



# Climatic control on primary productivity changes during development of the Late Eocene Kiliran Jao lake, Central Sumatra Basin, Indonesia

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## ABSTRACT

A 102 m long core section of the late Eocene Kiliran Jao oil shale has been studied by means of palynofacies and inorganic geochemistry to examine the role of climate change on the development of the Kiliran Jao paleo-lake. Climate changes during deposition of the studied oil shale are interpreted from the abundance variation of fungal remains. Higher abundance of fungal remains in the middle part of the oil shale profile indicates relatively warmer climate during deposition. The warmer climate is thought to have led to changes in lake productivity. Carbon isotopic compositions of organic matter ( $\delta^{13}\text{C}$ ) range from  $-27.0$  to  $-30.5\%$ . These are generally more depleted in the middle part of the profile indicating lower primary productivity of the lake during deposition. *Botryococcus braunii* varies from 3 to 16% and is generally more abundant in the middle part of the profile. This is consistent with the less trophic preference of this algal blooming. The warmer climate is thought to have induced stratification, limiting the introduction of recycled nutrients to the epilimnion, thereby reducing the lake productivity.

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## 1. Introduction

The late Eocene Kiliran Jao oil shale is an immature organic-rich shale which was deposited in the Central Sumatra Basin. Sedimentological investigation revealed that the oil shale was deposited in lacustrine and anoxic environments (Sunardi, 2015). In a more regional framework, geochemical and palynological studies indicate that paleoclimate was responsible for the deposition of Paleogene source rocks in the Central Sumatra Basin (Cole and Crittenden, 1997; Rodriguez and Philp, 2012). The authors discussed that the tropical paleoclimate controlled the chemical stratification of the water column and thus bottom water anoxia of lakes in the basin. Although paleoclimate has been identified as the significant factor on source rocks deposition, a detailed discussion of the links between climate change and sediment deposition in Indonesian basins has been less reported previously.

In the present study, the depositional environment changes of Kiliran Jao oil shale are investigated using palynofacies and geochemical

analyses in order to characterize the organic matter and geochemical composition of the oil shale. Based on these results, an improved reconstruction of the climatic conditions governing the Kiliran Jao paleo-lake is provided.

## 2. Geological setting of the study area

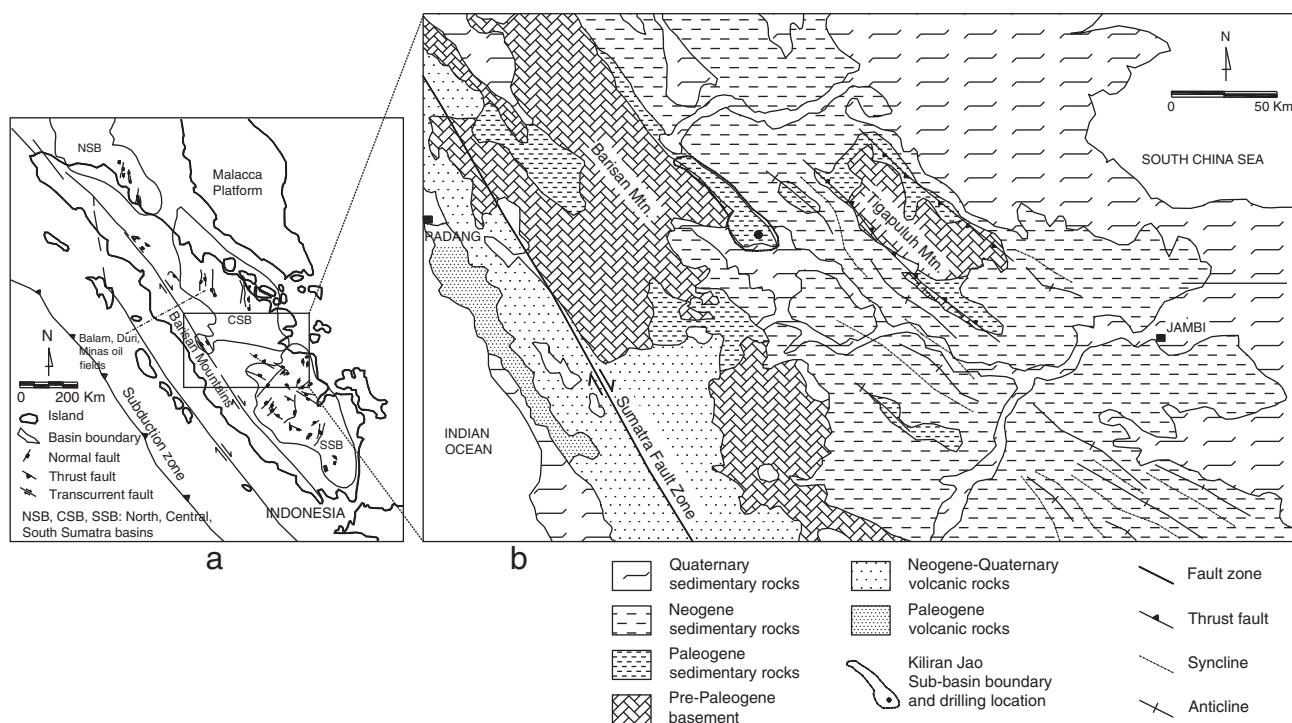
Three main basins developed in Sumatra during the Paleogene: the North, Central and South Sumatra Basins (NSB, CSB and SSB respectively) (Fig. 1a). The Central and South Sumatra Basins are considered as one large basin with many troughs and grabens, as they show similar and related geological histories (Crow and Barber, 2005; de Smet and Barber, 2005). The area of the present study is located in the Kiliran Jao Sub-basin, one of source rock depocenters at the transition of the Central and South Sumatra Basins (Fig. 1b). The Kiliran Jao Sub-basin is referred as part of the Central Sumatra Basin, since it shows analogous sediment successions (Sunardi, 2015).

### 2.1. Central Sumatra Basin

The geological setting and history of the Central Sumatra Basin have been described in detail by Crow and Barber (2005), Darman and Sidi (2000), de Smet and Barber (2005) and Doust and Noble (2008). This

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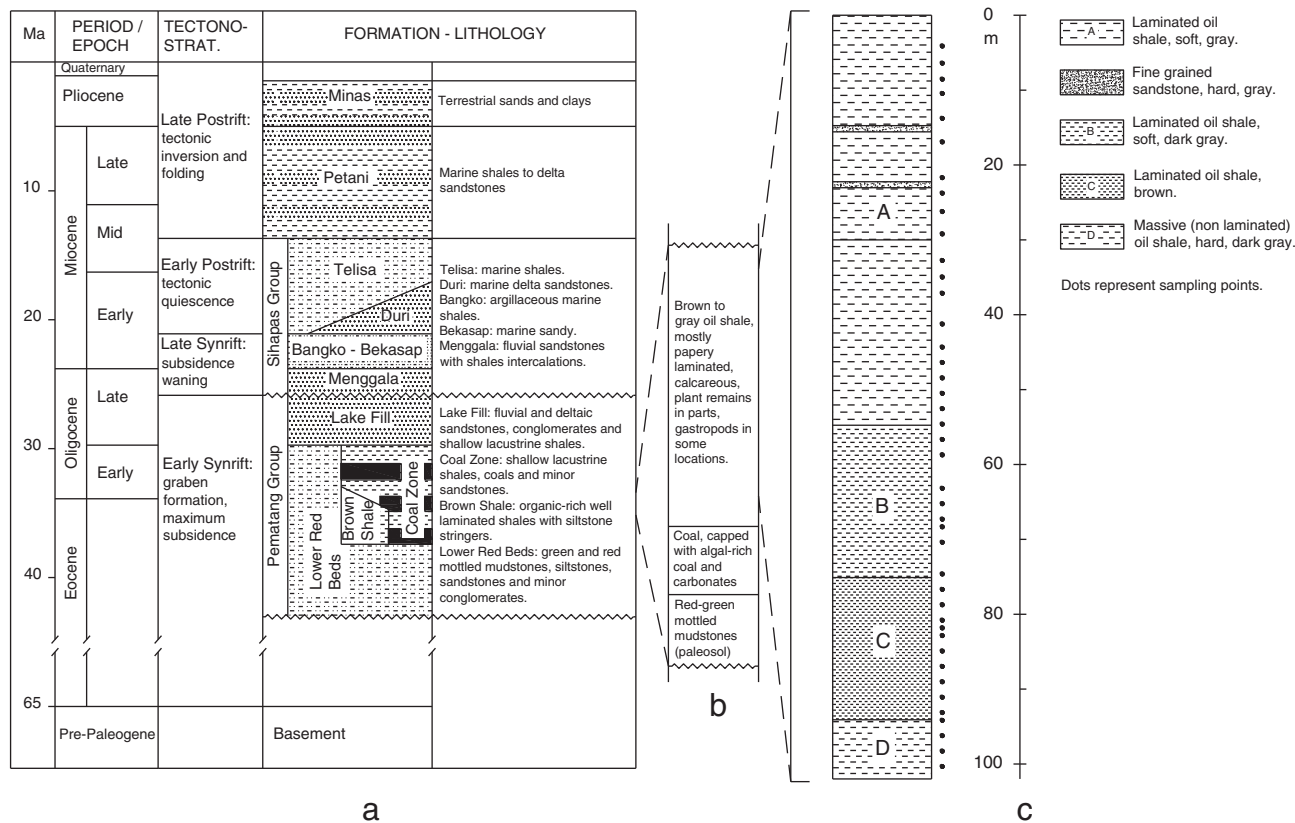
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**Fig. 1.** Map of Sumatra Basins with main graben structures (a), enlargement of the transition of Central and South Sumatra Basins showing the Kiliran Jao Sub-basin and drilling locations (b), modified after Darman and Sidi (2000).

basin is situated in a tectonically active region and originated as a result of the subduction of the Indian-Australian plate beneath the Eurasian plate. The basin development can be divided into four stages of

tectonostratigraphic evolution which were responsible for petroleum system formation (Fig. 2a): early synrift (late Eocene to Oligocene), late synrift (late Oligocene to early Miocene), early postrift (early to



**Fig. 2.** Generalized stratigraphic column of the Central Sumatra Basin (adopted from Doust and Noble, 2008; Williams and Eubank, 1995) (a) and Kiliran Jao Sub-basin (based on Iqbal et al., 2014; Sunardi, 2015; and the references therein) (b), and drill core profile of the oil shale in Kiliran Jao Sub-basin (c).

mid Miocene) and late postrift (mid Miocene to Quaternary) (Doust and Noble, 2008).

The early synrift phase corresponds to a period of rift graben formation and a maximum in subsidence rates. This rifting was triggered by an East-West extension during northward movement of both the Australian plate to the East and the Indian plate to the West. During this stage, the Pematang Group was deposited above the basement. The group consists of an association of alluvial, shallow to deep lacustrine and fluvio-deltaic facies represented by laminated shales, silts, sands with coals and conglomeratic intervals. The Brown Shale Formation (Fm) belongs to the Pematang Group and represents excellent petroleum source rocks in the basin. The late synrift phase corresponds to the period when subsidence rates slowed down. In this stage, sea level was starting to rise and influenced the deposition of the Sihapas Group. The Menggala Fm is still fluvial and overlain by shallow marine sandy (Bekasap Fm) and argillaceous (Bangko Fm) facies. The Menggala and Bekasap Fms represent excellent reservoirs, whereas the Bangko Fm is a regional seal. The early postrift phase corresponds to a period of tectonic quiescence. In this stage, marine transgression continued and then maximized forming distal marine facies of the Duri and Telisa Fms. The late postrift phase corresponds to a period of inversion and folding. In this stage, the Petani and Minas Fms which consist of regressive deltaic and alluvial sediments were deposited during a major falling of sea levels (de Smet and Barber, 2005; Doust and Noble, 2008).

## 2.2. Pematang group development

The tectonostratigraphy of the Pematang Group has been discussed by Darman and Sidi (2000), Doust and Noble (2008) and Williams and Eubank (1995). The Lower Red Beds Fm (Fig. 2a) was deposited during pre-graben stage, when the basin was undergoing initial rifting (late Eocene). It consists of gray, green and red mottled mudstones, siltstones, sandstones and minor conglomerates deposited in alluvial-lacustrine settings. Shallow lacustrine or marsh/bog environments existed in the deepest basinal areas.

The Brown Shale Fm either conformably overlies the Lower Red Beds Fm, or forms in some parts a lateral equivalent to the Lower Red Beds Fm. The formation is composed of organic-rich well-laminated shales with siltstone stringers and deposition started during rapid rift development (early synrift) in deep and shallow lakes. Based on oxygen isotopic data, Williams and Eubank (1995) suggested that the Brown Shale Fm deposition ended with the Eocene-Oligocene global cooling. The Coal Zone Fm only occurs in a few sub-basins and consists of interbedded shallow lacustrine shales, coals and minor sandstones. This formation is laterally equivalent to the Brown Shale Fm and partly younger. In the Oligocene, a compressional phase led to uplift of the Lower Red Beds and Brown Shale Fms. During the Oligocene to early Miocene rapid deposition of the Lake Fill Fm occurred and was characterized by uplift and rapid erosion of highland areas. It comprises fluvial and deltaic sandstones, conglomerates and shallow lacustrine shales. The deposition of this formation ended with a major unconformity.

## 2.3. Geology of the Kiliran Jao Sub-basin

The Kiliran Jao Sub-basin is regarded as a small rift basin formed during the early synrift stage. The morphology of the sub-basin is uncertain, since it has been integrated into the Barisan compressional belt and is now fragmented and faulted on both flanks. The general sediment succession of the Kiliran Jao Sub-basin is presented in Fig. 2b based on Iqbal et al. (2014), Sunardi (2015) and the references therein. The pre-graben paleosol most probably corresponds to the Lower Red Beds Fm. It is composed of carbonaceous and gray mudstones with locally red and green mottles. Above the paleosol, coal beds varying from thin to 17.5 m thick were deposited in a slowly subsiding reed swamp. A more rapid subsidence rate later resulted in the deposition of algal-rich coal interbeds which pass laterally into freshwater carbonates. A

conformably lithofacies change occurred by the deposition of >90 m of thick brown to gray colored calcareous lacustrine shales. There is no exposure which corresponds to the Oligocene Lake Fill Fm and younger lithostratigraphical units in this area.

## 3. Methods and materials

Forty two samples were collected from a 102 m long drill core (representing about 90 m thick oil shale) available in the depository warehouse of the Center for Geological Resources (PSDG), Bandung, Indonesia. The drilling location is shown in Fig. 1b. The sampling points along the drill core are marked by dots in Fig. 2c. Plant remains are occasionally present in minor amount as woody organic detritus and leaves. The vertical section consists of fine-grained shales with the following variation of the physical characteristics:

- soft, gray and well-laminated oil shale in the upper part, thin fine sandstone intervals are present in the upper part (section A)
- soft, dark gray and well-laminated oil shale (section B)
- soft, brown and well-laminated oil shale (section C)
- hard, dark gray and non-laminated oil shale in the lowermost part (section D).

### 3.1. Palynofacies analysis

Palynological processing was carried out at the Natural History Museum of London, UK. The samples were treated with HCl (37%), and HF (40%) in alternating steps to remove carbonates and silicates, respectively, and, after washing to neutrality, sieved with a 15 µm mesh sieve. The slides were made with Elvacite polymer resin. Organic matter particles (minimum 300) were counted using a transmitted-light microscope (400× magnification) at constant-interval points following the method described by Tyson (1995). The slides are stored in the Laboratory of Mineralogy, Microscopy and Geochemistry, Institut Teknologi Bandung, Indonesia.

### 3.2. Geochemical analysis

Oil shale rock samples were first crushed, pulverized and sieved to obtain particle size <63 µm. Major and trace elements were analyzed by Actlabs, Ancaster, Canada. A 0.25 g sample was digested with four acids beginning with HF, followed by a mixture of HNO<sub>3</sub> and HClO<sub>4</sub>, heated using precise programmer controlled heating in several ramping and holding cycles until dryness and all volatile elements were released. The sample was then brought back into solution using HCl and HNO<sub>3</sub> and analyzed using a Perkin Elmer ELAN 9000 ICP-MS (inductively coupled plasma – mass spectrometry). Total organic carbon contents (TOC) and total sulfur (S) were analyzed using Euro EA (CAP 20) Elemental Analyzer. For TOC determination, pulverized samples were treated with HCl (10%) prior to the analysis to remove carbonates from the sample and then rinsed with distilled water until neutrality. The TOC values were then corrected to the original sample weight due to carbonate loss.

For analysis of carbon isotopic composition of bulk organic matter, the carbonate free samples were measured with an IsoPrime™ (GV Instruments, UK) continuous-flow isotope ratio mass spectrometer. Isotope ratios are given in δ-notation,  $\delta = (R_s / R_{st} - 1) \times 1000$ , with  $R_s$  and  $R_{st}$  as isotope ratios of sample and the standards VPDB. Analytical precision was 0.08‰.

## 4. Results

### 4.1. Organic matter composition

The palynofacies of the oil shale is dominated by amorphous organic matter (AOM), contributing about 76–96% of organic matter. The

structured organic matter account only in minor amount, consists of *Botryococcus braunii*, pollen, spores, phytoclasts and fungal palynomorphs. Fig. 3 shows the organic matter observed under the microscope. Palynofacies data is shown in Table 1 and Fig. 4.

#### 4.1.1. Amorphous organic matter

AOM is dominant, its structure generally can be recognized as fibrous and membraneous debris as shown in Fig. 3a. The structure supports a lacustrine depositional environment, as suggested by Batten (1983) that palynofacies dominated by fibrous and/or membraneous debris commonly originate from *Botryococcus braunii*, *Pediastrum* or other non-marine algae. Along the drill core profile, the proportion between amorphous and structured organic matter is shown in Fig. 4a. AOM is less abundant and decreases upwards in lower part of section A and section B, and is more abundant in the upper part of section A and section D. Higher amounts of AOM are observed in the section C.

#### 4.1.2. Structured organic matter

*Botryococcus braunii* shows thick botryal structure as it originated from a colony of thick-walled unicellular algae (Fig. 3b). It accounts for the most dominant palynomorph and varies from 3 to 16% with an average value of 8% (Table 1). The proportion of *Botryococcus braunii* is inversely correlated with that of AOM (Fig. 4b). Phytoclasts consist of cuticles and wood debris (Fig. 3c,d), varying from 0 to 3% (average 1%, not listed). Pollen accounts in minor amount and is mostly dominated by non-saccate taxa (Fig. 3c). The proportion of pollen ranges from ~0 to 6% averaging at 2% and shows moderately higher proportion in section D, lower in sections C and B, and generally increasing proportion upwards in section A (Fig. 4c). Bisaccate pollen are present only in a few samples with very low amount (<1%). Although some pollen grains smaller than 15  $\mu\text{m}$  might have been lost during sieving, the pollen abundance observed under the microscope is still representative for palynofacies study. Our data of higher plants-derived biomarkers such as des-A-ursane (not presented) and pollen show similar abundance variation along the sections. Spores are mostly observed as trilete

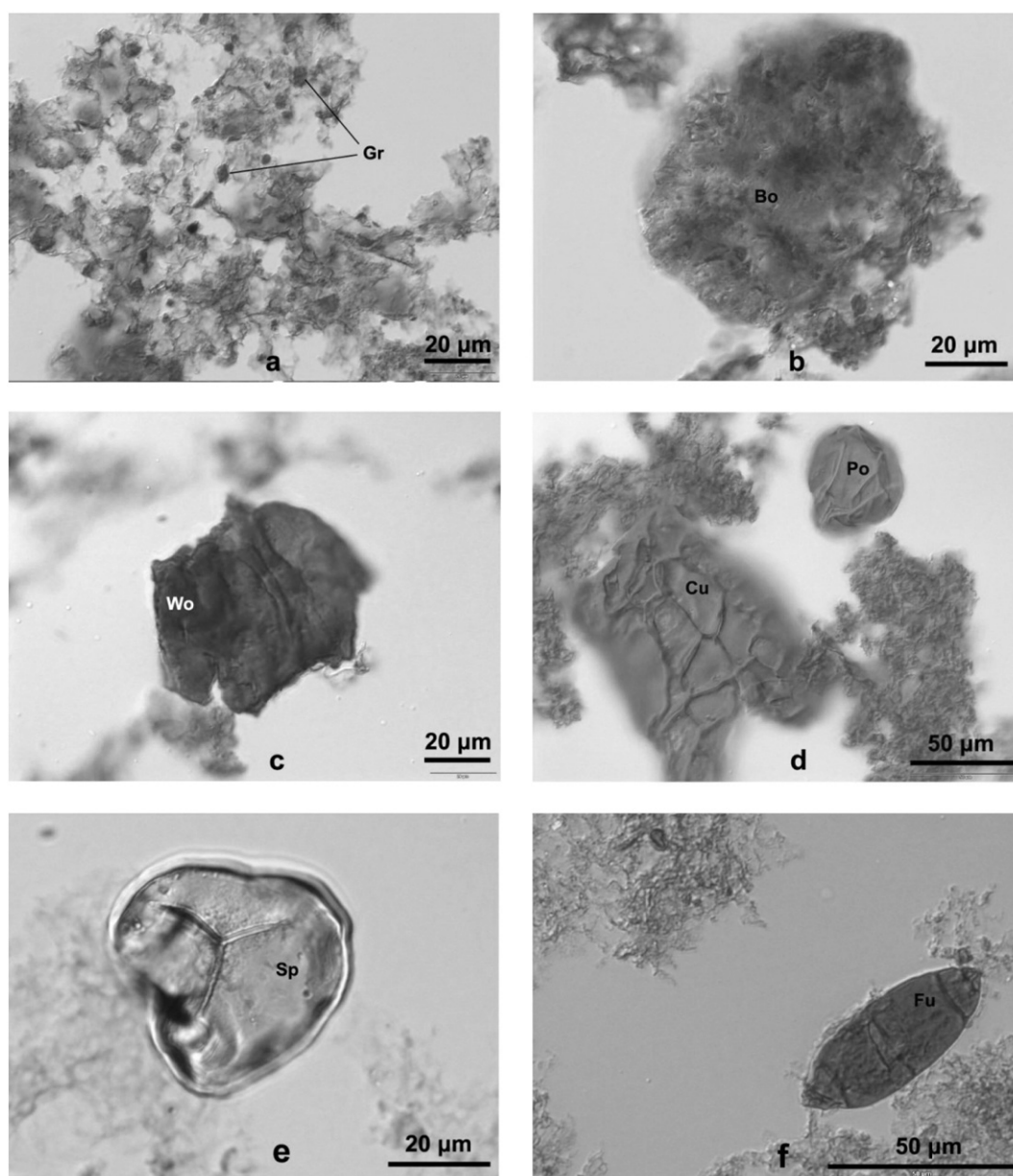


Fig. 3. Photomicrographs of the Kiliran Jao oil shale organic matter showing amorphous organic matter (AOM) dominated by fibrous and membraneous debris with granular features (Gr) (a), *Botryococcus braunii* (Bo) (b), wood debris (Wo) (c), cuticles (Cu) and pollen (Po) (d), trilete spore (Sp) (e) and fungal remains (Fu) (f).



**Table 1**

Sample data including sample depth and result of palynofacies and geochemical analyses.

Sample Nr.	Depth m	AOM % (vol.)	<i>B. braunii</i>	Pollen	Fungi	Al % (weight)	TOC	S	$\delta^{13}\text{C}$ ‰	U ppm	Mo
B3-01	4.0	89.3	4.3	5.0	0.0	5.34	3.19	0.69	−27.01	4.3	1.3
B3-03	6.1	89.0	7.0	3.0	0.0	6.08	3.73	0.52		4.0	1.5
B3-05	8.3	88.3	6.7	4.3	0.0	4.08	3.15	0.39	−27.96	3.2	1.8
B3-06	10.2	91.5	4.7	3.0	0.0	6.52	3.22	1.09	−28.36	4.5	1.8
B3-11	17.4	84.7	8.7	5.3	0.0	6.26	3.82	0.55	−28.18	3.8	1.2
B3-14	21.1	79.0	13.3	6.0	0.0	6.09	1.86	0.12	−27.53	3.8	0.2
B3-16	23.1	76.0	16.0	5.0	0.3	7.62	2.58	0.35	−28.93	4.0	0.7
B3-20	28.4	83.7	9.0	4.7	0.7	6.11	3.47	0.38	−27.55	3.8	1.3
B3-22	31.8	82.7	11.3	3.7	1.3	5.33	3.04	0.95	−27.42	4.0	1.9
B3-24	34.0	80.3	13.7	3.7	1.7	7.26	3.77	1.07	−29.51	4.8	1.8
B3-26	36.1	79.0	14.3	5.0	1.0	6.48	3.59	0.69	−30.54	3.6	1.7
B3-28	40.1	76.7	16.0	3.0	2.7	5.45	4.84	0.95	−28.15	3.9	2.1
B3-30	43.1	84.3	9.3	3.3	1.3	6.02	4.83	0.60	−29.05	3.8	1.8
B3-32	45.1	79.0	13.7	3.7	2.3	6.01	4.57	0.83	−28.94	4.1	2.1
B3-34	47.1	86.7	8.7	1.7	2.0	8.11	4.48	0.64	−29.53	4.4	1.9
B3-36	49.1	79.3	15.3	2.3	1.7	6.33	4.42	1.10	−29.32	3.7	1.6
B3-38	51.1	83.3	8.3	3.3	3.0	6.20	4.09	0.56	−28.72	4.1	1.8
B3-40	53.1	87.3	9.0	2.0	0.7	5.57	4.88	0.81	−28.51	3.5	1.5
B3-42	55.1	90.5	7.0	1.8	0.0	4.06	7.20	0.75	−27.03	3.8	2.2
B3-44	57.1	91.5	6.5	1.0	0.8	5.36	6.72	0.65		4.5	2.0
B3-50	63.1	91.0	7.5	1.3	0.0	3.71	8.71	1.29	−27.53	4.0	4.6
B3-52	65.1	87.7	9.0	1.7	1.0	4.13	4.76	0.66	−29.13	4.1	3.0
B3-54	67.1	88.3	9.7	0.7	1.0	5.62	6.83	1.02	−28.58	4.8	3.8
B3-55	68.1	88.0	8.7	0.7	1.3	4.05	7.54	1.08	−27.78	5.5	3.6
B3-57	70.1	89.1	7.9	1.7	0.7	5.58	6.13	1.38	−28.15	5.0	3.7
B3-62	75.1	94.3	3.8	1.0	0.8	4.25	7.85	1.39	−28.34	6.4	4.7
B3-64	77.1	94.3	4.3	0.8	0.5	5.00	10.25	1.34	−27.02	6.6	6.8
B3-66	79.1	96.0	3.0	0.3	0.5	4.01	9.87	1.82	−27.83	5.7	5.9
B3-68	81.1	92.5	5.3	1.3	0.5	4.60	12.45	1.51	−28.03	7.5	6.3
B3-70	83.1	93.5	5.3	0.8	0.0	3.90	10.59	1.76	−27.44	6.0	5.6
B3-72	85.1	95.0	4.0	1.0	0.0	3.78	8.31	1.67	−28.15	5.4	3.5
B3-74	87.1	93.3	6.0	0.8	0.0	3.73	9.06	1.47	−27.97	4.0	2.8
B3-76	89.1	94.0	5.3	0.8	0.0	3.87	10.00	1.64	−27.55	5.8	4.0
B3-78	91.1	94.0	4.3	0.8	0.0	3.78	7.85	1.77	−27.27	4.9	3.4
B3-80	93.1	93.3	4.7	1.0	0.0	3.55	7.45	1.74	−29.45	4.2	5.0
B3-81	94.1	91.3	7.4	1.3	0.0	3.69	6.55	1.42	−28.12	4.1	2.8
B3-83	96.1	87.7	8.7	2.0	0.0	4.58	5.05	2.04	−28.80	3.4	2.1
B3-85	98.1	90.7	5.3	0.3	0.3	4.55	6.37	1.23	−28.88	3.8	2.1
B3-87	100.1	88.7	7.0	2.0	0.3	6.54	4.40	0.89	−29.00	3.7	1.7

morphotypes (Fig. 3e), and represent a minor component in the oil shale (<1%, not listed). Fungi are present in most samples as hyphae, spores and fruiting bodies (Fig. 3f). The proportion of fungal remains ranges from 0 to 3% with an average value of 1%. It shows moderately higher abundances in section B and higher abundances in the lower part of section A (Fig. 4d).

*Botryococcus braunii* represents the only autochthonous organism which could be recognized as structured organic matter in the oil shale. *Botryococcus braunii* is a green colonial alga that is widely dispersed in temperate and tropical regions, and tolerant to seasonally cold climates. It lives in freshwater and brackish lakes, ponds and bogs (Metzger and Largeau, 2005). Pollen are mainly derived from angiosperms. The encountered fungi are mostly derived from saprotrophic soil organisms, which degrade dead plants or other fungi. The higher plants and fungal palynomorphs represent terrigenous organic matter input in the oil shale. As pollen originate from terrestrial plants, the generally upwards increase of pollen along the profile especially in section A might indicate a general shallowing upwards depositional environment of oil shale in the Kiliran Jao graben.

#### 4.2. Geochemical composition

Major elements of the oil shale detected from the ICP-MS analysis consist of Ca, Al and Fe, averaging at 9.8%, 5.2% and 4.19%, respectively. K, Mg and Na account only in minor amount (<1%). The high amount of Ca in the shale confirms that Paleogene source rocks in the most

depocenters of the basin are typically calcareous as previously reported by Iqbal et al. (2014), Sunardi (2015). The occurrence of carbonates in the lacustrine Kiliran Jao oil shale is interesting and will be discussed elsewhere. In the present study, the elements are limited to those strictly associated with terrigenous input such as Al, K, and Na, and autochthonous input such as TOC, S, U, and Mo.

Geochemical data are shown in Table 1 and Fig. 4, including abundances of Al, TOC, S, U and Mo, and carbon isotopic composition of bulk organic matter ( $\delta^{13}\text{C}$ ) along the drill core profile. The vertical variations of K and Na are similar to that of Al and not presented here. Vertical variations of the major element Al and the trace elements U and Mo exhibit two distinct patterns. Concentrations of Al generally increase upwards in the profile ranging from 3.6 to 8.1% with an average value of 5.2%. The Al concentrations are moderately higher in section D, lower in section C and increase subsequently in two steps at the beginning of deposition of sections B and A (Fig. 4e). TOC varies from 1.9 to 12.5% (average 5.9%) and generally decrease upwards (Fig. 4f). S percentages range from 0.1 to 2.0% averaging at 1.0% (Fig. 4g) with a comparable variation along the profile as observed for the TOC proportion. The  $\delta^{13}\text{C}$  values of bulk organic matter vary along the profile, ranging from −27.0 to −30.5‰ with an average value of −28.3‰ (Fig. 4h). The concentrations of U and Mo vary from 3.2 to 7.5 ppm (average 4.5 ppm) and from 0.2 to 6.8 ppm (average 2.7 ppm), respectively (Figs. 4i,j). The vertical concentration variations of U and Mo are also similar with those of TOC and S percentages along the profile.

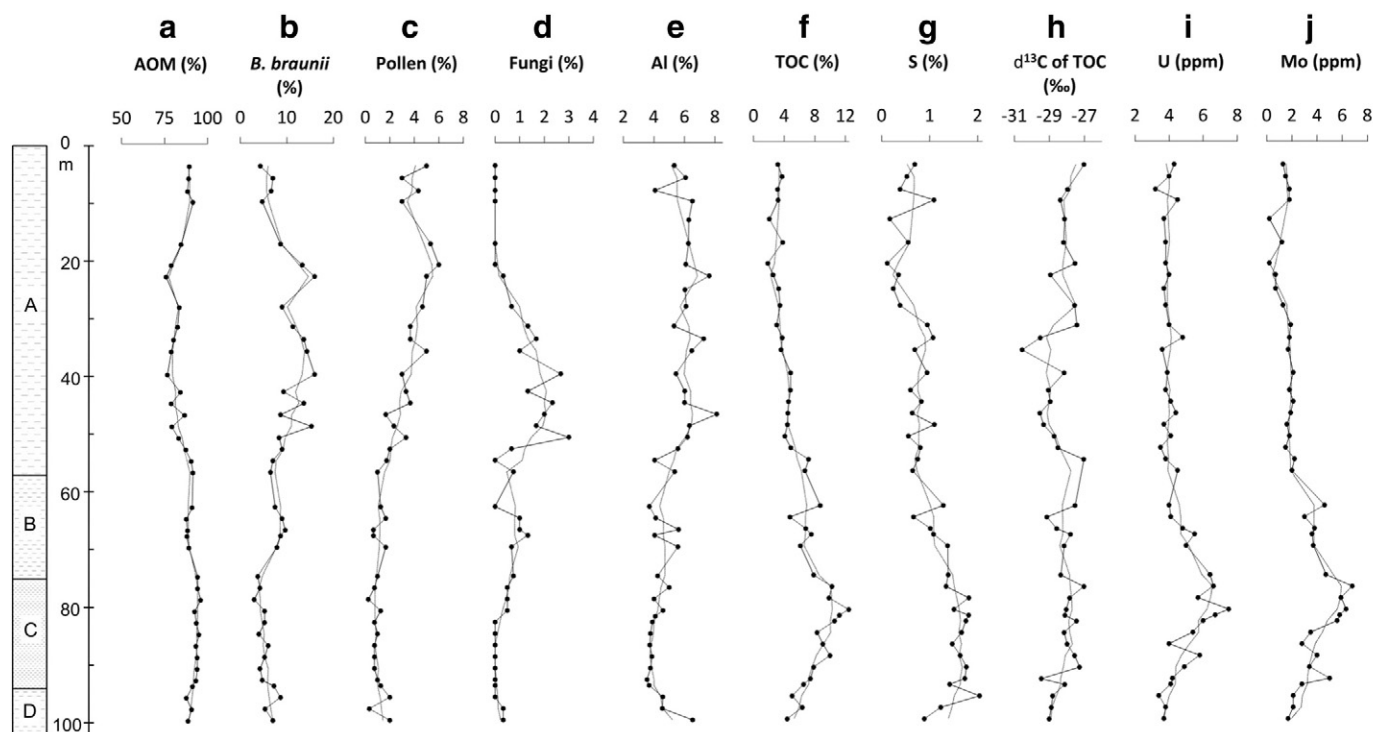


Fig. 4. Vertical profile of abundances of the oil shale organic matter components along the profile: AOM (a), *Botryococcus braunii* (b), pollen (c) and fungal remains (d); and element concentrations: Al (e), TOC (f), S (g),  $\delta^{13}\text{C}$  of bulk organic matter (h), U (i), Mo (j). Smoothed curves based on moving average calculation are superimposed in each figure.

## 5. Discussion

### 5.1. Variations of autochthonous and terrigenous contributions

The higher concentrations of aluminum (Al) in section A indicate that in this part the terrigenous input is higher than in the other parts. Al is well known to predominate in detrital material. Its presence in sediments has been used as a terrigenous proxy considering its immobility during diagenesis (Dypvik and Harris, 2001; Tribouillard et al., 2006). In section A pollen originating from terrestrial environment also show higher abundances and increase upwards successively, while in the lower sections pollen are generally less abundant, generally consistent with the Al concentration trend along the profile. Plot Al vs pollen results moderate positive correlation ( $r = 0.61$ ) as shown in Fig. 5a.

In contrast, the higher concentrations of TOC, S, U and Mo in the lower part of the profile especially in section C suggest a higher autochthonous input compared to the upper part of the profile. The co-occurrence of these elements usually indicates sedimentation of autochthonous material due to the presence of anoxic bottom water in both marine and lacustrine environments (Eusterhues et al., 2005; Tribouillard et al., 2006). In the presence of organic matter, anoxic conditions also promote reduction of sulfate into hydrogen sulfide which can react with reduced iron to form pyrite either in the bottom water or below the sediment-water interface (Bernier, 1984; Kasper et al., 2013). U and Mo are mobile in oxic water and immobile or precipitated in anoxic water (Eusterhues et al., 2005; Tribouillard et al., 2006). In addition, the presence of organic matter also accelerates the precipitation and accumulation of these trace elements in the sediment (McManus et al., 2006; Tribouillard et al., 2006) resulting in their co-variation. Moderate to strong positive correlations are indicated from plots of the elements, for example Mo vs TOC ( $r = 0.90$ ) as shown in Fig. 5b. Plot of Mo vs pollen results relatively strong negative correlation ( $r = -0.72$ , Fig. 5c), indicating contribution contrast between autochthonous and terrigenous inputs along the oil shale profile.

### 5.2. Variation of trophic level

The occurrence of *Botryococcus braunii* has been widely reported to be favoured by oligotrophic-mesotrophic conditions (Tyson, 1995). Hence, eutrophication does promote the demise of *Botryococcus braunii* (Smittenberg et al., 2005; Tyson, 1995; Xu and Jaffé, 2009). The disappearance of *Botryococcus braunii* in response to eutrophication has been related to the slow growth rate characteristic of this alga. With increasing availability of nutrients, *Botryococcus braunii* is outcompeted by faster-growing algae such as *Pediastrum* (Tyson, 1995), diatoms (Smittenberg et al., 2005) and freshwater dinoflagellates (Herrmann, 2010). Considering its trophic level dependence, variation of the abundance of *Botryococcus braunii* might therefore be used as a paleoenvironmental indicator for trophic level change, both anthropogenically or naturally-induced (Smittenberg et al., 2005).

*Botryococcus braunii*, together with *Pediastrum* and dinoflagellates, represent the main biological source material for petroleum generation in lacustrine basins throughout Southeast Asia especially in the Central Sumatra Basin (Sladen, 1997). Additionally, Cole and Crittenden (1997) and Williams and Eubank (1995) reported that Paleogene oil source rocks of Central Sumatra are characterized either by *Pediastrum*-dominated organic matter in sediments originating from shallower lake environments or by *Botryococcus braunii*-dominated organic matter in sediments originating from deeper lake environments.

In the studied oil shale section, the variation of *Botryococcus braunii* abundance (Fig. 4b) likely reflects trophic level changes during development of the former Kiliran Jao lake. Other algae which might take advantage from the trophic level change based on their ecological preferences could not be observed in palynological analysis since most phytoplankton has been degraded. However, the variation of  $\delta^{13}\text{C}$  along the oil shale profile is in agreement with that of the abundance variation of *Botryococcus braunii* with respect to the lake eutrophication development. The carbon isotopic composition of sedimentary organic matter has been used as an indicator to constrain primary productivity in lake systems (Heyng et al., 2014; Hodel and Schelske, 1998;

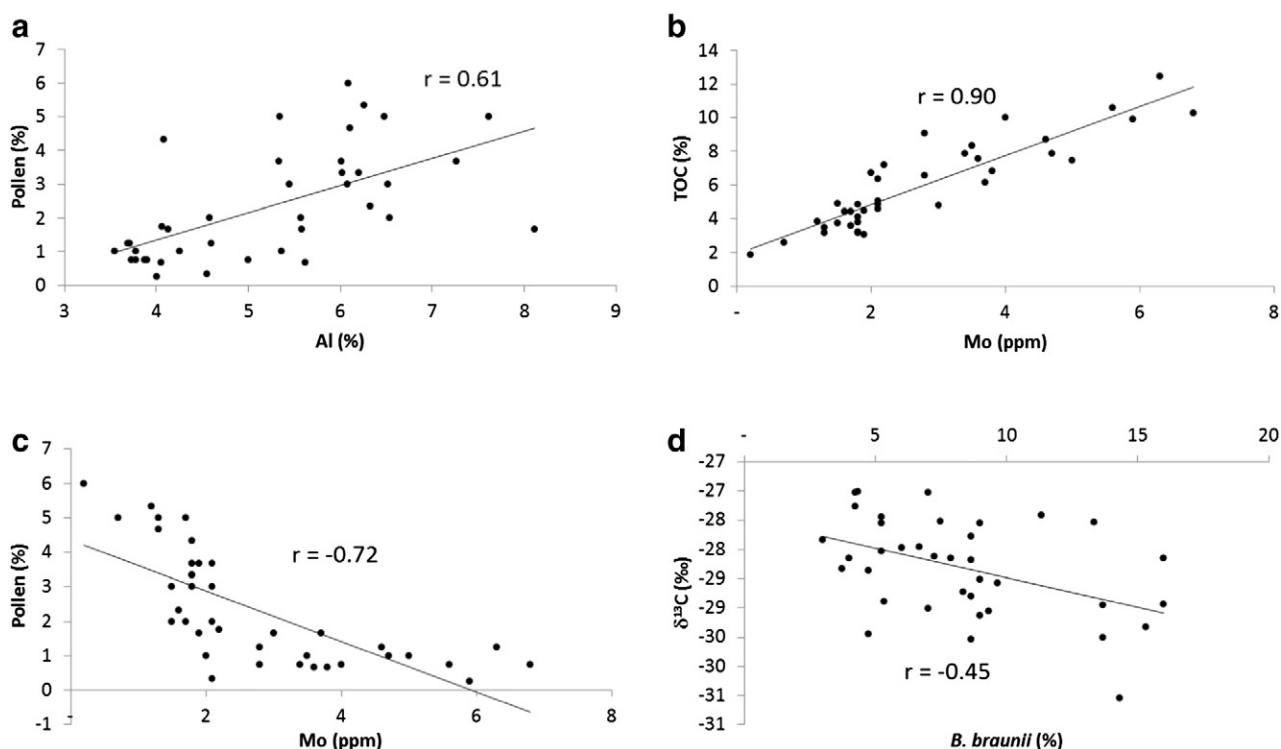


Fig. 5. Some plots of elements and palynomorphs abundances in the Kiliran Jao oil shale.

Meyers and Ishiwatari, 1993; O'Reilly et al., 2003). In lakes where primary productivity is the main control on carbon cycling, organic matter is progressively enriched in  $^{13}\text{C}$  with increasing productivity and vice versa. In the Kiliran Jao oil shale, the abundance of *Botryococcus braunii* (Fig. 4b) shows an opposite trend when compared with  $\delta^{13}\text{C}$  values of the organic matter (Fig. 4h). Their scatter plot indicates negative correlation ( $r = -0.45$ ) as presented in Fig. 5d. This confirms that lake trophic levels fluctuated during deposition of the oil shale and that the abundances of *Botryococcus braunii* can be used to infer trophic level changes. A sudden decrease of  $\delta^{13}\text{C}$  values of bulk organic matter and a rapid increase of *Botryococcus braunii* abundance are distinctly observed at the beginning of deposition of section A, indicating a decrease of trophic level. This sudden decrease cannot be attributed to the input of terrestrial organic matter which contributed to the oil shale in only small amounts.

Nutrients, particularly nitrate and phosphate, are the limiting factors controlling growth of aquatic plants in lakes (Nara et al., 2014; Seip, 1994). Nitrogen fixation occurs mainly due to soil microbes and the fixed nitrogen can be transferred into the lake by soil erosion from the surrounding land. Phosphates in lakes originate predominantly from weathering of continental rocks (Peters et al., 2005). The input of these external nutrients is therefore important to trigger eutrophication in lakes. However, external nutrients are only relevant in the initial stage of lacustrine systems to develop the nutrient pool (Katz, 2001). In most ancient lacustrine systems responsible for organic-rich sediment deposition, long-term availability of nutrients in the epilimnion appears to be maintained more by remineralization (decomposition) of organic matter in anoxic hypolimnion and water overturn. Once liberated, the nutrients are reintroduced into the epilimnion through partial or complete water overturn, which can either be continuous or seasonal (Katz, 2001; Lewis, 1987).

Bacterial processes, such as denitrification, control nutrients regeneration and mediate sulfate reduction and methanogenesis in the anoxic hypolimnion (Katz, 2001). In the Kiliran Jao paleo-lake, the availability of nutrients in the epilimnion was likely depending on remineralization of organic matter rather than on the additional input

of external nutrients. The presence of anoxic bottom water during deposition of the entire oil shale section enabled regeneration of nutrients and thus methanogenesis. The latter is evident by the occurrence of methanotrophic bacteria biomarkers in all studied samples. 30-Norneohop-13(18)-ene and neohop-13(18)-ene were identified in high amounts (not presented). Compound specific isotope analysis for carbon (CSIA) of the biomarkers revealed extreme  $\delta^{13}\text{C}$  depletion values from  $-45.2$  to  $-50.2$ ‰. Methanogenesis produces methane with extreme depleted carbon isotope composition ranging from  $-50$  to  $-60$ ‰ (e.g., Whiticar, 1999). Fixation of the methane by the methanotrophic bacteria results in a depletion of  $\delta^{13}\text{C}$  values of their biomass. The rapid decrease of the trophic level in the lower part of section A, therefore, should be related to a limitation of nutrient supply from the hypolimnion.

Increase of surface temperature is likely one of the possibilities controlling the marked decrease of trophic level in the former Kiliran Jao lake especially at the beginning of deposition of section A. O'Reilly et al. (2003) reported the successive decreases of aquatic productivity and  $\delta^{13}\text{C}$  of sedimentary organic matter since the mid 1900s in tropical Tanganyika lake, Africa. They concluded that the productivity decrease is the effect of the present global warming. The surface temperature increase of about  $0.5$  °C is decreasing aquatic productivity by about 20%. The increase of surface temperature is suggested to induce the thermal stratification establishment and oxycline shoaling of the lake, and thus limiting the nutrients supply from remineralization in the anoxic hypolimnion.

Data supporting the role of temperature changes during deposition of the Kiliran Jao oil shale include variation of fungal remains along the profile (Fig. 4d). The proportion of fungal remains develops differently from the terrigenous constituents such as pollen and Al abundances along the profile. The abundance of fungal remains generally changes concomitant with the abundance of *Botryococcus braunii*. Changes of diversity and relative abundance of fungal remains has been suggested to reflect changes in paleoclimate during deposition of Cenozoic sediments (Elsik, 1996; Staplin et al., 1976). The fungal remains are most diverse and abundant in sediments of the cyclic

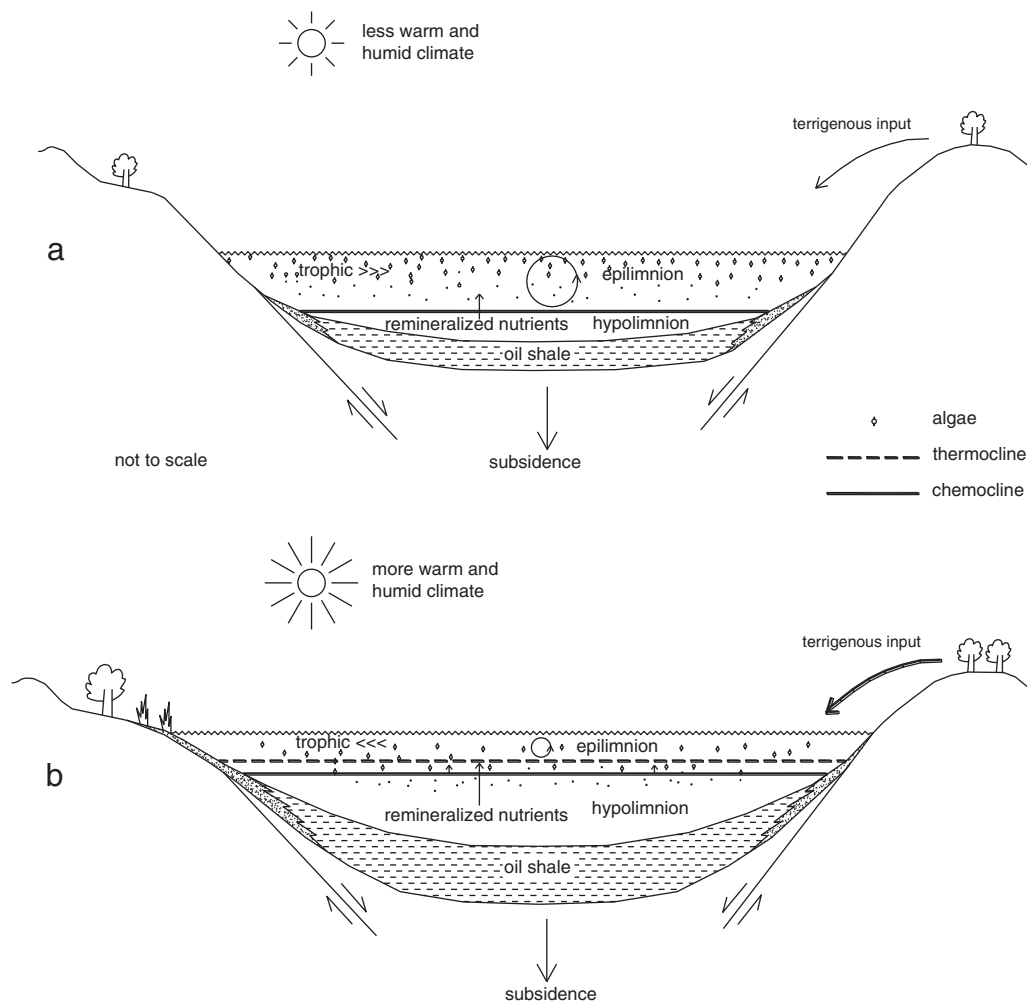
warm periods (Elsik, 1996). Additionally, the abundances of fungal remains in Paleogene–Neogene sediments have also been regarded to correspond with warm and humid climates during deposition (El Atfy et al., 2013; Du et al., 2012; Kalgutkar, 1997; Kar et al., 2010; Kumar, 1990). The variation of fungal remains in the oil shale profile might indicate relative changes of temperature or humidity during the oil shale deposition. The increasing abundance of fungal remains in the sediments reflects more humid climate and vice versa. Additionally, under the more humid climate during deposition of the lower part of section A and section B (Fig. 4d), thermal stratification might have developed, limiting the remineralized nutrients input to epilimnion and thus supporting the disappearance of faster-growing algae and stimulating *Botryococcus braunii* to grow. Fig. 6 shows the lake depositional environment model representing the depositions of section C when the climate was less warm and section B when the climate was relatively warmer.

### 5.3. Redox sensitive elements

Redox sensitive elements including U and Mo have been widely used for reconstruction of bottom water redox conditions of marine systems (Tribouillard et al., 2006). Eusterhues et al. (2005) assessed the utility of the redox sensitive elements in lake settings and found that most trace element-based redox indices failed to infer anoxicity of bottom water in Steisslingen lake (Germany). This was suggested to be due to the strong variability of the detrital input to this lake. However, they reported

parallel tendency of the variation of U and Mo concentrations in sediments as a result of changes in bottom water anoxicity. These elements are relatively more abundant in sediments deposited under anoxic (sulfidic) depositional environments and are less abundant in sediments from less anoxic (non-sulfidic) environments.

In the present case, U and Mo concentrations show a remarkable variation along the profile (Figs. 4i,j). The distinct concentration decrease of these elements from section B to A may lead to an interpretation of bottom water anoxicity decrease. However, the decrease of the trophic level at the beginning of deposition of section A requires stronger thermal stratification in the epilimnion and thus shoaling of the chemocline separating the anoxic hypolimnion from the oxic epilimnion. This implicates that U and Mo concentrations should not be used to infer anoxicity change during the deposition of these sections. It seems that the decrease of these elements concentrations rather relates to the lower primary productivity due to warmer climate. Lower amounts of organic matter sinking to hypolimnion would decrease acceleration of U and Mo precipitation. On the other hand, low productivity would also relatively increase the fraction of detrital/terrigenous material in the sediments resulting in the dilution of organic matter especially in the lower part of section A (Fig. 4f). Additionally, higher precipitation during warmer climate also will increase water supply and detrital flux to the lake. But the lake might have been deep enough and thermal stratification might have been sufficiently strong to prevent water body mixing. In the present study higher concentrations of U and Mo coincide with higher concentrations of organic matter



**Fig. 6.** Reconstructed aquatic systems and trophic levels during deposition of section C (a) and the lower part of section A (b). The presence of thermocline in (b) would limit the reintroduction of remineralized nutrients to epilimnion and thus decrease the primary productivity of the lake.



(Figs. 4f–j), and thus reflect the input of autochthonous material into the sediment.

## 6. Conclusions

Palynological and geochemical data show paleoenvironmental changes in the late Eocene Kiliran Jao lake as the result of climate change during the lake development. The higher abundance of fungal remains in the middle part of the profile (section B and lower part of section A) probably indicate relatively warmer climate during deposition. The warmer climate might promote thermocline establishment of the lake and thus limiting the supply of nutrients from hypolimnion. This would decrease the lake productivity in the epilimnion. The decrease of productivity is recognized by the higher abundance of *Botryococcus braunii* and relatively lower value of  $\delta^{13}\text{C}$  especially in oil shale samples from the lower part of section A.

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