



## Precipitation of Calcite during the Deposition of Paleogene Sangkarewang Oil Shale, Ombilin Basin, West Sumatra, Indonesia

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**Abstract** - Geochemical and petrographical analyses were carried out to investigate the occurrence of calcite in the former Ombilin lacustrine lake. The study involves eight samples taken from a 56 m long drill core of Sangkarewang oil shale. Geochemical investigation showed that the samples consist of varied terrigenous input represented by Si, Al, K, and Ti, and autochthonous input represented by S, total organic carbon (TOC), and  $\delta^{13}\text{C}$  of bulk organic matter. Along the drill core profile the abundance of autochthonous input decreases upwards, while that of terrigenous input oppositely increases upwards. Petrographical analysis revealed that calcite is a major mineral in the samples. In this study, the abundance of calcite could be represented by the abundance of Ca, as calcite is the only significant Ca containing mineral. Ca is abundant in the samples (8.4% in average) and its concentration varies similarly with those of S, TOC, and  $\delta^{13}\text{C}$ , suggesting that the element as well as calcite incorporates the autochthonous input. The variation of calcite abundance in the drill core profile is considered to be related with primary productivity changes during the development of the former lake. Higher primary productivity represented by more positive of  $\delta^{13}\text{C}$  value (-24.8‰) during the deposition of the lower part of the drill core profile promoted the higher amount of deposited organic matter. In such environment, the supersaturation of carbonate ion in lake water was also reached and significant precipitation of authigenic calcite occurred. As the lake developed, the primary productivity decreased as indicated by more negative of  $\delta^{13}\text{C}$  value (eventually -26.8‰). This condition led to the decreases of deposited organic matter and calcite in the lake sediments.

**Keywords:** calcite precipitation, oil shale, depositional environment, primary productivity, Ombilin Basin

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### INTRODUCTION

The occurrence of Sangkarewang oil shale has been discussed extensively by many authors. Silitonga and Kastowo (1975) firstly introduced Sangkarewang Formation as the strata consists of dark brown to blackish marly-shale interbedded with arkosic sandstone and locally andesitic

breccia. The formation was deposited in terrestrial environments, as interpreted based on the presence of freshwater fish fossil (Koesoemadinata and Matasak, 1981). The shale layers contains significant amount of organic matter, which has been discussed in detail by means of sedimentology (Koesoemadinata and Matasak, 1981), petroleum geology (Koning, 1985), organic

petrology (Fatimah and Ward, 2009; Widayat *et al.*, 2013) and organic geochemistry (Anggayana *et al.*, 2014; Widayat *et al.*, 2013). With respect to the presence of organic matter in the oil shale, the authors have demonstrated the depositional environments responsible for the organic matter preservation. Euxinic bottom water existed in the former Ombilin lake was thought as the key factor for the preservation of organic debris sinking from top water into sediment zone (Anggayana *et al.*, 2014; Koesoemadinata and Matasak, 1981).

The Sangkarewang oil shale is calcareous as reported by *e.g.* Koesoemadinata and Matasak (1981) with carbonate content in Talawi area is up to 55% (wt) (Anggayana *et al.*, 2014). The mineralogy of Sangkarewang oil shale has been discussed in detail by Fatimah and Ward (2009). The oil shale consists of mainly quartz, feldspar, carbonates, and a range of clay minerals. The authors reported that calcite is the only carbonate mineral found in the oil shale based on XRD study.

Although mineralogy of the Sangkarewang oil shale has been discussed by many authors, the mineral composition with respect to the depositional environments has never been studied in detail. Moreover, the presence of abundant calcite in the shales deposited in freshwater environments is interesting. This study will investigate the composition of major elements especially calcium composing the shales and its relationship with the paleoenvironments occurred in the former Ombilin lake. Some methods including elemental analysis, petrographical analysis, and carbon isotope analysis will be performed.

### GEOLOGICAL SETTING

The Ombilin Basin is located in the Barisan Mountain, central part of Sumatra Island, Indonesia (Figure 1). It is a pull-apart intramontane basin resulted from Early Tertiary tensional tectonics related to strike-slip movement along the Sumatra Fault Zone (Koning, 1985). The basement of Ombilin Basin is Permo-Carboniferous slates, phyllites, marble, and limestones (Kuantan

Formation). The generalized stratigraphy of Ombilin Basin according to Koesoemadinata and Matasak (1981) and de Smet and Barber (2005) is presented in Figure 2 and described as follows:

1. Brani Formation is the oldest strata in the basin, consists of a sequence of purple-brown coloured breccias and polymictic pebble to cobble conglomerates, formed partly as alluvial fan and coastal deposits.
2. Sangkarewang Formation is composed of dark bluish grey to black fine, calcareous, carbonaceous and laminated shales deposited in lacustrine environments. The oil shale investigated in this study is part of Sangkarewang Formation in Talawi area (Figure 1).
3. Sawahlunto Formation comprises a sequence of brownish shales, silty shales, coal layers, and siltstones and inter-bedded quartz sandstones. This formation was deposited in flood plains.
4. Sawahtambang Formation consists of a thick massive sequence of cross-bedded sandstones, which typically quartzose to feldspathic.
5. Ombilin Formation comprises dark grey carbonaceous and calcareous shales.

### MATERIALS AND METHODS

#### Materials

Oil shale samples are taken from 56 m long drill core (WL-2) of Sangkarewang Formation. The drilling program was conducted by Center of Geological Resources (PSDG) in 2005. The core comprises typically fine grained papery laminated oil shale, dark brown in color, hard and show plant remains in some parts. Grab sampling was applied at eight points distributed along the core as shown in Figure 3.

#### Methods

##### Elemental Analysis

Elemental analysis was conducted to determine major inorganic elements including Si, Al, Ti, K, Ca, and S and the contents of total organic carbon (TOC). The eight oil shale samples were

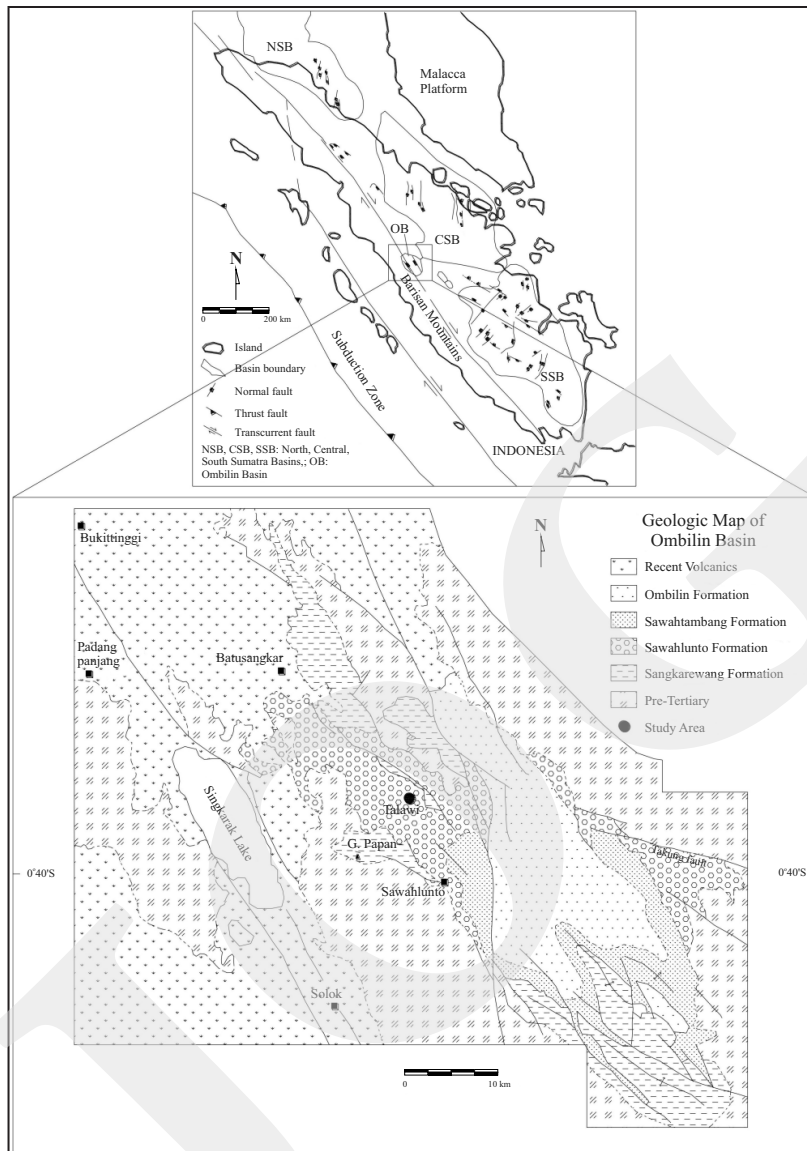


Figure 1. Ombilin Basin and tectonic settings of Sumatra (modified from Koesoemadinata and Matasak, 1981; and Koning, 1985).

crushed and ground to obtain pulverized samples with grain size <200 micron. Inorganic elements were measured using X-ray fluorescence spectrometry. The powdered samples were calcined at 1,050 °C and the lost-on-ignition is determined. The samples were then analyzed using ARL 9900 XRF at the Laboratory of Center of Geological Survey (PSG), Geological Agency, Bandung.

For TOC measurement, the samples were treated first with diluted (10%) hydrochloric acid to remove carbonates completely and then rinsed with distilled water until a neutral condition. TOC measurement was performed using Leco SC-632

Elemental Analyzer at the Laboratory of Center for Geological Resources (PSDG), Geological Agency, Bandung.

#### Carbon Isotope Analysis

Carbon isotope analysis was performed to measure the  $\delta^{13}\text{C}$  of bulk organic matter. The carbonate free samples were analyzed with an IsoPrime<sup>TM</sup> (GV Instruments, UK) continuous-flow isotope ratio mass spectrometer. Isotope ratios are given in  $\delta$ -notation,  $\delta = (R_s/R_{st} - 1) \times 1000$ , with  $R_s$  and  $R_{st}$  as isotope ratios of sample and the VPDB standard (Vienna Peedee Belemnite) re-

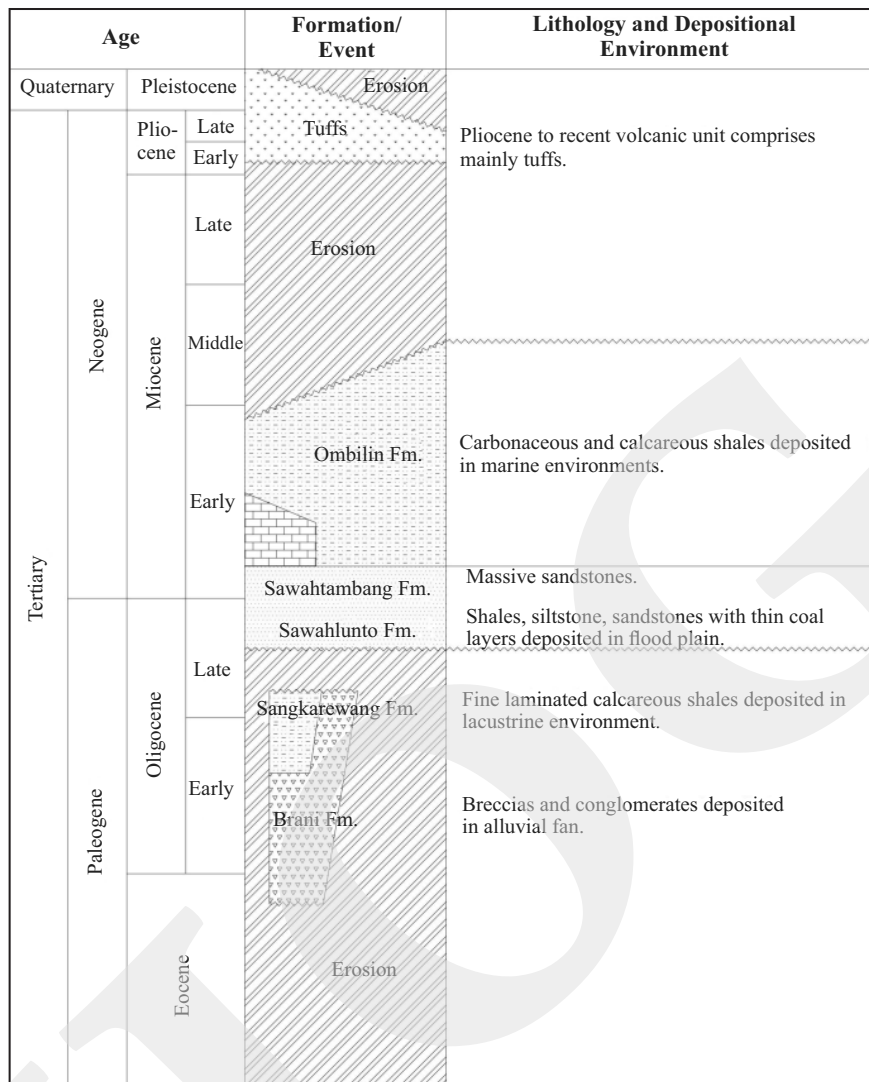


Figure 2. Stratigraphic column of the Ombilin Basin (modified from Koesoemadinata and Matasak,1981; and de Smet and Barber, 2005).

spectively. Analytical precision was 0.08‰. The carbon isotope analysis was done in the Institute of Chemistry and Dynamics of the Geosphere 4: Agrosphere, Research Center Jülich, Germany.

**Petrographical Analysis**

Petrographical analysis was conducted to investigate the occurrence of calcite in the Sangkarewang oil shale. Transmitted-light polarization microscope Nikon Eclipse LV100POL was used to identify calcite mineral in thin section of oil shale. The petrographical analysis was done in the Laboratory of Mineral Deposit, Faculty of Mining and Petroleum Engineering, Institut Teknologi Bandung.

**RESULTS**

**Elemental and Isotope Analyses**

Major elements will be discussed in detail are Si, Al, K, Ti, Ca, S, and TOC, with their values as shown in Table 1. These elements have been widely used to infer depositional environments and geochemical facies of fine-grained siliclastic sedimentary rocks by many authors (Dypvik and Harris, 2001; Eusterhues *et al.*, 2005; Tribovillard *et al.*, 2006). Si is the most abundant elements found in the Sangkarewang oil shale, ranging from 10.4 - 22.0% with an average value of 17.3%. Al is the second most abundant which varies between 5.9 - 11.9%, averaging at 9.6%,

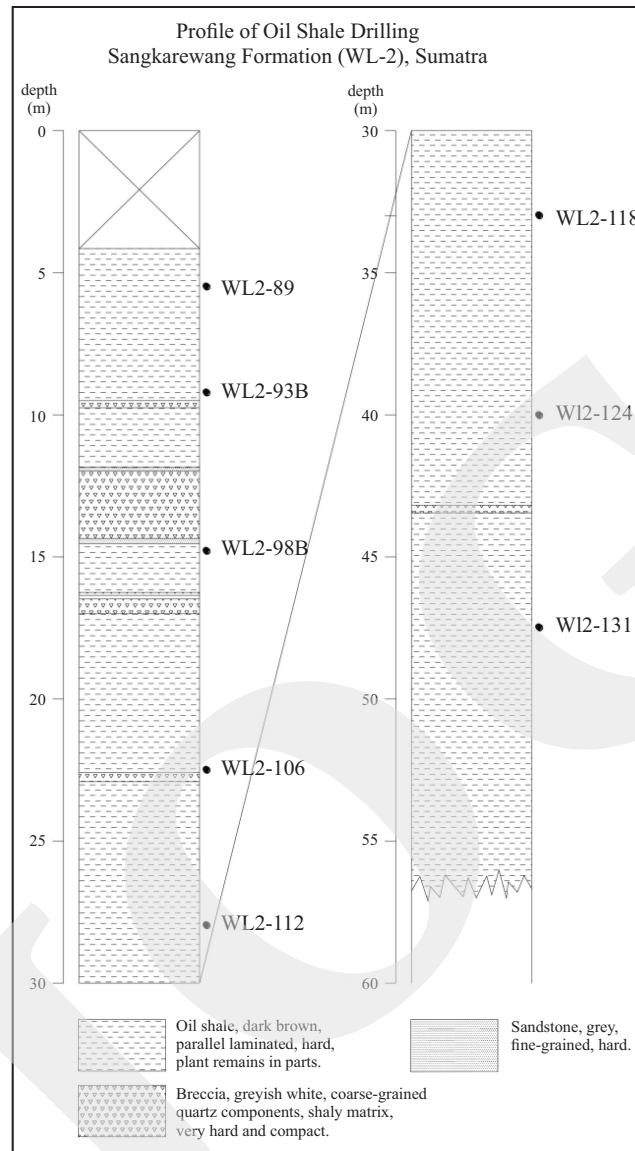


Figure 3. Stratigraphic column of the Ombilin Basin (modified from Koesoemadinata and Matasak, 1981; and de Smet and Barber, 2005).

whilst K and Ti are typically low in amount, about 1.33 to 0.36%, respectively. Along the drill core profile, these elements show upwards increasing variation as shown in Figures 4a - d.

Ca is generally abundant in the oil shale samples, ranging from 2.4% - 19.5%, with an average value of 8.4% (Table 1). As calcite is the only carbonate mineral in Sangkarewang oil shale and there is no other mineral containing Ca in significant amount (Fatimah and Ward, 2009), the carbonate content of the oil shale samples can be estimated to be 6 - 49%. This condition suggests that the oil shale samples are calcareous, as

generally reported for Sangkarewang shales by previous authors.

The concentration of S in the oil shale samples is relatively low, typically below 0.8%. TOC content varies between 1.55 and 11.12%, averaging at 4.99%. Only five samples were measured for bulk organic carbon isotope composition ( $\delta^{13}\text{C}$ ). The  $\delta^{13}\text{C}$  values range from -27.5‰ to -24.8‰. The elements Ca, S, TOC and  $\delta^{13}\text{C}$  generally vary upwards decreasing along the drill core profile as shown in Figures 4e - h. These vertical variations are in opposite condition with those of Si, Al, K, and Ti mentioned previously.

Table 1. Results of TOC, some Major Elements, and Carbon Isotope Analyses

Sample	Depth (m)	Concentration (%)							$\delta^{13}C^*$ (‰)
		Si	Al	K	Ti	Ca	S	TOC	
WL2-89	5.0	18.5	10.0	1.54	0.41	7.0	0.24	3.71	-26.8
WL2-93B	9.5	18.6	10.2	1.55	0.41	6.8	0.28	3.57	
WL2-98B	14.5	22.0	11.9	1.68	0.56	2.4	0.11	1.55	-27.5
WL2-106	22.0	18.4	11.1	1.53	0.44	5.9	0.16	3.38	-26.4
WL2-112	28.0	16.6	10.3	1.26	0.33	7.6	0.77	6.90	
WL2-118	33.0	17.1	10.5	1.27	0.36	8.2	0.36	5.33	-25.1
WL2-124	40.0	16.8	9.1	1.18	0.23	10.1	0.48	4.35	
WL2-131	47.0	10.4	5.9	0.65	0.15	19.5	0.60	11.12	-24.8
<b>Average</b>		<b>17.3</b>	<b>9.6</b>	<b>1.33</b>	<b>0.36</b>	<b>8.4</b>	<b>0.38</b>	<b>4.99</b>	<b>-26.1</b>

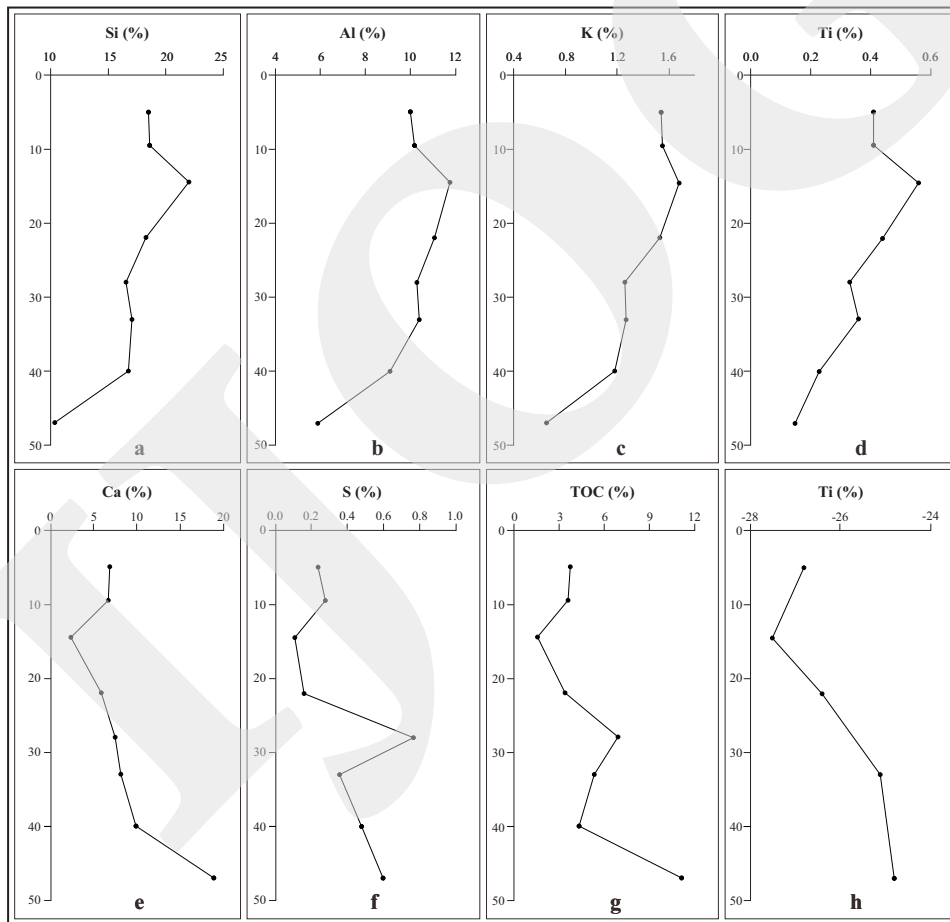


Figure 4. Vertical profiles of the drill core, in general, showing upward increasing concentration trends of Si, Al, K, and Ti (a-d); and upward decreasing concentration trends of Ca, S, TOC, and  $\delta^{13}C$  (e-h), except in 15 m and around 28 m deep zones.

### Petrographical Analysis

Under the microscope, the oil shale shows mostly micro-laminations structure, where each lamination is up to 700 micron thick. Each

lamination indicates different mineral texture. More homogenous grain size lamination is typically rich in calcite as, mostly, subhedral crystals (Figure 5). Coarse to fine grains lamination is

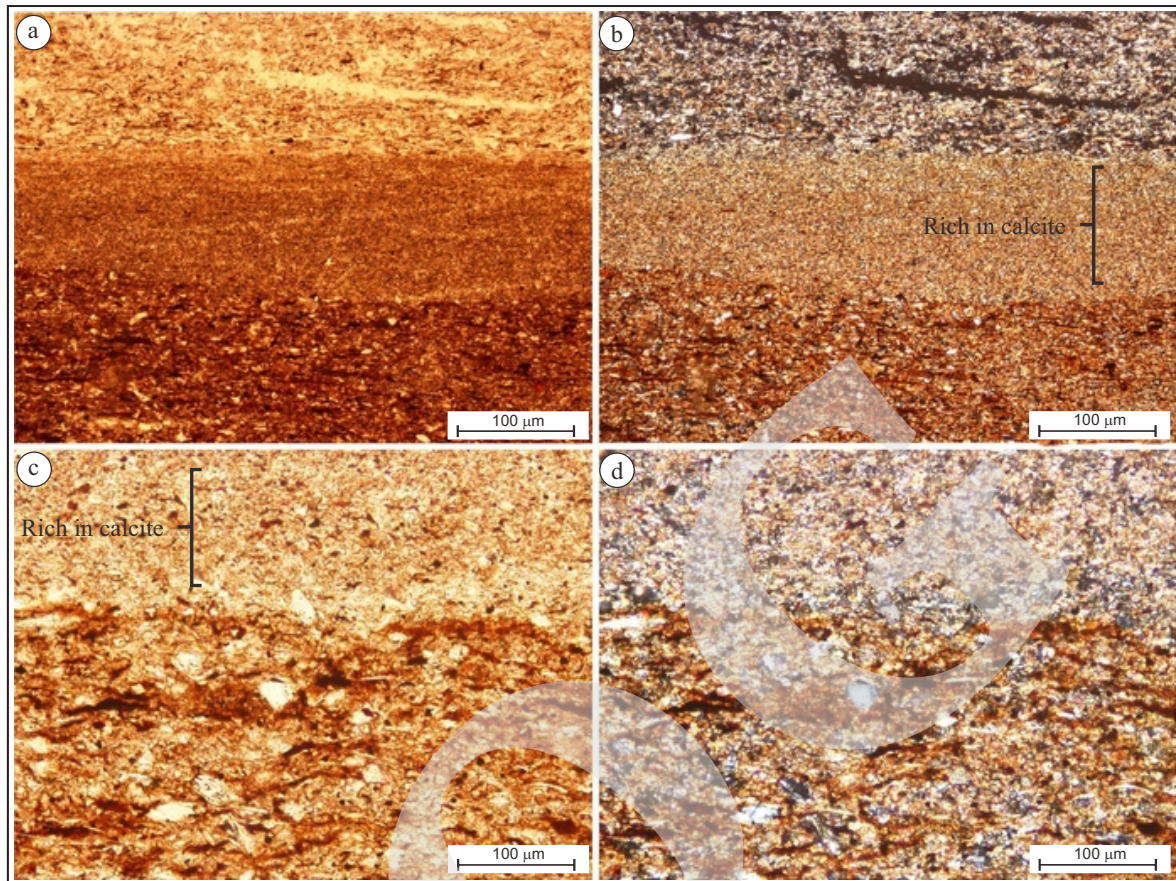


Figure 5. Photomicrograph of WL-106 sample thin section in parallel nicols (left: a, c) and crossed nicols (right: b, d). The oil shale samples show typically micro-laminations. Homogenous and finer grain size lamination is rich in calcite (middle part of b and upper part of c), while coarser to finer grain size lamination is generally a mixture of quartz, plagioclase, clay minerals, and calcite. The scale bars represent 500 (a and b) and 100 (c and d) micron long.

generally mixture of quartz, plagioclase, and clay minerals as anhedral crystals, and lesser calcite.

## DISCUSSIONS

### Lake Ombilin Sediment Sources

In aquatic settings including lakes, sediments deposited below the bottom water consist of two major sources: terrigenous and autochthonous or aquatic sources (Einsele and Hinderer, 1998; Meyers and Ishiwatari, 1993). Terrigenous sources come from the surrounding area of the lakes and are generally detrital of rocks and sometimes plants. The presence of these material in lake sediments is controlled by mechanical transportation. Autochthonous or aquatic sources are usually organic components originate from organisms living in the lakes and inorganic components

which crystallize in the lakes, either in the water column or sediment zone.

Along the drill core profile, the concentrations of Si, Al, K, and Ti show similar upwards increasing variation, suggesting that these elements coexisted during the deposition of Ombilin lake sediment. This coexistence is also exhibited by the plots of several elements, which one of them is presented in Figure 6a. The coefficient of correlations between the elements are listed in Table 2. The plots show that the elements are positively correlated where the coefficient of correlations ( $r$ ) are typically more than 0.8. These indicate that the elements are likely similar in origin in the Sangkarewang oil shale. Si, Al, and K are commonly found in detrital material composing fine grained siliciclastic sedimentary rocks as silica, feldspar, and clay minerals. Ti is commonly found in resistant minerals such as rutile and ilmenite

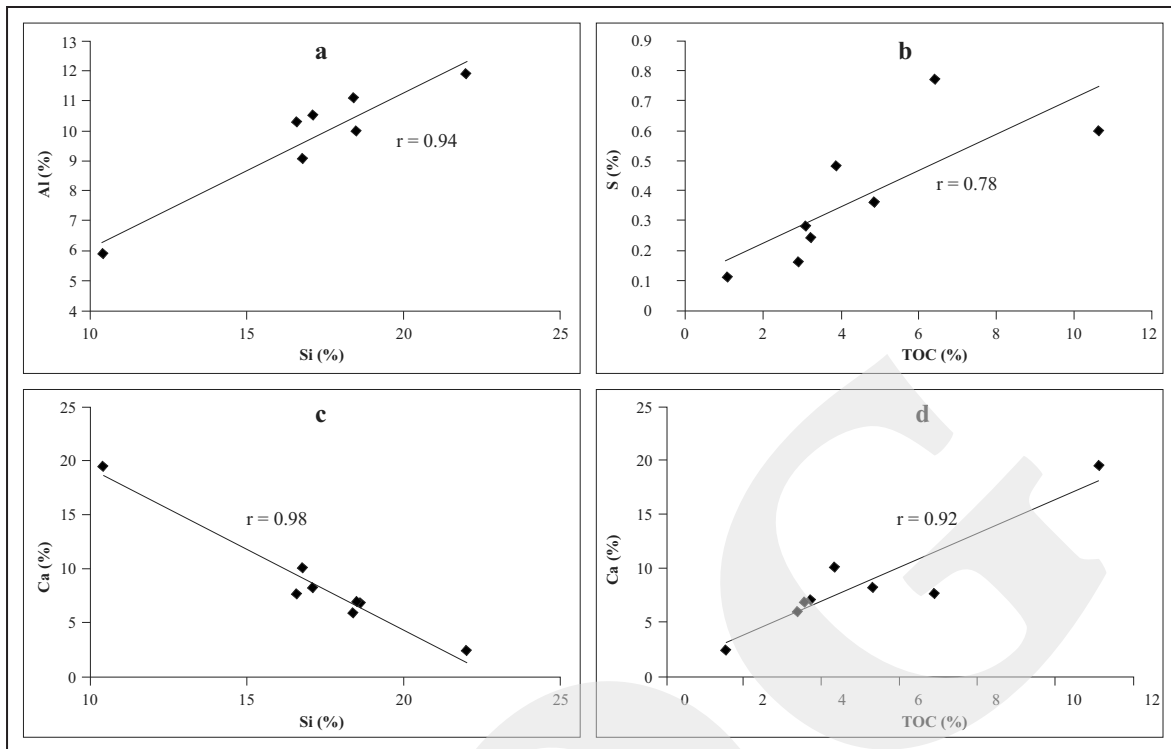


Figure 6. Plots of major elements of the Sangkarewang oil shales. a. Si vs. Al; b. TOC vs. S; c. Si vs. Ca, and d. TOC vs. Ca.

Table 2. Coefficient of Correlations (r) of Plots between the Major Elements

	Si	Al	K	Ti	Ca	S	TOC	$\delta^{13}\text{C}$
Si	-	0.94	0.96	0.92	-0.98	-0.70	-0.97	-0.87
Al	0.94	-	0.92	0.91	-0.98	-0.58	-0.88	-0.73
K	0.96	0.92	-	0.93	-0.96	-0.73	-0.95	-0.88
Ti	0.92	0.91	0.93	-	-0.92	-0.76	-0.85	-0.89
Ca	-0.98	-0.98	-0.96	-0.92	-	0.61	0.92	0.82
S	-0.70	-0.58	-0.73	-0.76	0.61	-	0.78	0.89
TOC	-0.97	-0.88	-0.95	-0.85	0.92	0.78	-	0.87
$\delta^{13}\text{C}$	-0.87	-0.73	-0.88	-0.89	0.82	0.89	0.87	-

associated with the sedimentary rocks. The elements are also known usually to be immobile during diagenesis. By these characteristics, Si, Al, K, and Ti have been considered as terrigenous origin in most fine grained sedimentary rocks (e.g. Eusterhues *et al.*, 2005; Tribovillard *et al.*, 2006; and the references therein). The coexistence of the elements, therefore, suggests them as terrigenous origin in the Sangkarewang oil shale. The vertical variation of the elements concentrations might indicate that terrigenous input increased during the development of the Lake Ombilin.

TOC and S concentrations show similar upwards decreasing along the drill core profile. Plot of TOC vs. S as shown in Figure 6b exhibits positive correlation with good coefficient of correlation ( $r = 0.78$ ). This indicates that the two elements coexist in the studied oil shale. Coexistence of TOC and S in ancient sediments has been related to anoxic or euxinic depositional environments of aquatic settings. In such environments, the presence of organic matter will promote bacteria activity for sulfate reduction into hydrogen sulfide which can further react with reduced iron to form pyrite (Berner, 1984; Kasper *et al.*, 2013;



Raiswell and Berner, 1985). Under such circumstance, the TOC and S could be considered as autochthonous elements in the studied oil shale. Their vertical concentration variations suggest that autochthonous input decreased during the development of the Lake Ombilin.

### Calcite Mode of Formation

Ca constitutes major amount in the Sangkarewang oil shale. Along the drill core profile, Ca shows opposite concentration variation with those of Si, Al, K, and Ti. Plot of Si vs. Ca reveals negative correlation with high coefficient of correlation ( $r = -0.98$ ) as shown in Figure 6c. On the other hand, Ca shows similar concentration variation with those of TOC and S. Plot of Ca vs. TOC exhibits positive correlation with high coefficient of correlation ( $r = 0.92$ ) as shown in Figure 6d. The variation of Ca concentration thus indicates that Ca is part of autochthonous input in the former Lake Ombilin.

As discussed above, Ca mostly represents calcite mineral in the Sangkarewang oil shale. Carbonate minerals are common constituents in both recent and ancient lacustrine sediments (Hodell *et al.*, 1999; Hollander and Smith, 2001; Wu *et al.*, 2015; Yu *et al.*, 2014). Kelts and Hsu (1978) summarized four processes responsible for the occurrence of carbonate in sediments: (1) clastic input from the erosion and transport, (2) production of calcareous skeleton, structural parts, and internal waste products of living organisms, (3) primary inorganic precipitation and sedimentation of carbonate minerals, and (4) postdepositional changes or early diagenetic reactions. The processes (1), (2), and (4) are unlikely to be the case for the occurrence of calcite in the Sangkarewang oil shale. Petrographical analysis reveals that carbonate in the oil shale is present as mostly subhedral crystals of calcite with relatively homogenous and fine grain size. There is no indication of weathering in the calcite mineral grains which might occur during clastic transport. Skeleton or structure of fossil is also not found under the microscope observation. The calcite minerals form the main structure of micro-

laminations (Figure 5) and there is no evidence that the mineral is present as infilling material in cracks or voids. Precipitation and sedimentation are therefore thought as the processes responsible for the presence of authigenic calcite in the Sangkarewang oil shale.

Calcite precipitation and sedimentation have been widely reported in both recent and ancient lakes (Hodell *et al.*, 1999; Hollander and Smith 2001; Vogel *et al.*, 2010; Wu *et al.*, 2015; Xu *et al.*, 2006; Yu *et al.*, 2014; and the references therein). Calcite precipitation in lakes is commonly induced by primary productivity. When the primary productivity is high, significant amount of CO<sub>2</sub> in the epilimnion is fixed by photoautotrophs for photosynthesis. This will lead to the increasing of lake water pH and carbonate ion concentration. When carbonate ion supersaturation is reached, authigenic calcite will be precipitated (Teranes *et al.*, 1999; Hollander and Smith, 2001; Vogel *et al.*, 2010). The coexistence of TOC and Ca in the Sangkarewang oil shale does confirm that primary precipitation and sedimentation of calcite occurred during the development of Lake Ombilin. The fine and homogenous crystal size of calcite may indicate that the precipitation occurred rapidly due to higher rate of primary productivity.

### Development of Lake Ombilin

In this study, the primary productivity is represented by the abundance of TOC. This presumes that primary productivity is the major control on the accumulation of organic matter in the sediment as proposed by Calvert and Pederson (1992) and Pederson and Calvert (1990). However, anoxia has also been ascribed to the higher accumulation of organic matter in sediments (Demaison and Moore, 1980) as anaerobic degradation of organic matter is thermodynamically less efficient than aerobic degradation (Claypool and Kaplan, 1974). Anoxia in the Lake Ombilin has been reported by some authors and considered as the significant factor on the abundant of preserved organic matter (Koesoemadinata and Matasak, 1981; Anggayana *et al.*, 2014).

Variation of  $\delta^{13}\text{C}$  in sediments and sedimentary rocks deposited in lacustrine environments has commonly been related to primary productivity changes in epilimnion. During photosynthesis, photoautotrophs prefer to fix  $\text{CO}_2$  with lighter carbon ( $^{12}\text{C}$ ). Thus, in normal primary productivity, photoautotrophs and the deposited organic matter would usually be depleted in  $^{13}\text{C}$ . When the primary productivity is very high, the concentration of dissolved  $\text{CO}_2$  decreases with relatively high  $^{13}\text{C}$ . In such condition, there will be less carbon isotope fractionation during photosynthesis. Photoautotrophs would fix  $\text{CO}_2$  with both lighter and heavier carbons. Thus, in lakes with high primary productivity, photoautotrophs and the deposited organic matter are typically enriched in  $^{13}\text{C}$  (Heyng *et al.*, 2014; Hollander *et al.*, 1993; Hollander and Smith, 2001; Meyers, 2003; Teranes and Bernasconi, 2005).

Along the drill core profile, the  $\delta^{13}\text{C}$  values generally decrease upwards as shown in Figure 4h. This indicates that primary productivity of Lake Ombilin decreased successively during the deposition of the studied oil shale. This trend is in agreement with the vertical variation of TOC. The coefficient of determination  $\delta^{13}\text{C}$  vs. TOC is 0.75 (Table 1). This suggests that primary productivity is the main control on the

accumulation of organic matter in the former Lake Ombilin. Anoxia is still considered as the significant control in the accumulation of the organic matter. When the Lake Ombilin was high in primary productivity, the anoxic bottom water would be thicker and promoted the preservation of organic matter. Drljepan *et al.* (2014) and Smittenberg *et al.* (2004) demonstrated that increase of primary productivity would lead to limited  $\text{O}_2$  in the water column due to respiration of photoautotrophs, and anoxia in bottom water would be expanded.

Figure 7 illustrates the development of Lake Ombilin during the deposition of the segment of Sangkarewang oil shale with respect to the primary productivity.

During deposition of lower part of the drill core, the Lake Ombilin underwent severe eutrophication (Figure 7a). The algal bloom required  $\text{CO}_2$  in significant amount for photosynthesis. At beginning of the severe eutrophication, the photoautotrophs fixed lighter carbon ( $^{12}\text{C}$ ) of  $\text{CO}_2$ . As the severe eutrophication progressed, the availability of lighter carbon of  $\text{CO}_2$  was limited. The photoautotrophs began to fix heavier carbon ( $^{13}\text{C}$ ) of  $\text{CO}_2$ . Biomass of the organisms was thus enriched in  $^{13}\text{C}$ . Organic matter deposited in the sediment zone would be more abundant and en-

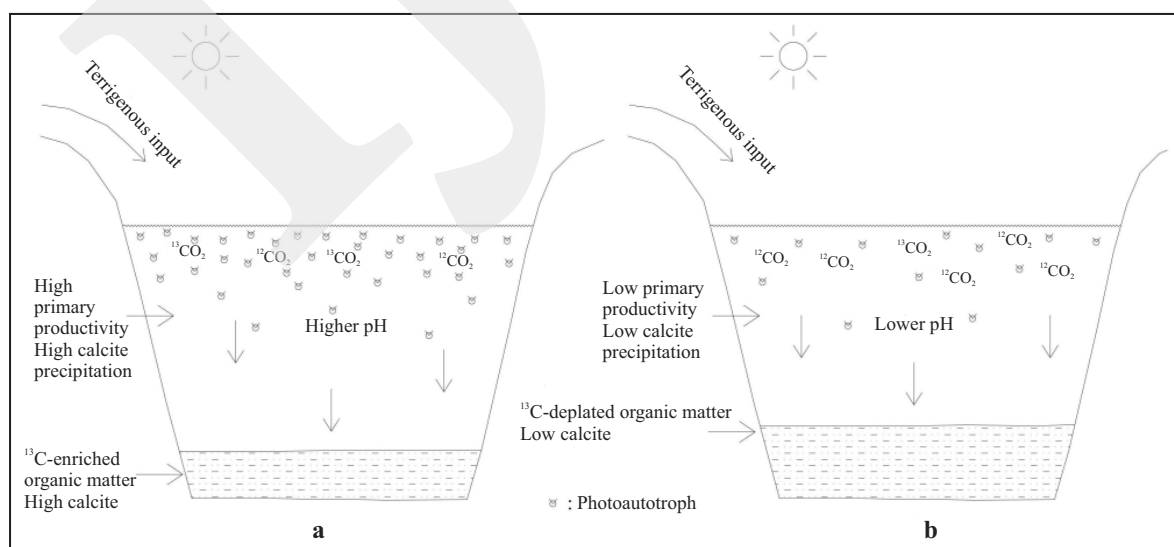


Figure 7. Illustrations of Lake Ombilin conditions during deposition of lower (a) and upper (b) parts of the Sangkarewang oil shale drill core.

riched in  $^{13}\text{C}$  as indicated by higher TOC values and more positive  $\delta^{13}\text{C}$  values, respectively, in the lower part profile. The limited concentration of dissolved  $\text{CO}_2$  led to higher pH of the lake water and higher concentration of carbonate ion. When supersaturation was reached, the calcite began to precipitate. Abundant calcite was deposited in the Lake Ombilin as revealed by the higher amount of Ca in the lower part profile. Under such lake development, the sediment would be abundant in autochthonous input.

As the development of Lake Ombilin progressed, the lake underwent successive decreasing of trophic level. During deposition of upper part of the drill core, fewer photoautotrophs lived in the lake. Relatively normal concentration of dissolved  $\text{CO}_2$  led fractionation of carbon isotope, as most of the organisms fixed lighter carbon of  $\text{CO}_2$ . The biomass of the organisms and the deposited organic matter would therefore be depleted in  $^{13}\text{C}$ . The amount of organic matter accumulation was also lower. These are shown by more negative of  $\delta^{13}\text{C}$  values and lower amount of TOC in the upper part of drill core. The pH and carbonate ion were not as high as those during deposition of lower part of the drill core. Such condition resulted lower amount of calcite precipitation and deposition as indicated by lower concentration of Ca in upper part of the drill core. Under such development, the Lake Ombilin sediments would be less in autochthonous input.

### CONCLUSIONS

Geochemical analysis of the lacustrine Sangkarewang oil shale revealed two opposite trends of elements abundance along the drill core profile. The abundances of elements commonly associated with detrital material (Si, Al, K, and Ti) show generally upwards increasing variation, suggesting that terrigenous input was relatively increasing during the development of the former lake. On the other hand, the abundances of elements considered to be closely related with aquatic processes (S, TOC, and  $\delta^{13}\text{C}$  of bulk organic matter)

exhibit generally upwards decreasing variation, indicating that autochthonous input was relatively decreasing during the former lake development.

Petrographical analysis found that calcite is abundant in the oil shale. Calcite is the only Ca containing mineral found significantly in the samples. Along the drill core profile, Ca abundance varies in the same way as those of S, TOC, and  $\delta^{13}\text{C}$ , suggesting that Ca, as well as calcite, represents autochthonous input in the oil shale. The occurrence of calcite is considered to be controlled by primary productivity variation during development of the former Lake Ombilin. When the lake underwent higher primary productivity, which could be reconstructed by more positive of  $\delta^{13}\text{C}$  value, the lake water would be less of dissolved  $\text{CO}_2$ . Such condition will lead to higher pH of the lake water and carbonate ion concentration. When the carbonate ion supersaturation was reached, authigenic calcite would be precipitated to the lake sediment.

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