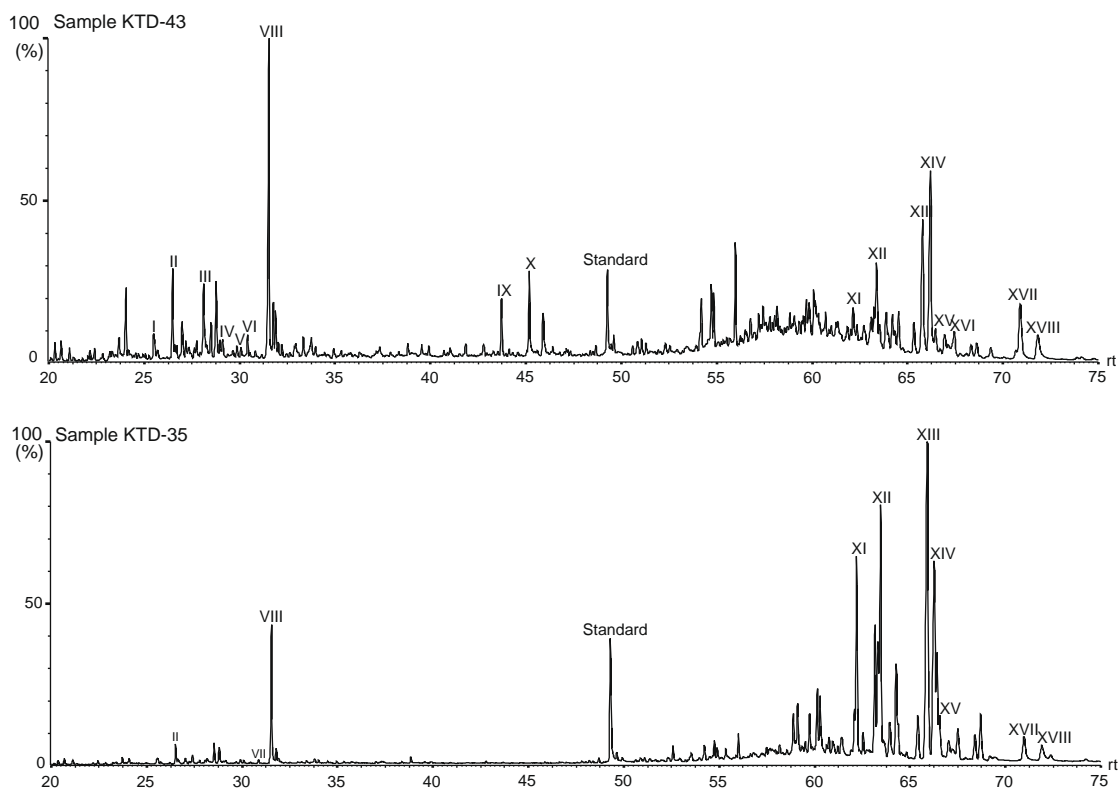


Fig. 3. Two examples of gas chromatograms of aromatic fractions from Embalut coal seam 12 (sample KTD-43) and seam 17 (sample KTD-35).

Various picene derivatives have been detected in the coal samples. These are composed of ring-A-monoaromatic triterpenoids (XI) and (XII), 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydronicene (XIII), 1,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydronicene (XIV), 1,2-dimethyl-1,2,3,4-tetrahydronicene (XV), 2,2-dimethyl-1,2,3,4-tetrahydronicene (XVI), 1,2,9-trimethyl-1,2,3,4-tetrahydronicene (XVII), and 2,2,9-trimethyl-1,2,3,4-tetrahydronicene (XVIII) based on mass spectral data and retention times published by Spycerelle (1975), Wakeham et al. (1980a,b), Philp (1985), Hazai et al. (1986), Chaffee and Fookes (1988), and Dehmer (1988).

#### 4.3.1. Concentration and vertical variation of naphthalene derivatives

The concentration variation of naphthalene derivatives are shown in Table 3. Compound 2,2,7,8-tetramethyl-1,2,3,4-tetrahydronaphthalene (I) has been found in seams 21, 12, 9, 8 and 7 with the highest concentration in the seam 12 (22.17  $\mu\text{g/g}$  TOC) from the Balikpapan Formation. Along the seam profile no systematic variation can be observed (Table 3). The concentration of 1,1,5,6-tetramethyl-1,2,3,4-tetrahydronaphthalene (II) decreases in the Balikpapan Formation successively from the upper seam (seam 22) to the seams 21 and 18, increases from seam 17 to the seam

**Table 2**

Peaks assignment for biomarkers in the aromatic hydrocarbon fractions of the Embalut coal samples.

Peaks	Compounds	M.Wt.	Base peak
I	2,2,7,8-tetramethyl-1,2,3,4-tetrahydronaphthalene	188	132
II	1,1,5,6-tetramethyl-1,2,3,4-tetrahydronaphthalene	188	173
III	1,2,7-trimethylnaphthalene	170	155
IV	1,2,5-trimethylnaphthalene	170	155
V	5,6,7,8-tetrahydrocadalene	202	187
VI	1,6-dimethyl-3-ethylnaphthalene (norcadalene)	184	169
VII	Calamenene	202	159
VIII	Cadalene	198	183
IX	Simonellite	252	237
X	Retene	234	219
XI	Ring-A-monoaromatic triterpenoid (1)	376	145
XII	Ring-A-monoaromatic triterpenoid (2)	378	145
XIII	2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydricene	342	342
XIV	1,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydricene	342	342
XV	1,2-dimethyl-1,2,3,4-tetrahydricene	310	295
XVI	2,2-dimethyl-1,2,3,4-tetrahydricene	310	254
XVII	1,2,9-trimethyl-1,2,3,4-tetrahydricene	324	324
XVIII	2,2,9-trimethyl-1,2,3,4-tetrahydricene	324	324

12, but is missing in seam 10 (Table 3). In the lower section of the coal profile, concentrations of (II) increase from seam 9 over seam 8 to seam 7. The highest concentration is found in the sample from seam 7 from Pulau Balang Formation at the bottom of the profile (Table 3). A tendency of concentration variations of compound (II) in the profile cannot be observed. The compound 1,2,7-trimethylnaphthalene (III) shows no systematic variation along the profile and the maximum concentration is also found in the seam 12 (52.22 µg/g TOC). 1,2,5-Trimethylnaphthalene (IV) is found only in three seams (seams 21, 22 from Balikpapan Formation and seam 8 Pulau Balang Formation), the maximum concentration is found in the sample from seam 8 (12.91 µg/g TOC). The concentration of compound 5,6,7,8-tetrahydrocadalene (V) shows a decrease on the top of the Balikpapan Formation (seams 22, 21, and 18 Table 3). The highest concentration of this compound is found again in the sample from seam 8 (57.94 µg/g TOC) from Pulau Balang Formation. 1,6-Dimethyl-3-ethylnaphthalene (VI) also has no systematic variation with the maximum concentration in the sample from seam 8 (58.87 µg/g TOC). The concentration of calamenene (VII) is relatively low in the coal samples. The maximum concentration has been found in the seam 10 (43.98 µg/g TOC) of the Balikpapan Formation. The highest concentration of all naphthalene derivatives was observed for cadalene (VIII) with particular high concentrations in the upper (seams 22 and 21) and middle part of the profile (seam 12) from Balikpapan Formation and with the maximum concentration of 267.37 µg/g TOC in seam 8 from Pulau Balang Formation (see Table 3 and Fig. 4).

The origin of the naphthalenes can be attributed to at least two different sources. The higher alkylated naphthalenes (15 carbon atoms) have been reported to occur in many sediments, coals and crude oils in the fully aromatized form as cadalene (e.g. Bendoraitis, 1974; Baset et al., 1980; Simoneit and Mazurek, 1982; Noble et al., 1991; van Aarssen et al., 1992; Curiale et al., 1994, 2005; Singh et al., 1994; Stankiewicz et al., 1996; Kalkreuth et al., 1998; Stefanova et al., 2002, 2005; Sun et al., 2002; Bechtel et al., 2004, 2007b) and were suggested to originate from sesquiterpenoids such as naturally occurring cadinanes or cadinols as possible precursors (Simoneit et al., 1986). The partially aromatized form of cadalene such as calamenene and 5,6,7,8-tetrahydrocadalene were often identified in geological samples containing cadalene at the same time (Simoneit et al., 1986). According to Dev (1989) the main sources for these sesquiterpenoids are *Compositae*, *Dipterocarpaceae* and *Myrtaceae* all belonging to the angiosperm plant family

and additionally *Cupressaceae* belonging to the gymnosperm plant family. van Aarssen et al. (1990, 1994) have shown that the so-called dammar resin from *Dipterocarpaceae* is composed of a polycadinene biopolymer which upon diagenesis and catagenesis will be degraded to monomers such as cadalene and cadinane. In pyrolysis products of a fossil Miocene resin from Kalimantan, cadinanes and bicadinanes were associated with abundant triterpenoids which were partly composed of the amyryn type skeleton (van Aarssen et al., 1990). Noble et al. (1991) investigated Talang Akar coals and shales offshore from northwest Java, Indonesia and detected aromatic compounds with angiosperm affinities including cadalene and 1,2,7-trimethylnaphthalene (1,2,7-TMN). All of these molecular features strongly indicate a significant correlation between the occurrence of cadalene and angiosperm (flowering plant) input to coals and sediments from southeast Asia.

However, the widespread occurrence of cadalene in Tertiary coal basins from Central Europe (Bechtel et al., 2002a, 2004, 2007b; Stefanova et al., 2002, 2005) has to be attributed to the high abundance of *Cupressaceae* and possibly at minor extent to further conifer species (Otto and Wilde, 2001). The occurrence of *Dipterocarpaceae* as possible bioproducers of cadalene and related compounds can be ruled out for central Europe, since *Dipterocarpaceae* were not contributing to the coal forming vegetation in this area. On the other hand, in the Tertiary flora of southeast Asia, *Cupressaceae* and further conifers did not play an important role during the whole Tertiary. During the Miocene the vegetation of the Kutai Basin was dominated by *Dipterocarpaceae* (Prasad, 1993; Appanah and Turnbull, 1998). Prasad (1993) concluded that many taxa such as members of the *Dipterocarpaceae* and *Fabaceae*, which were found during the Paleogene in southeast Asia were also present in the Neogene on the Indian subcontinent. Angiosperms are also the dominant plants in Tertiary coals and recent ombrogenous peats from the Malay-Indonesian area (Anderson and Muller, 1975; Morley, 1981; Demchuck and Moore, 1993; Amijaya et al., 2006). However, in Holocene peat deposits from northwest Kalimantan some conifer pollen grains (*Dacrydium* and *Podocarpus*) and *Burseraceae* pollen grains in clay layers underlying a peat deposit were also found in low abundance (Anderson and Muller, 1975).

The co-occurrence of cadinanes and bicadinanes was suggested to be a good argument for the origin of the cadinanes from *Dipterocarpaceae* (van Aarssen et al., 1992). However, the aromatic hydrocarbon fractions of the coal extracts from the Kutai basin investigated here do not contain aromatic bicadinanes. This is consistent with the observation of van Aarssen et al. (1990), who found bicadinane type structures not in solvent extracts and only in pyrolysis products of the Miocene outcrop resin from Kalimantan.

A second precursor of naphthalenes in the geological record is β-amyryn from angiosperms which upon aromatization and C-ring cleavage yields trimethylnaphthalenes (1,2,5- and 1,2,7-trimethylnaphthalene) associated with 2,2,7,8-tetramethyl-1,2,3,4-tetrahydronaphthalene. The related degradation pathway has been described in detail by Püttmann and Villar (1987) and was confirmed by several other studies (Strachan et al., 1988; Murray et al., 1997). Particularly, for 1,2,7-trimethylnaphthalene (III) the origin from β-amyryn is rather exclusive whereas for 1,2,5-trimethylnaphthalene (IV) further possible precursor molecules can be postulated.

All aromatic sesquiterpenoids listed in Table 3 can therefore be related to an origin from angiosperms according to the degradation pathway proposed by Villar et al. (1988), with the exception of one compound: 1,1,5,6-tetramethyl-1,2,3,4-tetrahydronaphthalene (II). This compound was first detected in Green River shale by Anders et al. (1973) and was suggested to be a diagenetic product of polycyclic lipids. Radke et al. (1986) also found the compound accompanied by 1,2,5-trimethylnaphthalene (IV) in the aromatic hydrocarbon fractions of a type III kerogen containing rock sample with a relation to non-specified resinous source material.

**Table 3**  
Concentrations of individual aromatic hydrocarbons in the coal seams from Embalut mine ( $\mu\text{g/g}$  TOC).

Peak	Compounds	Concentration of aromatic compounds ( $\mu\text{g/g}$ TOC)										Total content ( $\mu\text{g/g}$ TOC)
		Balikpapan formation					Pulau Balang form					
		Seam 22	Seam 21	Seam 18	Seam 17	Seam 12	Seam 10	Seam 9	Seam 8	Seam 7		
I	2,2,7,8-TeM-1,2,3,4-TeHN	-	10.88	-	-	22.17	-	-	14.10	18.75	74.86	
II	1,1,5,6-TeM-1,2,3,4-TeHN	23.23	17.23	4.02	10.60	58.42	-	-	47.47	66.21	256.19	
III	1,2,7-TMN	10.63	22.68	-	3.57	52.22	7.25	-	45.31	12.38	165.09	
IV	1,2,5-TMN	-	6.18	-	-	6.35	-	-	12.91	-	25.44	
V	5,6,7,8-Tetrahydrocadalene	20.92	15.87	2.99	6.93	12.33	26.06	-	57.94	1.43	151.57	
VI	1,6-DM-3-ethylnaphthalene	28.19	34.92	7.47	9.11	45.12	-	-	58.87	7.28	208.64	
VII	Calamene	4.47	6.47	0.67	18.93	5.27	43.98	-	8.22	-	87.98	
VIII	Cadalene	179.24	173.32	49.91	61.11	201.15	34.92	-	267.37	139.95	1199.2	
IX	Simonellite	2.11	1.07	0.55	-	33.59	0.69	-	2.78	12.26	55.36	
X	Retene	-	-	-	-	59.76	3.18	-	-	19.00	138.84	
XI	MATTP (1)	26.52	13.22	20.54	132.76	15.86	28.30	-	25.23	7.40	269.83	
XII	MATTP (2)	30.20	65.68	14.80	137.56	71.77	47.40	-	69.62	100.95	557.01	
XIII	2,2,4a,9-TeM-1,2,3,4,4a,5,6,14b-OHP	198.20	236.08	175.29	266.20	119.37	32.23	-	87.12	70.49	826.84	
XIV	1,2,4a,9-TeM-1,2,3,4,4a,5,6,14b-OHP	107.94	159.84	90.66	162.97	199.89	8.70	-	20.86	68.63	850.70	
XV	1,2,3,4-TeH-1,2-TeHP	55.00	-	24.74	23.79	23.86	5.24	-	8.05	21.23	173.96	
XVI	2,2-DM-1,2,3,4-TeHP	12.16	16.46	-	-	-	1.67	-	-	18.88	49.17	
XVII	1,2,9-TM-1,2,3,4-TeHP	38.45	26.90	25.67	29.71	80.73	6.88	-	14.85	70.69	309.61	
XVIII	2,2,9-TM-1,2,3,4-TeHP	43.32	39.50	18.23	23.12	48.74	7.57	-	11.16	66.68	277.87	

#### 4.3.2. Concentration and vertical variation of phenanthrene derivatives

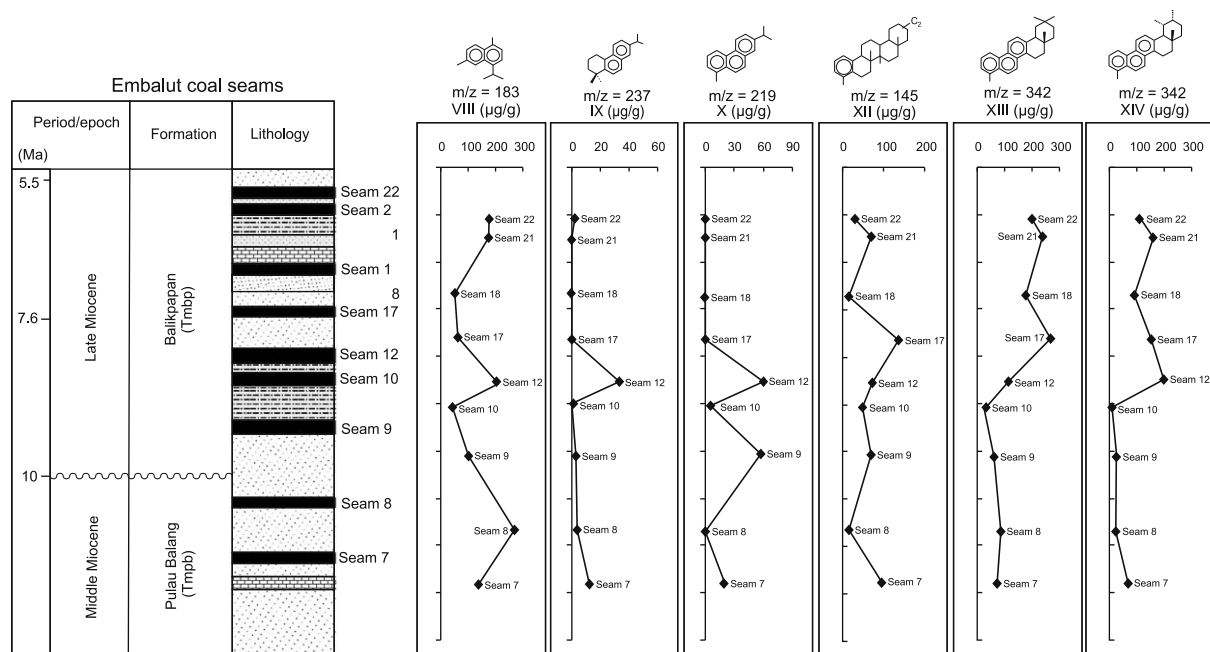
The contribution of phenanthrene derivatives to the aromatic hydrocarbon fractions is low overall. Only simonellite (IX) and retene (X) were detected in three coal samples at concentrations above  $0.5 \mu\text{g/g}$  TOC. Simonellite (IX) is present in the coal seams 7 ( $12.26 \mu\text{g/g}$  TOC), 8 ( $2.78 \mu\text{g/g}$  TOC), 9 ( $2.31 \mu\text{g/g}$  TOC), 10 ( $0.69 \mu\text{g/g}$  TOC), 12 ( $33.59 \mu\text{g/g}$  TOC), 18 ( $0.55 \mu\text{g/g}$  TOC), 21 ( $1.07 \mu\text{g/g}$  TOC), and 22 ( $2.11 \mu\text{g/g}$  TOC). Retene (X) is only detectable in the seams 7 ( $19.00 \mu\text{g/g}$  TOC), 9 ( $56.90 \mu\text{g/g}$  TOC), 10 ( $3.18 \mu\text{g/g}$  TOC), and 12 ( $59.76 \mu\text{g/g}$  TOC) (see Table 3, Figs. 3 and 4).

There is no systematic vertical variation of phenanthrene derivatives in the profile from the upper seam to the bottom seam but phenanthrene derivative are preferentially present in the lower part of the profile (in the seams 12 and 9 from Balikpapan and seams 8 and 7 from Pulau Balang Formation), whereas in the upper part of the profile, the compounds are detectable in trace amounts.

Phenanthrene derivatives such as simonellite (IX) and retene (X) are diagenetic compounds from diterpenoids present in higher plant resins, mostly gymnosperms (Simoneit et al., 1986; Chaffee et al., 1986; Killips et al., 1995; Otto et al., 2005; Stefanova et al., 2005; Bechtel et al., 2007b). The presence of these phenanthrene derivatives in a few of the coal samples can be suggests that gymnosperms contributed to the coal swamp vegetation in low proportions only in some coal seams from the Middle and from the beginning of Late Miocene (seams 12, 10, 9, 8 and 7). Further upwards in the profile (Late Miocene) the compounds are only detectable in trace amounts (seams 22, 21 and 18). Anggayana (1996) also identified some phenanthrene derivatives (diterpenoids) in the alkane fractions from some Miocene coal deposits in Sumatra and East Kalimantan, Indonesia, suggesting that apart from the dominating angiosperms, also material from gymnosperm (conifer) contributed to the coal formation. This is consistent with findings of Morley (1981), who studied the development and vegetation dynamics of lowland ombrogenous peat swamp in the Palangkaraya, Central Kalimantan, Indonesia by means of palynological methods using material from sediment cores. The deeper peat was built up from a forest dominated by *Dacrydium* sp. (conifer) and *Combretocarpus rotundatus* (angiosperm). Caratini and Tissot, 1988 also observed *Dacrydium* pollen in their palynological study of Quaternary and Late Pliocene sediments and coals in the MISEDOR core from the Mahakam Delta, Indonesia. These palynological studies confirm that conifers were present in low abundance in Kalimantan from the Miocene over Pliocene to present day.

#### 4.3.3. Concentration and vertical variation of picene derivatives

Several picene derivatives (non-hopanoid triterpenoids) were found in the aromatic hydrocarbon fractions of the coal sample (see Table 3): aromatic ursanes, aromatic oleananes, ring-A-monoaromatic triterpenoid (XI) and ring-A-monoaromatic triterpenoid (XII), 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydricene (XIII) and 1,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydricene (XIV), 1,2,3,4-tetrahydro-1,2-dimethylpicene (XV), 2,2-dimethyl-1,2,3,4-tetrahydricene (XVI), 1,2,9-trimethyl-1,2,3,4-tetrahydricene (XVII) and 2,2,9-trimethyl-1,2,3,4-tetrahydricene (XVIII). The concentration of aromatic picene derivatives (non-hopanoid triterpenoids) are shown in Table 3. The concentrations of ring-A-monoaromatic triterpenoids XI and XII vary from 7.4 to  $132.76 \mu\text{g/g}$  TOC and from 14.8 to  $137.56 \mu\text{g/g}$  TOC, respectively. The maximum concentration of compounds XI and XII ( $132.76$  and  $137.56 \mu\text{g/g}$  TOC) was found in the Balikpapan Formation (coal seam 17) (see Table 3 and also Fig. 4 for compound I). The compounds 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydricene (XIII) and 1,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydricene (XIV) were the dominant triaromatic com-



**Fig. 4.** Lithological profile of Embalut coal seams and vertical variation of concentrations of some aromatic hydrocarbons ( $\mu\text{g/g}$  TOC) detected in the aromatic hydrocarbon fractions (VIII = cadalene, IX = simonellite and X = retene, XII = ring-A-monoaromatic triterpenoid (2), XIII = 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydricene, XIV = 1,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydricene) (Fig. is not to scale).

pounds in all samples and the concentrations range from 32.23 to 266.20  $\mu\text{g/g}$  TOC (compound XIII) and 8.70 to 199.89  $\mu\text{g/g}$  TOC (compound XIV) (see Table 3 and Fig. 4). The tetraaromatic pines 1,2-dimethyl-1,2,3,4-tetrahydricene (XV) and 2,2-dimethyl-1,2,3,4-tetrahydricene (XVI) tend to be also enriched in the bottom and top of the profile with lower concentrations in the Balikpapan Formation (the concentrations vary from 5.24 to 55  $\mu\text{g/g}$  TOC for compound XV and 1.67 to 18.88  $\mu\text{g/g}$  TOC for compound XVI) (Table 3). The maximum concentration (55  $\mu\text{g/g}$  TOC) of compound 1,2-dimethyl-1,2,3,4-tetrahydricene (XV) was detected in the seam 22 (Balikpapan Formation) and for compound 2,2-dimethyl-1,2,3,4-tetrahydricene (XVI) in seam 7 (18.88  $\mu\text{g/g}$  TOC, Pulau Balang Formation). The concentrations of the tetraaromatic compounds 1,2,9-trimethyl-1,2,3,4-tetrahydricene (XVII) and 2,2,9-trimethyl-1,2,3,4-tetrahydricene (XVIII) are largely parallel along the profile of coal seams (see Table 3). Compounds XVII and XVIII show highly variable concentrations from 6.88 to 80.73  $\mu\text{g/g}$  TOC and 7.57 to 66.68  $\mu\text{g/g}$  TOC.

These pincene derivatives dominate by far among the pentacyclic compounds in the aromatic hydrocarbon fractions of the coals from Embalut. The compounds belong to both the oleanane and ursane type and are present mostly in the form of alkylated-tetrahydro- (XV, XVI, XVII, XVIII) and octahydricenes (XIII, XIV) as shown in Table 3. Aromatic hydrocarbons with hopanoid skeletons are only present in trace amounts. The pincene derivatives originate from both  $\alpha$ - and  $\beta$ -amyrins. Concentrations of  $\alpha$ -amyrin derivatives predominate over  $\beta$ -amyrin derivatives in most of the coal samples (Table 3). Dehmer (1993) also detected polyaromatic triterpenoids such as 1,2-dimethyl-1,2,3,4-tetrahydro-pincene (XV), 2,2-dimethyl-1,2,3,4-tetrahydricene (XVI), 1,2,9-trimethyl-1,2,3,4-tetrahydricene (XVII) and 2,2,9-trimethyl-1,2,3,4-tetrahydricene (XVIII) in the peat samples from Palangkaraya (Central Kalimantan). Some of these aromatic derivatives of  $\alpha$ - and  $\beta$ -amyrin were also present in the extracts of coals from Australian Late Oligocene to Early Miocene coal (Chaffee and Johns, 1983) and German Miocene brown coals (Dehmer, 1988). Stout (1992) identified pincene derivatives in the Tertiary angiospermous Brandon lignite (southeast USA). The occurrence of pincene derivatives already in re-

cent sediments and in peat suggests that aromatisation of  $\beta$ -amyrin may be mediated by microbial activity or clay catalytic processes during early diagenesis (Wakeham et al., 1980b; Dehmer 1988).

Based on Karsten et al. (1962) and Brackman et al. (1984) all known triterpenoid resins originate from angiosperms, such as *Dipterocarpaceae* of the southeast Asian forests and the Mediterranean *Pistacia lenticus* (*Anacardiaceae*). However, the resin bearing angiosperms predominate in the tropics (Taylor et al., 1998; Langenheim, 2003). van Aarssen et al. (1990) investigated commercially available dammar resins from *Dipterocarpaceae* (species unknown) and found that the amyrins were associated by a polycadinene resin which upon heating yields monomeric, dimeric and trimeric cadinenes. Dammar resins are well known for their protective properties against insects and fungi (Langenheim, 2003). The most prominent resin producing genera of *Dipterocarpaceae* is *Shorea*, a plant typically found in modern ombrogenous tropical lowland peat swamps of Indonesia, especially Sumatra and Kalimantan (Anderson and Muller, 1975; Morley, 1981; Demchuck and Moore, 1993). However, in resins from 35 species of the genus *Shorea*, only sesquiterpenoids, pentacyclic triterpenoids and derivatives of dammarene but no cadalenes have been detected (Bisset et al., 1971). Also in later studies the identification of cadalenes in *Shorea* failed (Kolhe et al., 1982). One explanation for the absence of cadinene derivatives in extant *Shorea* might be the missing of monomers in the polycadinane biopolymer. Alternatively, the genus *Shorea* might not contain the polycadinane biopolymer. This has to be clarified in further studies.

#### 4.4. Carbon isotopes of organic matter

The  $\delta^{13}\text{C}$  values of the Embalut coal vary in a narrow range from  $-27.0\text{‰}$  to  $-28.0\text{‰}$  (Table 1) and the vertical variation of the values is shown in Fig. 2. Based on stable carbon isotope analyses, coal samples (seams 7, 9, 10, and 12) that contain aromatic diterpenoids provide heavier isotopic values compared with the other coal samples (see profile in Fig. 2). Previous studies have shown that  $\delta^{13}\text{C}$  values of coals and fossil wood are strongly depending on the proportion of angiosperms versus gymnosperms in the coal

forming swamp (Bechtel et al., 2001, 2003, 2007a). A valuable parameter to assess the proportion of angiosperms versus gymnosperms in peat and coal vegetation swamp is the ratio of diterpenoids versus diterpenoids + triterpenoids (di-/(di- + triterpenoids)). The positive relationship between this ratio and the  $\delta^{13}\text{C}$  values indicates the major influence of variable contributions of angiosperms to the coal formation on the carbon isotopic composition of the coals (Bechtel et al., 2002b). A significant influence of gymnosperms on the carbon isotopic composition of the Embalut coal samples is shown in Fig. 5. Although the ratios of di-/(di- + triterpenoids) in the Embalut coal samples do not exceed values of 0.1 the influence of the gymnosperms on the  $\delta^{13}\text{C}$  values is high as reflected by a shift of almost 1.0‰ to heavier values. Miocene lignites from Zillingdorf (Austria) which are almost entirely composed of gymnosperms (conifers) provide  $\delta^{13}\text{C}$  values of organic matter in the range from  $-24\text{‰}$  to  $-25\text{‰}$  (Bechtel et al., 2007a) and with increasing proportions of angiosperms the values decrease to  $-27\text{‰}$  even when the ratio of di-/(di- + triterpenoids) was still as high as about 0.5, indicating a still significant contribution of gymnosperms.

Murray et al. (1998) investigated carbon isotopic ratios of fresh resins and fossil resins from various places of the world. Extant resins of gymnosperm (conifer) trees were collected from Australia, New Zealand and Brunei (Kalimantan) and extant resins of angiosperms were collected from various *Dipterocarpaceae* (*Shorea* sp., *Drybanolops* sp., *Vatica* sp.) in Temburong, Brunei. The investigated fossil resins were mainly of Tertiary age with only two samples from Cretaceous and one Holocene sample. The  $\delta^{13}\text{C}$  values of the extant gymnosperm resins provided mean values of  $-25.8\text{‰}$  and the angiosperm resins provided mean values of  $-31.0\text{‰}$  (resulting in a difference of  $5.2\text{‰}$  between both species on average). The  $\delta^{13}\text{C}$  values of the fossil gymnosperms were  $-22.8\text{‰}$  and the values for the fossil angiosperms were  $-27.3\text{‰}$  (resulting in a difference of  $4.5\text{‰}$  between these species). The difference in the  $\delta^{13}\text{C}$  values between the angiosperms and gymnosperms is similar comparing the fossil and the recent species, but the extant resins are in case of angiosperms on average  $3\text{‰}$  and in case of gymnosperms  $2.7\text{‰}$  lighter than the fossil resins. The reason for this difference might be a change in the isotopic composition and partial pressure of atmospheric  $\text{CO}_2$  and/or ecological stress and reduced canopy effect for trees more prone to fossilization (Murray et al., 1998).

Bechtel et al. (2007a) found that in a Miocene fossil wood from Austria (Zillingdorf) the remnants of angiosperms differed by  $2.6\text{‰}$  on average from the gymnosperm remnants. Lücke et al. (1999) determined the carbon isotopic composition of fossil wood pieces from the Lower Rhine Embayment and found a difference of  $2.8\text{‰}$  between gymnosperms and angiosperms. These differences

are lower than those observed by Murray et al. (1998) on fossil resins from angiosperms and gymnosperms ( $\Delta\delta^{13}\text{C} = 4.5$ ) but in the same range as those differences measured by Stuiver and Branzunias (1987) in the case of modern conifer and angiosperm carbon ( $\Delta\delta^{13}\text{C} = 3.0$ ).

In Fig. 6 the results obtained from the carbon isotope determination ( $\delta^{13}\text{C}$ ) in the Embalut coals are plotted versus the di-/(di- + triterpenoid) ratio and compared with results obtained from previous studies of lignites in central Europe.

Bechtel et al. (2007a) determined the  $\delta^{13}\text{C}$  values and the di-/(di- + triterpenoid) ratios of the coals from the Upper Miocene Zillingdorf lignite deposits (Austria). The  $\delta^{13}\text{C}$  values vary from  $-24.6\text{‰}$  to  $-27.2\text{‰}$  and the di-/(di- + triterpenoid) ratios vary from 0.46 to 0.96. In this case the positive correlation between the parameters provides evidence that the carbon isotopic composition is controlled by the peat forming vegetation (gymnosperm/angiosperm ratio), but samples with very high proportions of angiosperms are not available from this deposit. In another study of Bechtel et al. (2003) both parameters have been determined in the Miocene Hausruck lignite deposits of Lukasberg and Kalletsberg from the Alpine Foreland Basin, Austria.  $\delta^{13}\text{C}$  measurements provided values ranging from  $-24.9\text{‰}$  to  $-27.4\text{‰}$  and di-/(di- + triterpenoid) ratios ranging from 0.10 to 0.77. In these lignites the proportion of angiosperms is higher than in the Zillingdorf lignites as reflected by lower di-/(di- + triterpenoid) ratios but values below 0.10 were missing. In the correlation diagram (Fig. 6) the data points obtained from the Embalut coal extend the tendency observed in case of the lignites from the Miocene coals from Austria. When lignites and coals are exclusively composed of angiosperm remnants the  $\delta^{13}\text{C}$  values of the bulk material can be expected to be around  $-28.0\text{‰}$ .

#### 4.5. Paleoclimate in the Mahakam Delta during the Miocene

Fig. 7 shows the concentration ratio of di-/(di- + triterpenoids) along the profile of Miocene Embalut coals and the paleotemperature development during the Miocene in Asia as proposed by Jablonski (2005). According to the results of biomarker analyses the concentration ratios of di-/(di- + triterpenoids) in the extracts of coals from the Middle Miocene and from the beginning of the Late Miocene are higher compared to the ratio obtained from coal seams of the upper part of the profile representing the Late Miocene sequence. The biomarker composition suggests that the proportion of conifers in the coal samples are higher in the lower part of the profile (Middle Miocene to the beginning of Late Miocene, coal seams 7, 8, 9, 10 and 12) compared to the upper part of the profile (latter part of Late Miocene, coal seams 22, 21, 18

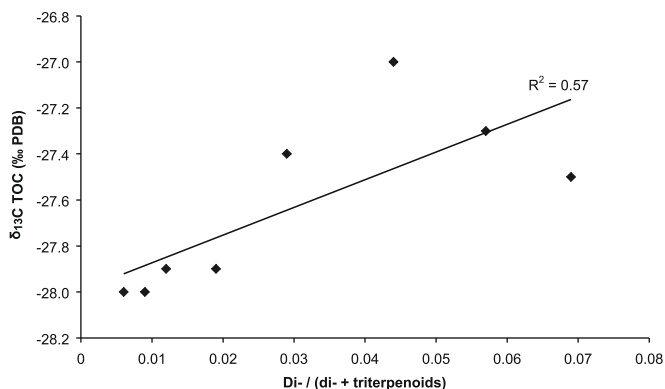


Fig. 5. Cross correlation between the di-/(di- + triterpenoids) ratio and the carbon isotopic composition of the Miocene coal seams (Embalut, East Kalimantan, Indonesia).

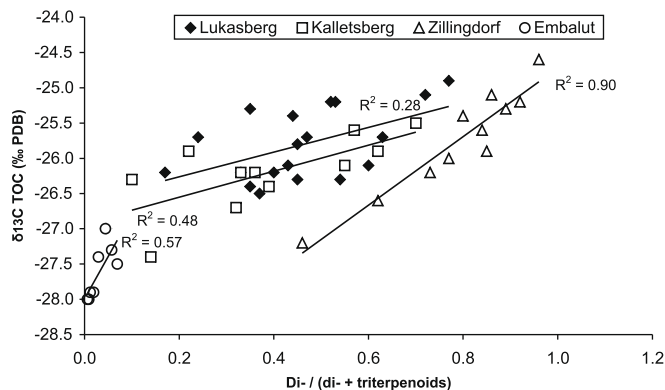


Fig. 6. Cross correlation between the di-/(di- + triterpenoid) ratio and the carbon isotopic composition of the Miocene coals from Embalut compared with the Miocene Zillingdorf lignite from Austria (Bechtel et al., 2007a); Lukasberg and Kalletsberg from the Alpine foreland Basin, Austria (Bechtel et al., 2003).

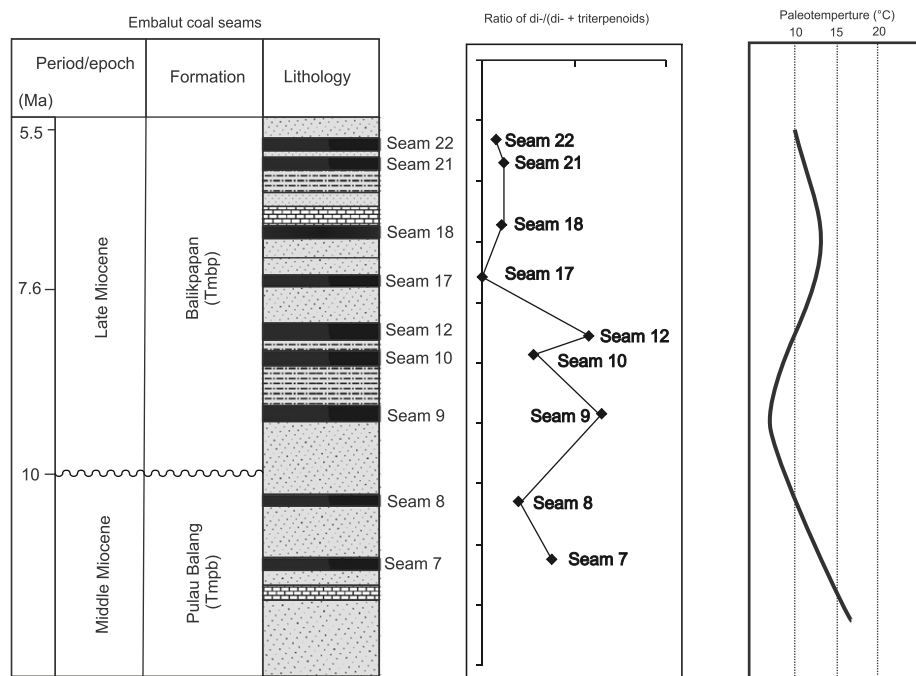


Fig. 7. Distribution of the di-/(di- + triterpenoids) ratio of the profile of Miocene Embalut coal seams (East Kalimantan, Indonesia) and the climatic conditions during peat formation in the Miocene (modified from Jablonski, 2005).

and 17) as shown in Fig. 7. This is consistent with the paleotemperature curve proposed by Jablonski (2005) for Asia, since lower temperatures at the beginning of Late Miocene are reflected by higher proportions of conifers in the coal forming vegetation.

However, these results are not fully consistent with palynological results of Morley (2000), who proposed the widespread expansion of more moist climates and in the expansion of rain forests across most of the Mahakam Delta region during the latter part of the Early and Middle Miocene. According to this study, the climate in the Mahakam Delta was drier (cooler) at the end of the Late Miocene supported more open savanna vegetation replacing the rain forests vegetation. This is reflected by the increasing proportion of *Gramineae* pollen in the Late Miocene sediment compared to the Early and Middle Miocene sediments. Conifer (montane vegetation) appears again in the Pliocene (Morley, 2000).

According to Morley (2000), the climate of southeast Asia in the Late Oligocene to earliest Miocene was cooler than the present day climate. Therefore, the presence of conifers at that time is favourable but only for the montane forests with altitudes between 1000 and 2000 m, whereas *Dipterocarpaceae* dominated in the lowland (altitude <1000 m) in southeast Asia (Morley, 2000). Moreover, the paleoclimate of southeast Asia was moister during the Middle Miocene, since the expansion of rain forests widespread in most areas.

Aston (1982) detected *Dipterocarpaceae* pollen in high proportions in southeast Asian Late Oligocene (30–25 Ma) and earliest Miocene sediments. At that time the parent plants are thought to have been important elements of strongly monsoonal vegetation, with dipterocarps radiating in wet rain forests after 20 Ma. The radiation of *Dipterocarpaceae* in southeast Asia occurred after the opening of the Makassar Straits.

## 5. Conclusions

The study of the biomarker composition of coals from Embalut reveals a vertical variation of aromatic hydrocarbon fractions. Aromatic sesquiterpenoids such as cadalene, tetrahydrocadalene and calamenene were detected with cadalene being present in very high concentration in most of the samples. These compounds are

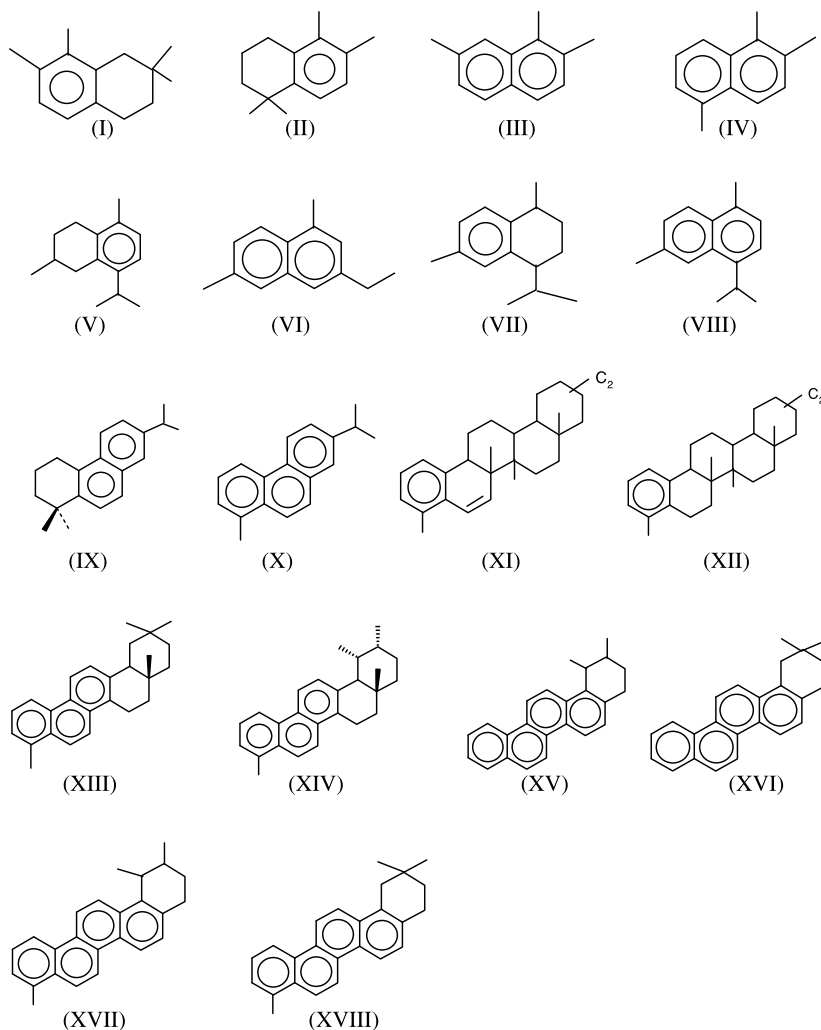
characteristic of angiosperms (mostly in angiosperm dammar resin). The angiosperm dammar resin can be attributed to the contribution of *Dipterocarpaceae*, a family plant typically found in modern ombrogenous tropical lowland peat swamps of Indonesia. Diterpenoids such as simonellite and retene were identified only in five of the nine coals samples. However the proportions were low. These compounds are considered to originate from gymnosperm (conifer) which contributed to the coal forming vegetation predominantly during the middle and at the beginning of the Late Miocene. Picene derivatives dominate by far among the pentacyclic compounds in the aromatic hydrocarbon fractions of the coal samples. Biomarkers in the aromatic fractions included polyaromatic triterpenoids derived from  $\alpha$ - and  $\beta$ -amyrin. Based on biomarker results in this study, Embalut coal seams were derived from angiosperm forests and mixed angiosperm-conifer forests (angiosperm dominant).

The results of stable carbon isotope investigations on organic matter ( $\delta^{13}\text{C}$ ) in the Embalut coals are consistent with their taxonomical classification as angiosperm derived ( $\delta^{13}\text{C}$  values between  $-27.0\text{‰}$  and  $-28.0\text{‰}$ ). The concentration ratios of di-/(di- + triterpenoids) in the extracts of coals from the Middle Miocene and the beginning of the Late Miocene are higher compared to the ratio obtained from coal seams of the upper part of the profile representing the Late Miocene sequence. The presence of conifer in the Embalut coal samples might be a result of cool climate during peat accumulation in the Kutai Basin.

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## Appendix A. Structures cited in the text



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