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Chemostratigraphy and Paleoenvironment of the Miocene Organic Rich Sediments in the East Kutai Sub-Basin, Indonesia

Kemostratigrafi dan Lingkungan Purba Batuan Sedimen Kaya Bahan Organik Berumur Miosen di Sub-Cekungan Kutai Timur, Indonesia

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Abstract - The Miocene sedimentary rocks in Samarinda area constrains organic rich sediments, which are considered as a good source rocks hydrocarbon in the East Kutai Sub-Basin, Kalimantan. The high organic material content within the sediments is related to the dynamics of depositional environment in deltaic setting. The accumulation and characteristics of organic matter in this area may be influenced by multiple factors, under a complex physical-chemical processes. Geochemical data of major and trace elements obtained for a total 309 outcrop samples from four locations were interpreted to define chemostratigraphic and paleoenvironmental conditions (paleoproductivity, detrital influx, paleoredox and paleosalinity) responsible for organic carbon accumulation and source rocks characterization. Stratigraphic variation in inorganic geochemistry allows two chemostratigraphic packages to be defined and correlated within the Miocene sedimentary sequences. These chemostratigraphic packages are geochemically differentiated using SiO_2/Al_2O_3, TiO_2/Al_2O_3, Na_2O/Al_2O_3, TiO_2/Nb and Sr/Ba ratio values. The chemical alteration index (CIA) suggests that the sedimentary unit was deposited in a hot and humid climate, with moderate to intensive weathering intensity. Detrital material input proxies (Si/Al, Ti/Al) indicate that the low Si/Al and Ti/Al ratios reflect a low material input providing an increasing organic matter accumulation in the Middle Miocene. However, paleoproductivity proxies (P/Ti, Ba/Al) show the organic matter enrichment is not restrained by water column productivity, as indicated by a weak correlation between TOC and productivity index. In addition, paleosalinity index (Sr/Ba) and redox indicators (V/Cr, V/Sc U/Th and Mo/Al) indicate that the sediments were deposited in a brackish environment with dysoxic to suboxic conditions and might be the main control in the enrichment of organic matter in the study area. Thus, the detrital material influx and paleoredox conditions controlled organic accumulation and source characteristics the Miocene sedimentary sequence of the Kutai Basin.

Keywords: Chemostratigraphy, Kutai Basin, paleoenvironment, source rocks.

Abstrak *- Batuan sedimen berumur Miosen di Daerah Samarinda kaya bahan organik dipertimbangan menjadi batuan induk hidrokarbon yang baik di Sub-Cekungan Kutai Timur, Kalimantan. Kelimpahan material organik di dalam batuan sedimen tersebut disebabkan oleh dinamika lingkungan pengendapan pada wilayah delta. Karakteristik dan akumulasi material organik pada daerah tersebut dipengaruhi oleh berbagai faktor dengan proses fisik dan kimiawi yang sangat kompleks. Data geokimia unsur utama dan unsur jejak yang diperoleh dari empat lokasi pengamatan dengan total 390 sampel telah dianalisis untuk mengetahui kemostratigrafi dan kondisi lingkungan pengendapan yang mempengaruhi kelimpahan material organik (produktivitas purba, input material, kondisi redoks purba, dan salinitas purba), dan karakteristik batuan induk. Variasi stratigrafi dari geokimia anorganik dapat dibedakan menjadi dua paket kemostratigrafi dan dapat dikorelasikan dalam sekuen batuan sedimen berumur Miosen. Paket kemostratigrafi tersebut secara geokimia dibedakan berdasarkan rasio nilai* SiO_2/Al_2O3, TiO_2/Al_2O_3, Na_2O/Al_2O_3, TiO_2*/Nb dan Sr/Ba. Indeks ubahan kimia menunjukkan bahwa unit batuan di daerah penelitian diendapkan pada lingkungan beriklim lembap dan kering, dengan tingkat pelapukan menengah sampai tinggi. Proksi input material sedimen melalui nilai rasio Si/Al, Ti/Al menunjukkan bahwa rasio Si/Al, Ti/Al rendah yang memperlihatkan rendah imput material sedimen yang menyebabkan tingginya akumulasi material organik pada Miosen Tengah. Proksi produktivitas purba dengan nilai rasio P/Ti, Ba/Al menunjukkan kelimpahan organik material organik tidak dikendalikan oleh produktivitas kolom air. Hal ini terlihat pada lemahnya hubungan antara TOC dan Indeks Produktivitas. Indeks salinitas purba (Sr/Ba) dan indikator kondisi redoks purba (V/Cr, V/Sc, U/Th dan Mo/Al) menunjukkan bahwa sedimen diendapkan pada lingkungan payau dengan kondisi diskoksik sampai suboksik, dan diperkirakan faktor utama penyebab pengayaan material organik di daerah studi. Dengan demikian dapat dikatakan bahwa input material dan kondisi redoks purba merupakan faktor yang mengontrol akumulasi material organik dan karakteristik batuan induk berumur Miosen di Cekungan Kutai.*

Katakunci: *Kemostratigrafi, Cekungan Kutai, lingkungan-purba, batuan sumber .*

INTRODUCTION

The petroleum source rocks have an important role on hydrocarbon exploration in the sedimentary basins. The presence favorable petroleum source rocks are usually defined by total organic carbon content in the sedimentary rocks. Organic rich sediments have been considered as oil and gas source rocks potential, both for conventional and unconventional hydrocarbon resources. However, the formation mechanism of organic rich sediment is not well understood due to a complicated process, and is depends on several factors, which includes biological productivity continental weathering, sedimentation rates, clay mineralogy, water column oxygenation levels, sea-level change, and sedimentary environment (Mayer,1994; Kennedy et al., 2002; Zonneveld et al., 2010; Bechtel et al., 2012; Shu et al., 2013). The main control factors of organic matter accumulation and preservation are still controversial. However, three fundamental mechanism have been identified for the accumulation of organic matter in organic rich sediments, includes organic productivity (Pedersen and Calvert, 1990; Sageman et al., 2003; Tyson, 2001, 2005; Wei et al., 2012), organic matter preservation associated with paleoredox conditions (Demaison and Moore, 1980; Arthur and Sageman, 1994; Mort et al., 2007), and rate of sedimentation (Creaney and Passey, 1993; Tyson, 2005).

The Miocene sequence in the East Kutai Sub-Basin dominantly comprise of organic rich sediments from the Balikpapan and Pulau Balang Formations, which are formed during the transition of transgression and regression phase of the deltaic environment. Shales and coals facies of this sequence are relatively high organic carbon contents (TOC) and considered to be a good source rocks in the Kutai Basin (Peters et al, 1999; Bachtiar, 2004; Bachtiar et al., 2013; and Permana et al., 2018). From the outcrops samples, the organic rich shales and mudstones of this sediment have high total organic content (TOC) values in range of 0.05 - 15.63% and coals are ranging from 2.25 - 57.11% (Permana et al., 2018). The source of organic matter in the Kutai Basin are considered to be a terrestrial origin derived from vegetal debris such as bark, wood and leaves (Bachtiar, 2004; Permana et al., 2018). However, the controlling factors of organic accumulation in this sequence are poorly understood.

Organic rich sediments are usually enriched of some trace elements, which can be used as geochemical proxies for interpreting the paleoenvironment and their association with the organic matter accumulation within the sediments (Kimura and Watanabe, 2001; Algeo and Maynard, 2004; Rimmer, 2004; Tribovillard et al., 2006). As described above that the organic geochemistry studies for source rocks characterization in the Kutai Sub-Basin, such as type and origin of organic matter, as well hydrocarbon generation potential have been established, however, the relationship between the organic matter accumulation, paleoproductivity and paleoredox conditions have not been studied in detail. Thus, this paper provides paleoenvironment conditions and organic matter accumulation in this basin, by using combined approach of organic facies, chemostratigraphy, and inorganic geochemical proxies as indicator for paleodepositional environments, includes provenance, paleoproductivity and paleoredox of organic rich sediments in the Early Miocene to Middle Miocene.

GEOLOGICAL SETTING

The study area is located at the eastern part of the Kutai Basin, as the second most prolific hydrocarbon resources in Indonesia. The Miocene organic rich sediments are well cropped out at around the Separi Anticline, Samarinda area, especially in four locations of Palaran, Loa Janan Ulu, Loa Bakung, and Sungai Kunjang areas (Figure 1). These sections are mainly consists interbedded shales, claystone, sandstones and coals of prograding deltaic sediments to fluvial sequences. This sedimentary sequence is part of the Early Miocene to Middle Miocene of the Pulau Balang and Balikpapan Formations (Figure 2). This Neogene succession is overlying the interfingerings of the Late Oligocene of the Pamaluan and Babuluh Formations. The Early Miocene Pulau Balang Formation was mainly deposited in deltaic to shallow marine environments, composed of greywacke quartz sandstone, limestone, claystone, dacitic tuff and coal interlamination. To the upward sequence, this formation changes gradually becomes much finer clastic sediments of Balikpapan Formation, which consists of interbedded sandstones, shales, claystone and coals seams. This formation was mostly deposited in deltaic environment during the Middle to Upper Miocene (Supriatna and Rustandi, 1986).

The organic rich sediments of the Pulau Balang and Balikpapan Formations was deposited in mixed fluvial deltaic systems which range from fluvial, upper delta plain, to prodelta facies setting. They are mainly divided into seven facies associations, fluvial channel, distributary channel, marsh, delta front mouth bar, delta front carbonate and prodelta mud (Permana et al., 2018). During the Miocene, the depositional setting in the study area changes by prograding systems from marine-deltaic setting to fluvial environments (Moss et al., 1997; Ahmad and Samuel, 1984; Van de Weerd and Armin, 1992). Organic petrological and geochemical studies from the Miocene sequence indicate that the lower part represents distal facies of delta which has lower concentration of organic matter, while in the upper part sequence represents proximal delta which are richer in organic matter (Permana et al., 2018). This pattern may be similar with the recent sediment in the Mahakam Delta, which shows that the organic contents in deltaic sediment decreasing from the inner part of deltas to the outer offshore areas (Allen et al., 1976). However, the factors controlling the accumulation and enrichment of organic matter in the Miocene sequence are well not understood, this research could lead to significant new insight of the source characteristics and unconventional hydrocarbon exploration in the Kutai Basin.

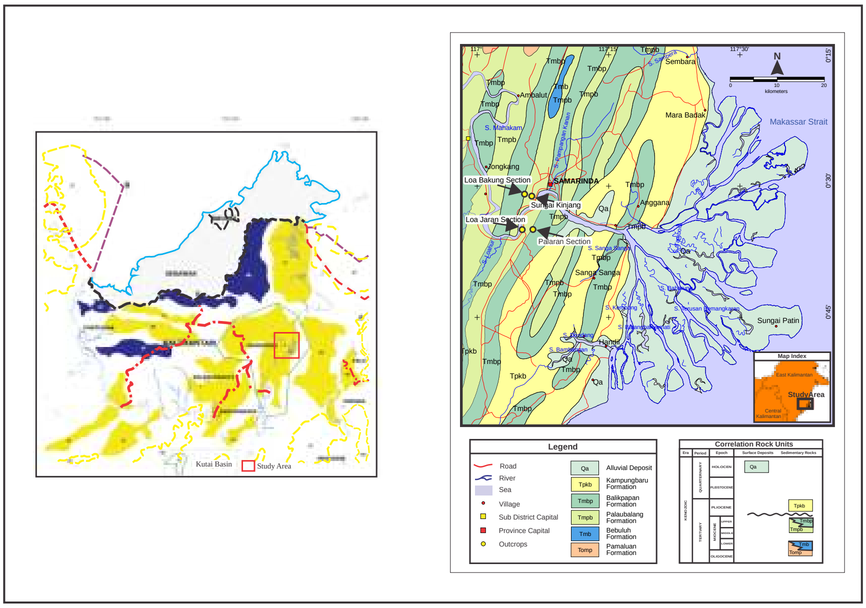
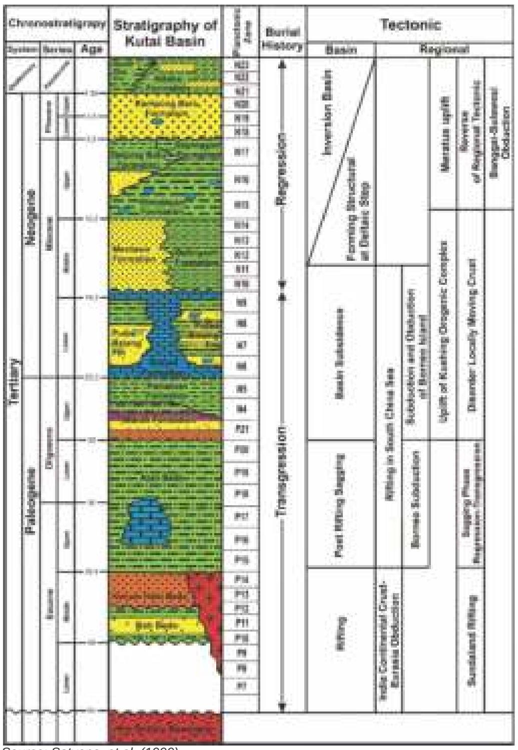


Figure 1. Basin and location map of the study area. Green polygonal mark as the Kutai Basin and the red rectangular box is the location of the studied area (left) and Geological map of study area, showing the lithological unit and stratigraphy of the Tertiary Formation. Full yellow circle and text mark the outcrop location and ID samples of the organic rich sediments (right).



Source: Satyana et al. (1999).

Figure 2. Regional stratigraphy of the Kutai Basin.

SAMPLES AND ANALYTICAL TECHNIQUES

A total 309 outcrop samples were collected from four locations around the Samarinda area, Palaran, Loa Janan, Loa Bakung, and Sungai Kunjang for sedimentary facies, TOC, organic petrology, and geochemical analysis. Fresh and representative samples were collected systematically, where increments are spaced evenly every one meter from bottom to the top of those stratigraphical sections (Figure 3). Samples were crushed into powder using mortar or mill and subsequently analyzed by multi elemental analyzer of Leco Instrumentation that provided for total carbon contents measurement (TOC).

For inorganic geochemistry, whole-rocks samples were determined by using X-Ray Fluorescence spectrometer (XRF) for major and some trace oxide composition and Inductively Couple Plasma – Mass Spectrometer (ICP-MS) for trace and rare elements concentration. For XRF analyses, 1 gram, 200 mesh powder samples were pressed pellets and determined by XRF Thermo ARL 9900 Series for 12 major oxides (SiO_2, Al_2O_3, K_2O, Fe_2O_3, Na_2O, CaO, MgO, NiO, Cr_2O_3, SO_3, TiO_2, and MnO), while for ICP-MS analyses, around 0.1 gram samples were dissolved with three acid leaching using nitric acid (HNO_3, ultrapure grade), formic acid (HCOOH, ultrapure grade), and perchloric acid ($HClO_4$, prograde analyses), and then determined by ICP-MS, iCAP-Q Thermo Fisher Scientific series for full suites of rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm,Yb, and Lu), as well as six other trace elements (V, Rb, Y, Ba, Th, and U) analyzed.

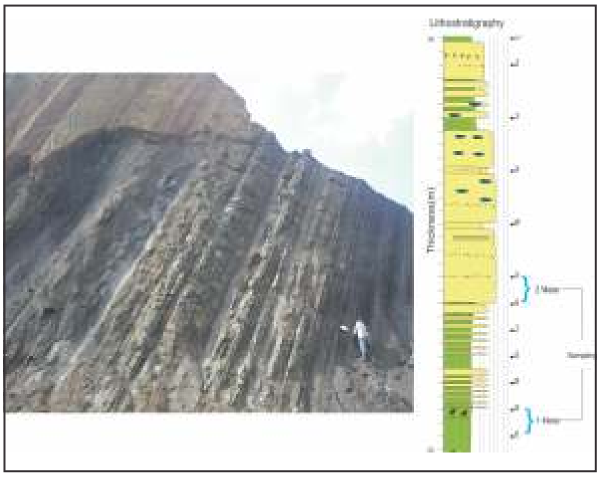


Figure 3. Systematic sampling technique. Representative samples were collected from the outcrop, every 1 m to 2 m from bottom to the top of stratigraphic section.

For petrological analyses, ninety three samples were also polished (block) and identified under the organic petrography microscope (oil immersion in plane polarized reflected light) and Scanning Electron Microscope (SEM). These analyses were used to identify maceral and mineral composition, as well as mode of occurrence minerals in association with macerals in shales and coals samples and mineral composition, as well as mode of occurrence minerals in association with macerals in shales and coals samples.

RESULTS

Petrological and Geochemical Characteristics

Organic Richness and Type of Organic Mater

The organic rich sediments of the Pulau Balang and Balikpapan formation have a relatively high total organic content (TOC), fair to excellent category (range 0.05 - 57.11 wt%, with average 7.33 wt%). Samples containing higher content of organic matter are mostly in shales or mudstone and coals. The shales or mudstones ranges from 0.05 - 15.63wt% TOC, with average 3.84 wt%, while coals are ranging from 2.25 - 57.11 wt%, with average 34.88 wt% (Table 1; Figure 4). In general, the TOC's values are increasing to the upward section, shows irregular pattern associated with the depth and lithological variations. This relatively high TOC's are commonly associated with delta plain environment, and increases from prodelta to delta plain facies (Permana et al., 2018).

Organic petrology analyses indicate that the Miocene organic rich sediments are dominantly composed of clay minerals, and significant amount of organic matter. The organic matter in this sedimentary rocks is mainly consists of vitrinite macerals, with minor inertinite and liptinite macerals. The sandstones are dominated by clay and oxide minerals, with significant dispersed organic matter of vitrinite and inertnite macerals. Most of shales samples are also mainly consist of mainly detritus clay sized-minerals, with vitrinite (huminite), minor liptinite and rarely inertinite macerals. Coal samples are dominated by organic matter, with moderate amount of clay minerals, and minor pyrite and carbonate minerals.

Combined of organic petrography and SEM analyses show the mode and association of macerals “dispersed organic matter” and minerals within the Miocene organic rich sediment of the East Kutai Sub-Basin. The vitrinite or huminite found in various textures and shapes, usually as sub rounded and finely-thick layered morphology, some occurs as detritus organic matter or fine huminitic particles. The inertinite mainly occurs as large lenses or thins bands, and some found as rounded isolated particles, while liptinite maceral occurs small isolated globular bodies or micro spore shaped. They are intimately bound together with clay minerals as the groundmass, lenses, and discrete particles with various shapes, and pyrite both frambiodal and non framdoidal morphology (Figure 5). The thick layered of dispersed organic matter associated with the clay minerals as shales matrix or ground mass indicate that this clay-rich organic matter were formed by syngenetic process (Figure 5 a, b), on the other hand detrital grains, small discrete particle and randomly of dispersed organic matter are considered to form by authigenic or epigenetic deposition (Figure 5 c, d).

Geochemistry of Major and Trace Elements

Geochemical composition of the major and trace elements for the organic rich sediment from the East Kutai Basin were used to gain further insight of the origin, type and preservation of organic matter and their relationship with the paleoenvironment conditions. The ternary plot of the major elements indicates that the majority of these sediments are enriched by SiO_2, relative to Al_2O_3 and CaO (Figure 6). All samples were obtained from Palaran, Loa Janan, Loa Bakung and Sungai Kunjang area shows a relatively high SiO_2 contents, with average is over than 60% (14.44 - 97.19%), followed by Al_2O_3, and Fe_2O_3, with an average concentration of 20.87% (1.73 - 29.25%), and 6.85% (0.54 - 70.15%) respectively. Other major elements such as CaO, K_2O, TiO_2, MgO, Na_2O and P_2O_5, are present in relatively low concentration, less than 3% in average.

The SiO_2 and Al_2O_3 are always changes in reverse direction, SiO_2 mainly associated with coarse grained sediments (sandstone), while Al_2O_3 is the dominant composition of the fine grained sediments (clay fraction). To identify which elements are associated with coarse fraction or clay fraction contents, Pearson's correlation coefficients was used to check the relationship between SiO_2 and Al_2O_3 and other major oxide elements (Table 2). There is very good positive correlation between Al_2O_3 and TiO_2 (coefficients correlation, r = 0.74), as well as K_2O (r = 0.65), suggesting that TiO_2 and K_2O are mostly component of aluminosilicate (clay) minerals. On the other hand, SiO_2 are have strong negative correlation with Fe_2O_3 (r = 0.74), CaO (r = 0.51), and MgO (0.69), suggests that associated with the coarse clastic fraction (sandstones) as terrigenous material input. The SiO_2/Al_2O_3 ratios are also relatively high, 3.78 in average, this confirm that SiO_2 is detrital quartz as terrigenous input material.

Table 1. TOC and organic petrological analyses of the Miocene organic rich sediment in the East Kutai Sub-Basin

Lithology	Average TOC Content (wt.%)	Average of organic petrological composition (%)					
		Maceral			Minerals		
		Vitrinite	Inertinite	Liptinite	Clay	Pyrite	Other mineral (oxide)
Sandstones	1.28	6.79	2.10	-	89.63	0.99	0.49
Shales	3.84	5.86	0.20	0.38	92.66	0.68	0.23
Coals	34.88	48.39	3.01	2.62	45.28	0.47	0.23
Limestones	0.5	2.5	0.40	-	95.82	0.80	0.40

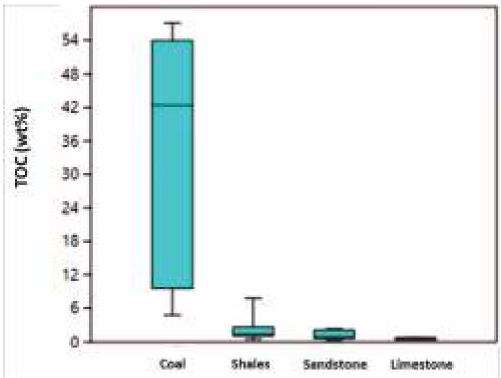


Figure 4. Boxplot showing the TOC contents from different type lithological facies.

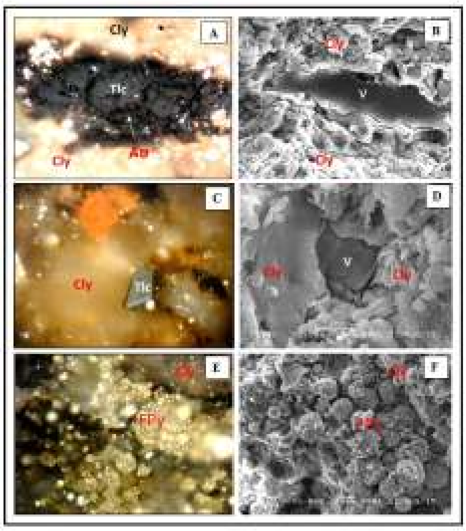


Figure 5. Organic matter images of the organic rich sediments under reflected light microscope and Scanning Electron Microscope (SEM), a) Masiive telocollinite (Tlc) macerals associated with atrinite (Atr) and clay mineral (Cly), reflected white light microscope, 25x; b) Vitrinite lenses maceral (V), associated with clay mineral (Cly), under SEM, 1000 x; c) fine large detrital grains of telocollinite maceral (Tlc) within the clay minerals (cly), reflected light microscope, 50x; d) fine detrital of vitrinite (V), associated with clay mineral in the shale matrix, SEM, 5000x; e) Framboidal pyrite (Fpy), reflected light microscope, 50x; e) Intimately of framboidal (Fpy) and clay mineral (Cly), SEM, 1000 x.

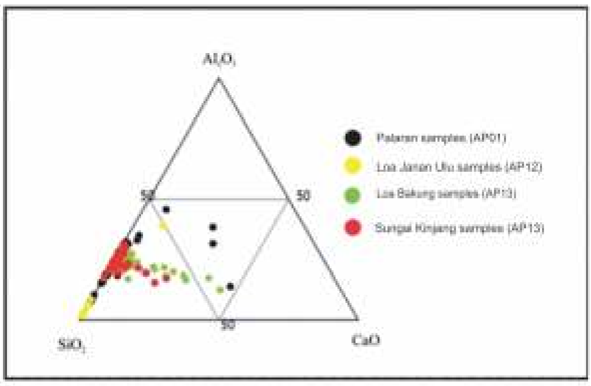


Figure 6. Ternary diagram showing the relative proportion of major element compositions of SiO_2 (quartz), Al_2O_3 (clay) and CaO (carbonates).

Trace elements data show that the Ba, Zn and Sr contents are prominent with average value more than 100 ppm, followed by V with average 72.84 ppm. Trace elements, Cr, Cu, Ni, Th, and Ga have average values ranges form 10 – 45 ppm, whilst Nb, U and Mo have average value less than 5 ppm. Trace elements of Cu, Zn, Th, Ni, U, and Mo are mostly enriched in shales and coal samples, while Ga, Nb, Sr and V predominantly associated with coarse clastic fraction, sandstones and carbonates. The enrichment Cu, Zn, Th and U in coals, and Ni and Mo in shales, suggests that these trace elements are associated with the organic matter preservation. Demaison and Moore (1980) indicate that the organic rich sediments are often enriched by organic matter and specific trace elements like Mo, V, Cu, Zn, Ni, Cd, Se, Pb and U.

Chemostratigraphy and Depositional Environments

Geochemical Characterization of Lithostratigraphic Units

Chemostratigraphic analysis was carried out on 309 organic rich samples collected from four sections (Palaran, Loa Janan Ulu, Loa Bakung and Sungai Kinjang), and samples at approximately 1 - 2 m intervals. Chemostratigraphic packages were identified by unique chemical signatures in a stratal sequence by the relative changes in chemical composition throughout the section. Using those unique geochemical signatures, the study interval was divided into two main chemostratigraphic packages (Figure 7).

Package 1 are mostly composed of the Early Miocene of marine deltaic sediments. This package occurs at the bottom of the interval, has low TOC values, high SiO_2/Al_2O_3 ratio and relatively high Na_2O/Al_2O_3 and TiO_2/Nb ratio. On the other hand, package 2, consist of mainly fluvial deltaic sediments, Middle Miocene age. This package is recognized by high TOC values, high Mo/Al ratio, relatively high Sr/Ba ratio, and low SiO_2/Al_2O_3 and TiO_2/Al_2O_3 ratio. The suddenly sharp increase of TiO_2/Nb, Mo/Al and TOC value represents the transition from marine deltaic sediment of the Pulau Balang Formation to fluvial deltaic sediments of the Balikpapan Formation. This suggests that there are changes in sediment provenance which contribute to organic matter accumulation and preservation during the Early Miocene to Middle Miocene in the study area.

Depositional Environment Signatures

The depositional environment for organic rich sediment of the study area was classified based on the ternary plot of Englund and Jorgenson (1973). This ternary plot employs the chemical classification on the basis (Al_2O_3)-(K_2O+Na_2O+CaO)-(Fe_2O_3+MgO) contents (AKF). The samples from four sections (Palaran, Loa Janan Ulu, Loa Bakung, and Sungai Kinjang) were plotted on the ternary diagram of the AKF plots which reveal that the sediments are deposited in gradual transitions of the sediments from continental to transitional environments, and somewhat depict of marine environments (Figure 8). As can be seen the samples from Palaran and Loa Janan Ulu falls under the continental zone, which mainly composed of argillaceous shales. On the other hand, the samples from Loa Bakung and Sungai Kinjang are dominantly of carbonaceous sediments and fall into transition to marine zone. This suggests that some of the sediments were transported from continental and transition environments before being deposited in marine environments.

DISCUSSION

Controlling Factors on the Organic Matter Accumulation

Paleoclimate and Detrital Input Material

Weathering process is strongly influenced by climatic factors. Various elements can be identified by using chemical composition of the weathering product in the sedimentary basin during the weathering phase. The chemical index of alteration (CIA) can be used to evaluate chemical weathering intensity and was applied to describe paleoclimate condition of sedimentary environment (Nesbit and Young, 1989). The CIA ranges from 50 to 70 (weak), indicating a low degree of chemical weathering, reflects cool and arid climate. When CIA ranges from 70 – 85 (intermediate), indicating moderate degree of chemical weathering, and classified as warm and humid climate. Furthermore, when the CIA exceed to 85, the value indicates a high degree of chemical weathering and associated with a hot and humid climate (Nesbit and Young, 1989). The CIA of the Miocene organic rich sediment in the East Kutai Sub-Basin ranges from 19.75 – 99.20, with average 78.89 (total samples, n = 297), higher than the Upper Continental Crust/UCC (56.9) and Post-Archean Australian Shale/PAAS (75.3) values (Taylor and Mc Clennan, 1985), which indicate the sediments mostly influenced by a moderate degree of chemical weathering and humid paleoclimate condition.

The CIA of the chemostratigraphic package 1 (Early Miocene of the Pulau Balang Formation) ranges form 19.75 – 99.20, with average 77.05, indicate moderate degree of chemical weathering, warm and humid climate. The CIA of the chemostratigraphic package 2 (Middle Miocene of the Balikpapan Formation) ranges from 40.90 – 82.69, average 98.34, reveals a high degree of chemical weathering, hot and humid climate condition. This shows that the climate changed during the deposition of these organic rich sediments from warm and humid to hot and humid paleoclimate conditions. Thus, this indicates that the paleoclimate has a great influence on the enrichment of the organic matter.

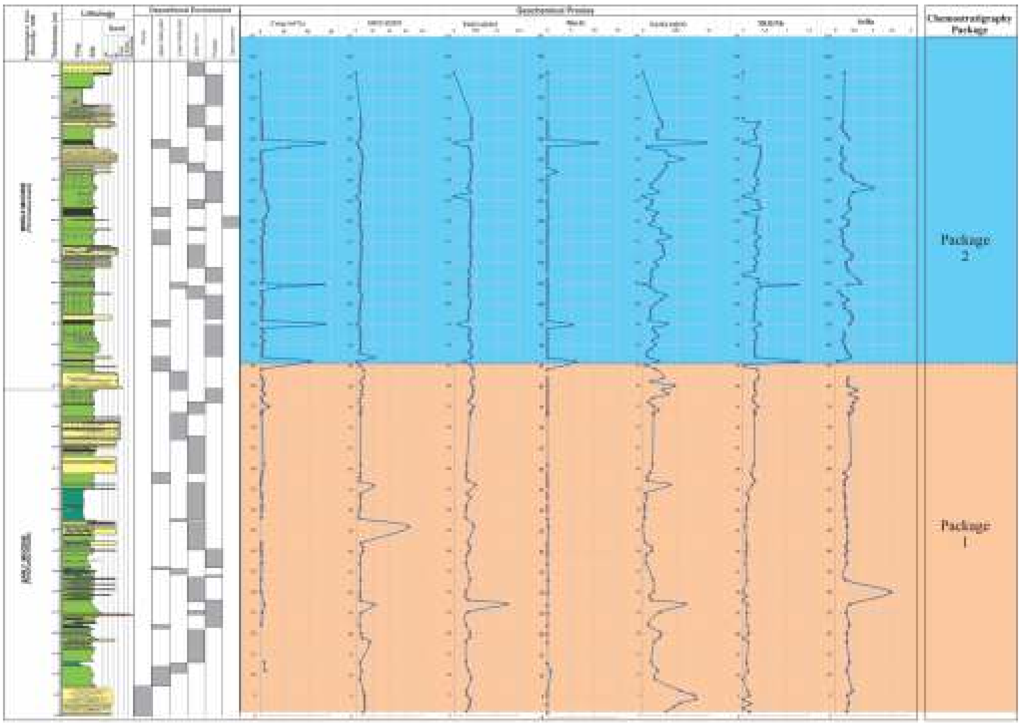


Figure 7. The lithostratigraphic of Palaran Section, distribution of TOC, geochemical proxies of detrital input, redox indicators, paleosalinity and chemostratigraphic packgaes in vertical section.

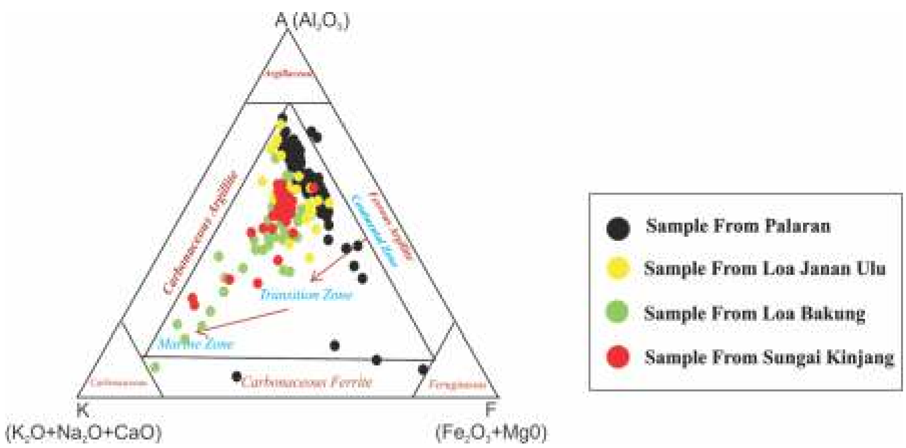


Figure 8. Ternary diagram (AKF plots, A: Al_2O_3, K: K_2O+Na_2O+CaO) and Fe: Fe_2O_3+MgO), showing depositional environments signatures of the Miocene organic rich sediment in the East Kutai Basin.

The elements of Al, Si, Ti, Zr and Th are relatively stable and widely used for detrital influx indicators (Tribovilard et al., 1994; Murphy et al., 2000). Al commonly found in the alumosilicate minerlas as fine grain clastic sediments (Calvert and Pederson, 2007). Ti mainly occurs in the clay minerals, as heavy minerals (ilmenite and rutile), while Si is mainly presents both as siliciclastic (quartz) and biogenic fraction (Kidder and Erwin, 2001). When elements Si, Ti, Zr and Th were normalized to Al, can provide changes of fluxes which are derived from detrital aluminosilicate sources. In general the Ti/Al ratio of the Miocene organic rich sediments in the East Kutai Sub-Basin (15-30), indicates that the sources of sediments are intermediate to felsic provenance. This suggests that the Miocene organic rich sediments in the study area are mainly derived from granitic and older sedimentary rock of the basement of the Kutai Basin.

Bivariate plot of TiO_2/Al_2O_3 shows a good positive correlation between TiO_2 and Al_2O_3, indicating the occurrence of Ti within clay mineral as detrital input material (Figure 9). The Al-normalized elements Al, Si, Th and Zr show a remarkable variation in organic rich sediments of the East Kutai Sub-Basin. In the vertical section show the Si/Al and Ti/Al ratios are decreasing upward. In the lower sequence of the chemostratigraphic package 1 (Early Miocene), the relatively high Si/Al and Ti/Al ratios are negative correlation with TOC values of organic rich sediments, indicating the high detrital influx from aluminosilicate decreases the concentration of organic matter. On the other hand, the upper part sequence of the chemostratigraphic package 2 (Middle Miocene) shows a relatively low detrital influx material (low Si/Al and Ti/Al), but higher TOC values, which indicate that decreases detrital flux probably increasing the organic matter preservation.

In lateral variation, there are no significant changes of the Si/Al and Ti/Al ratios. The Si/Al and Ti/Al of the Palaran Section (proximal/fluvial deltaic environment) and Si/Al and Ti/Al ratios of Sungai Kinjang Section (more distal/marine deltaic environment) have similar variation, however, Permana et al. (2018) revealed that the organic content decreases from proximal to distal of marine environment. This suggests that a detrital material influx of aluminosilicate minerals might be not the main factor on controlling the dilution of organic material. Bohacs et al. (2005) stated that the carbonate mineral and biogenic silica are also influenced the organic matter dilution of the sedimentary rocks. The relatively high CaO and Sr elements in the Sungai Kinjang Section are associated with more distal facies/marine environments, which may be influenced more largely by carbonate minerals or biogenic silica of marine environments setting and control the organic matter accumulation.

Paleosalinity and Paleoredox Conditions

Paleosalinity is very important proxy for indicating sedimentary environment and organic matter enrichment and preservation conditions. There are some elemental geochemical proxies for evaluating the paleosalinity, boron/gallium (B/Ga), sulfur total/organic carbon (S/TOC), and strontium/barium (Sr/Ba) ratios (Wei and Algeo, 2019). Therefore, in this study the Sr/Ba ratio was applied to identify the paleosalinity of the Miocene organic sediments in the East Kutai Basin. The higher Sr/Ba ratio indicate the higher paleosalinity, which classify into three categories, when Sr/Ba ratio <1, the sedimentary environment is terrestrial (freshwater) environment, Sr/Ba >1, Sr/Ba ratio between 0.5 and 1.0 indicate the transition environment (brackish water), and Sr/Ba >1 indicate the marine environment (saline water).

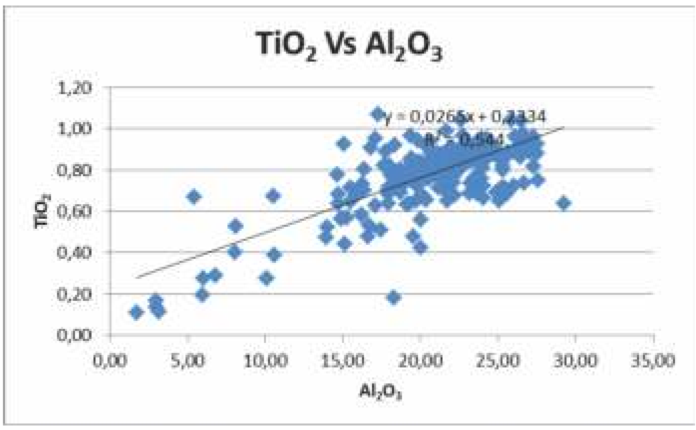


Figure 9. Bivariate plot TiO_2 and Al_2O_3, showing positive correlation between TiO_2 and Al_2O_3.

Table 2. Pearson's correlation coefficient for major elements within the organic-rich sediments, the blue highlight represents with high positive correlation and red highlight stands for high negative correlations

Lithology	Average TOC Content (wt.%)	Average of organic petrological composition (%)					
		Maceral			Minerals		
		Vitrinite	Inertinite	Liptinite	Clay	Pyrite	Other mineral (oxide)
Sandstones	1.28	6.79	2.10	-	89.63	0.99	0.49
Shales	3.84	5.86	0.20	0.38	92.66	0.68	0.23
Coals	34.88	48.39	3.01	2.62	45.28	0.47	0.23
Limestones	0.5	2.5	0.40	-	95.82	0.80	0.40

The Sr/Ba ratio of the Miocene rich sediment vary between 0.06 and 3.55, with average 0.71 (total samples n = 265), indicate that the Miocene organic rich sediment were mostly deposited in the transitional (brackish) environment. The wide ranges variation of Sr/Ba ratio in vertical section, indicating alternating of freshwater, brackish and saline conditions. Chemostratigraphic profile show that the fluctuation of Sr/Ba ratio is correlated with the variation of the TOC values. There are negative correlation between Sr/Ba ratio and TOC value, the Sr/Ba ratio is increasing when the TOC values is depleting, reflects that the salinity stratification of the water column during the deposition of sediment controls the organic preservation of the Miocene organic-rich sediment in the study area.

Some trace element are sensitive to paleoredox conditions and have been widely used as redox indicators, such as V, U and Mo (Algeo and Lyons, 2006; Tribovillard et al., 2006; Algeo and Rowe, 2012; Zeng et al., 2015). Paleoredox condition is controlled the organic accumulation in the sedimentary rocks during the deposition, which are commonly determined by using elemental ratios of V/Cr, V/SC, V/(V+Ni), U/Th, and Mo/Al. There are some reference standard published by previous researcher indicate that redox conditions of the sediments can be classified into oxic, suboxic, dysoxic and suboxic categories. Jones and Manning (1994) indicated that the V/Cr ratio <2 classify to oxic conditions, 2 - 4.25 to dysoxic conditions, and 4.25> to suboxic to anoxic conditions. The ratio V/Cr for the Miocene organic rich sediment in Kutai Basin varies from 0.16 to 23.95 (average 2.03), which suggest dominantly a dysoxic depositional environment with moderate oxygen level.

The variation of the V/Cr ratio relatively shows an increasing trend in the vertical section, indicating decreasing oxygen concentration to the upward section, from more oxic to sub oxic environments. In some part of the Palaran section the V/Cr ratio increase sharply (depths 85 m, 104 m and 140 m), which illustrates that the oxidation level of seawater decreases temporarily. This trend was correlated with the increasing of Mo/Al ratio and organic matter content (TOC values), which indicate that changes redox conditions (from sub-oxic to anoxic) implies on the preservation of organic matter. Thus, this suggests that the organic matter preservation in the Miocene organic rich sediments of the Kutai Basin was controlled by paleosalinity and paleoredox conditions.

Paleoproductivity

The elements of P and Ba are widely used to evaluate the paleoproductivity of organic matter in the sedimentary rocks (Algeo et al., 2011; Payton and Griffith, 2007). As discussed above that the Ti and Al are originally originates from terrigenous detrital material, so the P/Ti or P/Al were used to avoid the dilution effect of the sedimentary organic matter and authigenic minerals content of P in terrigenous clastic material (Algeo et al., 2011). Moreover, the Ba/Al or Ba/Ti ratios can also be used to qualitatively assess paloproductivity of sedimentary organic matter (Dean et al., 1997). The P/Ti ratio of the organic rich sediment of the Kutai Basin varies from 0.04 – 0.54, with average 0.13, which is quite closed to average shale values (0.15), but far below the elevated of the modern equatorial Pacific region 2 to 8 in average (Murray et al., 1993). This indicates from the P/Ti ratio that the Miocene organic-rich sediment of the Pulau Balang and Balikpapan Formations are poor paleoproductivity. Bivariate plot of the P/Ti and TOC shows a negative correlation which indicate that this proxies do not remarkable show the primary productivity organic matter in deltaic setting.

The Ba/Al ratio of Miocene organic rich sediment varies from 0.55 to 123.8, with average is 27.55 (total samples, n=261). This Ba/Al average shows a low paleoproductivity, and far below the average Ba/Al ratio of the upper continental crust in the Central California 100 – 200 in average (Dean et al., 1997). There is a weak positive correlation between the Ba/Al and TOC value for the Miocene organic rich sediments. Although the low Ba/Al ratio reflects low paleoproductivity, it shows slight correlative curve pattern between Ba/Al ratio and TOC value in vertical section. The Ba/Al ratio rises gradually to upward section, correlate with the increasing TOC value. The low P/Ti and Ba/Ti ratio, a weak positive correlation between Ba/Al and TOC values and negative correlation between Pa/Ti and TOC values, indicate that there is complex organic paleoproductivity in deltaic sediments. Thus, it can be summarized that the primary paleoproductivity does not significantly contribute to the organic accumulation in the deltaic setting.

Organic Matter Enrichment and Source Rocks Characteristics

The organic rich sediments in the East Kutai Sub-Basin was deposited in fluvial-deltaic systems, which influences both marine and river environments. The enrichment of organic matter is often related to organic matter accumulation and preservation. The organic matter accumulation is a result of multiple factors, such as paleoclimate conditions, paleoproductivity, and terrigenous influx material. The preservation of organic matter is mostly related to paleoredox and paleosalinity conditions (Demaison and Moore, 1980; Pedersen and Calvert, 1990; Murphy et al., 2000; Lash and Blood, 2014 Chen et al., 2016). However, every sedimentary setting may have specific factors that involve to the organic matter accumulation and preservation (Rimmer et al., 2014).

As discussed above, the accumulation and preservation of organic matter in the East Kutai Basin is mainly controlled by paleoclimate, influx detrital material, paleosalinity and paleoredox conditions.

During the Miocene, the organic rich sediments of Balikpapan and Pulau Balang Formations were deposited in a hot and humid climate, with moderate to intensive weathering intensity (Figure 10). This paleoclimate conditions was contributed to the abundant high plants as source of the organic matter preservation in the basin setting. The relatively high weathering degree of rocks provided high organic matter and terrigenous influx material, which transported by river and accumulated in delta environments. Permana et al. (2018) indicate that the accumulation and preservation of organic matter in proximal delta are relatively high than distal facies, which mainly consists of vegetal debris organic matter, such as bark, wood and leaves, associated with thick layer shales and coal facies. This variation of organic matter concentration is correlated to the process of organic matter accumulation in recent sediment of Mahakam Delta that the inner part of delta much higher organic matter content than the outer offshore area (Allen et al., 1976). These results indicate that the terrigenous material influx acted as the diluents for the organic matter in distal facies of study area. The detrital material increases and dilutes the organic matter by the mineral phases, and control the organic preservation in the basin setting. This also indicates from high concentration of carbonate mineral and biogenic silica in distal areas.

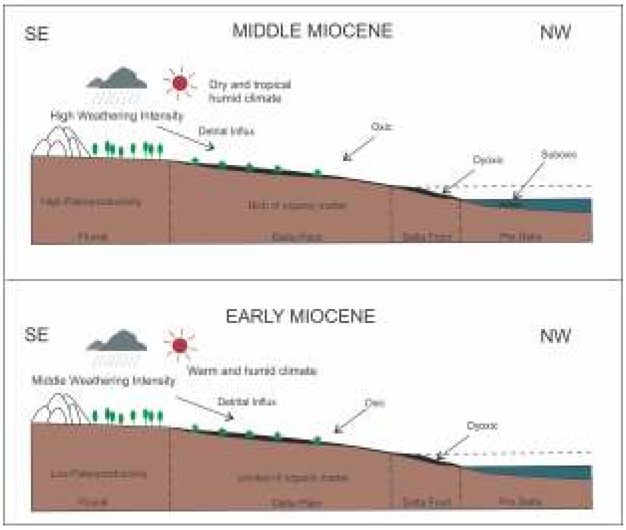


Figure 10. Schematic illustration to show the main controlling the organic matter enrichment in the Miocene organic rich sediments.

The multiple geochemical proxies were also recognized in controlling the organic matter accumulation in marine-continental transitional facies of the Upper Permian Longtan Formation, Western Guizhou, China (Liu et al., 2018). They reported that paleoclimate conditions contribute to the accumulation and preservation in marine-continental transitional shale. Geochemical proxies and chemostratigraphy analyses were clearly defined that the similar factors may also control the organic matter accumulation and preservation in Early Miocene and Middle Miocene of sedimentary sequence in the East Kutai Basin. The Early Miocene sediments are relatively limited organic matter (low TOC), warm and humid climate, and moderate weathering degree (Moderate CIA: 77.05), high clastic material input (high Si/Al ratio). These suggest that the high input clastic material key factor or controlling the organic matter accumulation in Early Miocene. On the other hand, the Middle Miocene sediment consist of high organic matter (high TOC), high chemical degree of chemical weathering, hot and humid climate condition (high CIA: 98.34), low input material (Si/Al ratio), and mainly deposited in brackish environment (high Sr/Ba ratio) with suboxic – anoxic redox conditions. These results indicate that paleoclimate, paleosalinity and paleoredox are key factors contributed to the accumulation and preservation organic matter in the upper part of the Middle Miocene organic rich sediments. Thus, this suggest that the enrichment of organic matter content in the Miocene organic rich sediment in the East Kutai Basin is the result of a combination factors, as discussed above.

The mechanism of organic matter accumulation and preservation in the study area influence the organic matter abundance, source rocks characteristics and hydrocarbon generation in the region. The organic matter mainly consists of higher land plants which are deposited close to source of organic matter at proximal delta, which mainly accumulated in thick layer of black shales and coal in delta plain facies. The terrigenous organic matter is more dominant compare to marine organic matter, which dominated by particle derived from terrestrial higher plant structures, kerogen type-III (Permana et al., 2018). The terrestrial organic debris then may be transported further distal to the basin, which accumulated in siltstone and claystone of prodelta facies. These indicate that the Miocene source rock in the study area were deposited mostly in brackish environment, suboxic to anoxic paleoredox conditions, warm to dry and humid paleoclimate conditions, provide high organic matter composition in proximal delta, however relatively high deposition rate, reduce organic matter preservation in distal delta environment (Figure 11). Rock-eval pyrolysis evaluation shows that the organic maturation of the samples from the study area ranges immature to early peak mature (Tmax vs HI), and considered to be good - excellent source rocks potential (PY vs TOC), which mainly type-III, gas prone potential (Peters et al., 1999; Bachtiar et al. 2013; and Permana et al., 2018). Thus the organic matter enrichment and source rock characteristic of the Miocene organic rich in the study area has favorable condition for generating shale gas.

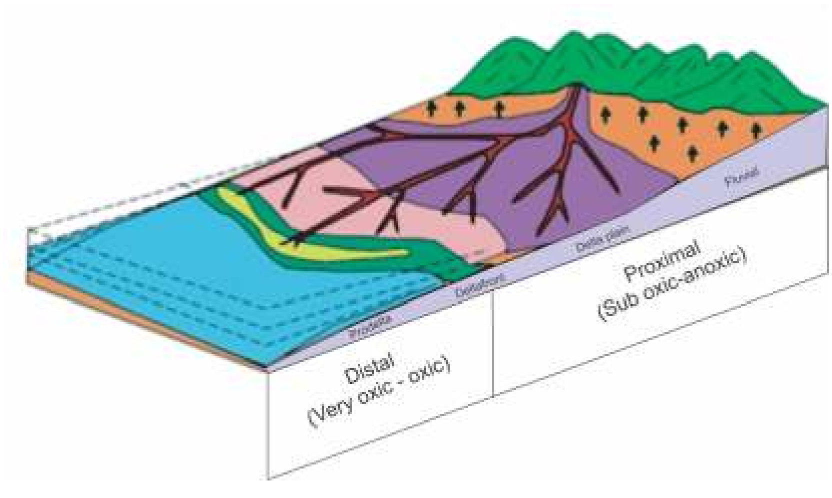


Figure 11. Schematic illustration of the lateral variation of source rocks characteristics, which that the basinal area might has a poor source rocks hydrocarbon.

Table 2. Pearson's correlation coefficient for major elements within the organic-rich sediments, the blue highlight represents with high positive correlation and red highlight stands for high negative correlations

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3
SiO_2	1.00000	-0.15487	-0.26725	-0.74113	-0.45577	-0.50077	-0.68719	-0.27138	-0.10562	-0.11728	-0.20053
TiO_2		1.00000	0.74283	-0.23061	-0.00025044	-0.16488	-0.15305	-0.098731	0.65037	0.30511	0.022875
Al_2O_3			1.00000	-0.078907	-0.19205	-0.28514	-0.13193	-0.24984	0.74511	0.17105	-0.070734
Fe_2O_3				1.00000	0.25298	0.12311	0.7154	0.21894	-0.10843	-0.046325	0.043827
MnO					1.00000	0.66641	0.34477	0.26294	-0.17272	0.20306	-0.064655
CaO						1.00000	0.32646	0.29308	-0.35374	0.073719	-0.0041863
MgO							1.00000	0.48542	-0.14888	0.11744	-0.13012
Na_2O								1.00000	-0.38873	0.35547	-0.062915
K_2O									1.00000	0.068571	-0.070478
P_2O_5										1.00000	-0.13342
SO_3											1.00000

CONCLUSIONS

The Miocene organic rich sediment is mostly influenced by a moderate degree of chemical weathering and humid paleoclimate conditions. These sediments were mainly deposited in the transitional (brackish) environment, which ranges from dysoxic to suboxic conditions. Thus, these might be the main control in the enrichment of organic matter in the study area.

Chemostratigraphy provides a good constraint on the organic matter enrichment of the Miocene organic rich sediments. The organic matter content in the Middle Miocene is higher than Early Miocene. For the Middle Miocene, there are positive correlations between TOC and climate condition (high CIA), paleosalinity and redox indicators (Sr/Ba, Mo/Al, V/Cr). This indicate that high sedimentation rate and sub oxic to anoxic bottom water conditions played an important role in the enrichment of organic matter. However, limited organic matter accumulation in the Early Miocene, which show by negative correlation between TOC and input clastic material (high Si/Al). This indicates that detrital input cannot be ignored for its influence on organic matter enrichment, which diluted the organic matter and decreased the concentration of TOC values in this sedimentary sequence.

The accumulation and preservation of organic material in proximal delta facies are relatively higher than distal delta facies. The relatively high chemical weathering intensity (high CIA) provides high organic matter and terrigenous input material, which transported by river and accumulated in proximal delta and further to distal delta environment. An increasing detrital input material in distal facies diluted and decreased the organic matter. This indicates that the distal delta facies appears to be a poor source rocks potential.

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REFERENCES

Ahmad, Z. and Samuel, L., 1984. Stratigraphy and Depositional Cycles in the N.E. Kalimantan Basin. *Indonesian Petroleum Association Proceedings 13th Annual Convention*, pp. 109–120.

Algeo, T.J. and Maynard, J.B., 2004. Trace-Element Behavior and Redox Facies in Core Shales of Upper Pennsylvanian Kansas-type Cyclothems. *Chemical Geology*, 206(3–4): 289-318.

Algeo, T.J. and Lyons, T.W., 2006. Total Organic Carbon Covariation in Modern Anoxic Marine Environments: Implications for Analysis of Paleoredox and Paleohydrographic Conditions. *Paleoceanography*, 21.

Algeo, T.J., Kuwahara, K., Sano, H., Bates, S., Lyons, T., Elswick, E., Hinnov, L., Ellwod, B., Moser, J., Maynard, J.B., 2011. Spatial Variation in Sediment Fluxes, Redox Conditions, and Productivity in the Permian-Triassic Panthalassic Ocean. *Paleogeogr. Paleoclimatol. Palaeoecol.*, 308: 65-85.

Algeo, T.J. and Rowe, H., 2012. Paleoceanographic Applications of Trace Metal Concentration Data. *Chemical Geology*, 324: 6-18.

Allen, G.P., Laurier, D., and Thouvenin, J., 1976. Sediment Distribution Patterns in the Modern Mahakam Delta. *Proceedings Indonesian Petroleum Association*, 5: 159-178.

Arthur, M.A. and and Sageman, B.B., 1994. Marine Black Shales: Depositional Mechanisms And Environments of Ancient Deposits. *Annual Review of Earth and Planetary Sciences*, 22: 499-551.

Bachtiar, A., 2004. Kerangka Stratigrafi Sikuen dan karakter batuan induk Miosen Awal di Cekungan Kutai Hilir, Kalimantan Timur. Disertasi, Institut Teknologi Bandung, 259 h.

Bachtiar, A., Heru, D.W., Azzaino, Z., Utomo, W., Krisyunianto, A., and Sani, M., 2013. Surface Data Re-Evaluation, Eocene Source Rock Potential and Hydrocarbon Seepage, and Eocene Sand Reservoir Prospectivity In West Sangatta, Northern Kutai Basin. *Proceedings of the Indonesian Petroleum Association, 37th Annual Convention and Exhibition*, paper IPA13-G-087, 10 p.

Bechtel, A., Jia, J.L., Strobl, S.A.I., Sachsenhofer, R.F., Liu, Z.J., Gratzer, R., and Püttmann, W., 2012. Paleoenvironmental Conditions During Deposition of the Upper Cretaceous Oil Shale Sequences in the Songliao Basin (NE China): Implications from Geochemical Analyses. *Org. Geochem.*, 46: 76-95.

Bohacs, K.M., Grabowski, G.J., Carroll, A.R., Mankiewicz, P.J., Gerhardt, K.J., Schwalbach, J.R., Wegner, M.B., Simo, J.A., 2005. Production, Destruction, and Dilution the Many Paths to Source Rock Development. In Harris, N.B. (ed.), The Deposition of Organic-Carbon-Rich Sediments: Models, Mechanism, and Consequences. *Society of Economic Paleontologist and Mineralogist Special Publication*, 82: 61-101.

Calvert, S.E. and Pederson, T.F., 2007. Elemental Proxies for Palaeclimatic and Palaeoceanographic Variability in Marine Sediments: Interpretation and Application. *Developments in Marine Geology*, 1: 567-664.

Chen, C., Mu, C.L., Zhou, K.K., Liang, W., Ge, X.Y., Wang, X.P., Zheng, B.S., 2016. The Geochemical Characteristics and actor Controlling the Organic Matter Accumulation of the Late Ordovician - Early Silurian Black Shale in the Upper Yangtze Basin, South China. *Marine Petroleum Geology*, 76: 159-175.

Creaney, S. and Passey, Q.R., 1993. Recurring Patterns of Total Organic Carbon and Source Rock Quality Within a Sequence Stratigraphic Framework. *American Association of Petroleum Geologists Bulletin*, 77: 386-401.

Demaison, G.J. and Moore, G.T., 1980. Anoxic Environments and Oil Source Bed Genesis. *American Association of Petroleum Geologists Bulletin*, 64: 1179-1209.

Dean, W.E., Gardner, J.V., and Piper, D.Z., 1997. Inorganic Geochemical Indicators of Glacial Interglacial Changes in Productivity and Anoxia on the California Continental Margin. *Geochimica Cosmochimica Acta*, 61(22): 4507-4518.

Englund, J.O. and Jørgensen, D.P., 1973. A Chemical Classification System for Argillaceous Sediments and Fact or Affecting Their Composition. *Geologiska Föreningens i Stockholm Förhandlingar*, 95(1): 87-97.

Kennedy, M.J., Pevear, D.R., and Hill, R.J., 2002. Mineral Surface Control of Organic Carbon in Black Shale. *Science*, 295: 657-660.

Kidder, D.I. and Erwin, D.H., 2001. Secular Distribution of Biogenic Silica Trough the Phanerozoic: Comparison of Silica-Replaced Fossil and Bedded Cherts at the Series Level. *Journal of Geology*, 109: 509-522.

Kimura, H. and Watanabe, Y., 2001. Oceanic Anoxia at the Precambrian-Cambrian Boudary. *Geology*, 29(11): 995-998.

Lash, G.G. and Blood, D.R., 2014. Organic Matter Accumulation, Redox, and Diagenetic History of Marcellus Formation, Southwestern Pennsylvania, Appalachian Basin. *Marine of Petroleum Geology*, 57: 244-26.

Mayer, L.M., 1994. Surface Area Control of Organic Carbon Accumulation in Continental Shelf Sediments. *Geochim. Cosmochim. Acta*, 58: 1271-1284.

Moss, S.J., Chambers, J., Cloke, I., Satria, D., Ali, J.R., Baker, S., Milsom, J., and Carter, A., 1997. New Observations on the Sedimentary and Tectonic Evolution of the Tertiary Kutai Basin, East Kalimantan, in A.J. Fraser, S.J. Matthews, and R.W. Murphy (eds), *Petroleum Geology of Southeast Asia*. Geological Society Special Publication, 126: 395-416.

Mort, H., Jacquat, O., Adatte, T., Steinmann, P., Föllmi, K., Matera, V., Berner, Z., and Stüben, D., 2007. The Cenomanian/Turonian Anoxic Event at the Bonarelli Level in Italy and Spain: Enhanced Productivity and/or Better Preservation?. Cretaceous Research, 28: 597-612. https://doi.org./10.1016/j.cretres.2006.09.003.

Murphy, A.E., Sageman, B.B., Hollander, D.J., Lyons, T.W., and Brett, C.E., 2000. Black Shale Deposition and Faunal Overturn in the Devonian Appalachian Basin: Starvation, Seasonal Water-Column Mixing, and E? cient Biolimiting Clastic Nutrient Recycling. *Paleogeography*, 15: 280-291.

Nesbitt, H.W. and Young, G.M., 1989. Formation and Diagenesis of Weathering Pro?les. *Journal of Geology*, 97: 129-147.

Payton, A. and Griffith, E.M., 2007. Marine Barite: Recorder of Variations in Ocean Export Productivity, Deep Sea Resources, Part II. *Study of Oceanography*, 54 (5-7): 687-705.

Pedersen, T.F. and Calvert, S.E., 1990, Anoxia vs. productivity: What controls the formation of organic-carbon-rich sediments and sedimentary rocks? *American Association of Petroleum Geologists Bulletin*, 74: 454-466.

Permana, A,K., Sendjadja, Y.A., Panggabean, H., and Fauxely, L., 2018. Depositional Environment and Source Rocks Potential of the Miocene Organic-Rich Sediments, Balikpapan Formation, East Kutai Sub-Basin, Kalimantan. *Journal of Geology and Mineral Resources*, 9(3): 171-186.

Peters, K.E., Snedden, J.W., Sulaeman, A., Sarg, J.F., and Enrico, R.J., 1999. New Deepwater Geochemical Model for the Mahakam Delta and Makassar Slope, Kalimantan. *Proceedings of the Indonesian Petroleum Association, 27th Annual Convention and Exhibition*, paper IPA99-G-094, 12 p.

Rimmer, S.M., 2004. Geochemical Paleoredox Indicators in Devonian Mississippian Black Shales, Central Appalachian Basin (USA). *Chemical Geology*, 206(3-4): 373-391.

Sageman, B.B., Murphy, A.E., Werne, J.P., Ver Straeten, C.A., Hollander, D.J., and Lyons, T.W., 2003. A Tale of Shales: The Relative Roles of Production, Decomposition, and Dilution in the Accumulation of Organic-Rich Strata, Middle–Upper Devonian, Appalachian Basin. *Chemical Geology*, 195: 229-273.

Shu, T., Dazhen, T., Hao, X., Jianlong, L., and Xuefeng, S., 2013. Organic Geochemistry and Elements Distribution in Dahuangshan Oil Shale, Southern Junggar Basin: Origin of Organic Matter and Depositional Environment. *Int. J. Coal Geol.*, 115: 41-51.

Supriatna, S. and Rustandi, E., 1986. *Geological Map of the Samarinda Quadrangle, Kalimantan, Scale 1:250.000*. Geological Research and Development Centre, Indonesia.

Taylor, S.R. and McClennan, S.M., 1985. *The Continental Crust: Iits Composition and Evolution*. Blackwell Scienti?c Publications, Oxford.

Tribovillard, N., Algeo, T.J., Lyons, T., and Riboulleau, A., 2006. Trace Metals as Paleoredox and Paleoproductivity Proxies: An Update. *Chemical Geology*, 232(1-2): 12-32.

Tribovillard, N.P., Desprairies, A., Lallier-Vergès, E., Bertrand, P., Moureau, N., Moureau, N., Ramdani, A., and Ramanampisoa, L., 1994. Geochemical Study of Organic-Matter Rich Cycles from the Kimmeridge Clay Formation of Yorkshire (UK): Productivity Versus Anoxia. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 108: 165-181.

Tyson, R.V., 2001. Sedimentation Rate, Dilution, Preservation, and Total Organic Carbon: Some Results of a Modeling Study. *Organic Geochemistry*, 32: 333-339.

Tyson, R.V., 2005. The Productivity versus Preservation Controversy: Cause, Faws, and Resolution, in Harris, N.B. (ed.), The Deposition of Organic-Carbon-Rich Sediments: Models, Mechanisms, and Consequences. *Society for Sedimentary Geology (SEPM) Special Publication*, 82: 17-33.

Van de Weerd, A. and Armin, R.A., 1992. Origin and Evolution of the Tertiary hydrocarbon-bearing Basins in Kalimantan (Borneo), Indonesia. *AAPG Bulletin*, 76: 1778-1803.

Wei, H.Y., Chen, D.Z., Wang, J.G., Yu, H., and Tucker, M.E., 2012. Organic Accumulation in the Lower Chihsia Formation (Middle Permian) of South China: Constraints from Pyrite Morphology and Multiple Geochemical Proxies. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 353: 73-86.

Wei, W. and Algeo, T.J., 2019. Elemental Proxies for Paleosalinity Analysis of Ancient Shales and Mudrocks. Geochimica Cosmochimica Acta (In Press), https://doi.org/10.1016/j.gca.2019.06.034.

Zeng, S.Q., Wang, J., Fu, X.G., Chen, W.B., Feng, X.L., Wang, D., Song, C.Y., and Wang, Z.W., 2015. Geochemical Characteristics, Redox Conditions, and Organic Matter Accumulation of Marine Oil Shale from the Changliang Mountain Area, Northern Tibet, China. *Marine Petroleum Geology*, 64: 203-221.

Zonneveld, K.A.F., Versteegh, G.J.M., Kasten, S., Eglinton, T.I., Emeis, K.C., Huguet, C., Koch, B.P., de Lange, G.J., de Leeuw, J.W., Middelburg, J.J., Mollenhauer, G., Prahl, F.G., Rethemeyer, J., and Wakeham, S.G., 2010. Selective Preservation of Organic Matter in Marine Environments: Processes and Impact on the Sedimentary Record. *Biogeosciences*, 7: 483-511 .