Clay minerals in the sediments as useful paleoclimate proxy: Lake Sentarum case study, West Kalimantan, Indonesia

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Abstract. Lake Sentarum is a flood-plains lake that will dry and flood as climate cycle that is interesting to be studied climate change from the past to near the present. The objective of this study is to reveals paleoclimate conditions by analysing clay minerals that present in the lake sediments. The study investigated clay mineral in lake sediments from 70 cm long core, X-RD analysis was obtained to identify various of clay minerals. The clay minerals of Lake Sentarum comprises of illite, chloride, and kaolinite. The relative change in abundance of clay minerals indicating climate conditions, besides numbers of chemistry and crystallinity of illite represents weathering mechanism. Our research reveals that climate history of Lake Sentarum from sediments core began cold and arid climate episode. This episode was characterized by low value of illite chemistry and illite crystallinity were 0.37-0.41 and 0.19°Δ2θ-0.2°Δ2θ, respectively, and slight decrease abundance of kaolinite. There was no significant changes until the middle of the sediments core. Significant changes of abundance of kaolinite and illite chemistry occurred in top of the core. The percentage of kaolinite and illite chemistry became the highest value that reflected strong chemical weathering occurred in the watershed with warm and high rainfall climate conditions.

1. Introduction
Clay minerals have been widely used to study paleoclimatic and regional paleoenvironmental reconstructions [1,2,3,4,5]. Variations of clay minerals in the sediments often reflect climatic changes particularly in tropical environments with efficient chemical weathering. In cold temperate, clay minerals are useful as source indicator [6]. Lacustrine clay minerals can be very important to understand the lacustrine processes responsible for deposition and alteration of the sediments [7]. A study has been conducted in the Lake Sentarum Wildlife Reserve of West Kalimantan, located in the central part of the Island of Borneo (Fig. 1). Lake Sentarum take 800 km² in upstream area of Kapuas River is bounded by mountainous areas, mainly by Kapuas Mountain in northern part, and Muller in eastern part [8] (Fig. 1). Land use changes and cultivations around the lake continue to increase, where natural forests are transformed into palm plantations. In 2013, it was reported that total of forest area was 2320 km², and it kept on decreasing to 143 km² within a period of 12 years [8].

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Lake Sentarum is a flood plain lake, which often floods during wet seasons when incoming rivers fill 80 lakes (6-14 meters water depth), instead partially or totally drain during dry periods [9]. Upper Kapuas River area experience wet tropical climate with annual rain fall 4000 mm [9]. Flood plain lake is example ecosystems that affected by meteorological factors. The objective of this study is to analyze paleoclimate using clay minerals as proxy indicators. To address this, sediments core was analyzed to define the clay types deposited and their weathering characteristic. Afterwards, clay mineralogy is used to untangle paleoclimate in Lake Sentarum.

2. Geological Setting
Physiography of Lake Sentarum area was divided in two parts, lake district plains and iselberg (Fig. 1). Lake district plains consist of quaternary deposit, the sequent generally contain of clay deposit that was deposited in a long time. Upper part of this sequent was formed during Holocene, which is mostly terrigenous materials from the surrounding forest forming a peat deposit [10]. Iselberg consists of felsic (granitic) rocks formation and mafic rocks formation. Granitic rocks formation was formed in Lower Cretaceous, whereas mafic rock formation was formed during Lower Cretaceous-Upper Jurassic [10].

3. Method
3.1 Study Site
Lake Sentarum is located in upper Kapuas River basin, West Kalimantan Province. Coring site was obtained in Lake Genali center part of Lake Sentarum (Fig. 1). The core was taken by hand coring while Lake Sentarum partially dried in September 2016.

3.2 XRD Analysis and Data Processing
Total 12 selected samples were taken from 70 cm long core for clay minerals analysis. The clay mineral analysis were performed by X-Ray diffraction (XRD) using PANalytical Pro with Cu-Kα radiation on the 2πm fraction. Analysis was conducted in State Key Laboratory of Marine Geology Tongji University, PRC. For the clay fraction the whole sediment was decarbonated with 0.5% HCl. For removal organic matter, samples were treated by 30% H2O2. Samples were mounted as oriented aggregates on glass slide [11].

![Figure 1. (a) Study site map; (b) Geological map of Lake Sentarum area](image-url)

For each sample resulted in three XRD patterns: air-dried (N), glycolated for 24h (EG), and heated at 500°C for 4h (H). Semiquantitative evaluation of the main clay mineral group of illite (10Å),
and kaolinite/chlorite (7Å) were carried out in glycolated conditions [12]. Calculated including peak, intensities, area, and Full Width at Half Maximum (FWHM) using the MacDiff 4.2.5 program. Relative amounts of kaolinite and chlorite were determined on the basis of the ratio from the 3.57/3.54Å peak areas [12].

4. Result

4.1 Illite
Illite (37-46%) was the most dominant clay mineral with an average of 43%. It was characterized by d(001) reflection peak about 10Å, this peak was unchanged in glycolated and heated conditions (Fig. 2). The intensity at 10Å shows that illite has high intensity compared to other minerals along (001) plane. Illite chemistry and illite crystallinity have also been calculated from the X-Ray diffractograms. Illite chemistry was calculated by dividing the areas ratio between illite 001 and illite 002. Illite crystallinity was acquired from FWHM of the 10Å peak [13]. The value of illite chemistry and crystallinity varied between 0.35-0.56, and 0.19°Δ2θ-0.22°Δ2θ, respectively.

Figure 2. Multiple X-Ray diffractograms of the clay fraction (<2µm) of the depths 3 cm (a), 48 cm (b), and 70 cm (c), showing interpretation of major clay mineral from the three types runs, i.e. in air-dried, glycolated, and heated conditions.

4.2 Kaolinite
Kaolinite (21-36%) comprised about 26% in each of sample. Kaolinite was characterized by reflection peak about 7.1Å d(001). It was unaffected under glycolated condition. Kaolinite (001) has the same peak with chlorite (002), although they have different structure and geological occurrence (Fig. 2). For identification these minerals in mixture, most of kaolinites have 002 peak at 24.9°2θ, and chlorite usually has reflection peak at 25.1°2θ. The peak of one of their minerals will sharp if the crystallinities are thick [13].

4.3 Chlorite
Chlorite (26-36%) comprised about 31% in each of sample. It was identified by reflection peak d(001) 14Å. X-ray diffractogram of chlorite under glycolated condition did not change. However, the d(001) intensities became poor under heated condition (Fig. 2). Reduce intensity after heated condition indicative of some primary clay degradation [4].
5. Discussion

5.1 Mineralogical Changes
Clay minerals are weathering products of surrounding rocks formation, variations of clay minerals abundance indicated paleoclimate changes [2,13]. Detrital clay will express weathering conditions in the source [2]. Clay minerals in the Lake Sentarum came from weathering of crystalline rocks formations that consist of igneous and metamorphic rocks.

The clay minerals of Lake Sentarum slightly differed throughout the core sediments. Illite mineral tend has an upward trend to the top of core with maximum percentage of 38%. In several parts abundance of illite went up and down mainly in the middle of the core but not significant (Fig. 3). Illite is considered to be the weathering product of rocks when physical rocks erosion is dominant under cold and dry climatic conditions [11]. Illite could be carried by granitic rocks formation that dispersed around the lake, predominantly were formed by weathering of the muscovite and feldspar minerals.

Kaolinite is shortly found in monosialitic soils [12]. Under warm and humid conditions pedogenic kaolinite is considered secondary mineral derived through chemical weathering of feldspar, mica, pyroxene, or amphibole [4]. Kaolinite in Lake Sentarum is formed by Paleozoic-Tertiary rocks formations. The abundance of kaolinite minerals along the core have many fluctuations particularly in the middle part (Fig. 3). Low percentage found in the bottom, while a significant percentage increased at depth of 25 cm to the surface, it showed how much chemical weathering intensity occurred.

Chlorite is a commonly formed mineral due to physical weathering with low hydrolysis level. Chlorite is generally derived from igneous rocks as an alteration product of mafic minerals such as pyroxene, amphibole and biotite, as well as from the erosion of sedimentary rocks [6]. These minerals are predominantly present in Mesozoic mafic rocks formations [10], which are scattered around the area of the lake. The reflection intensity d (001) of chlorite can be determined by the presence of some heavy metals such as Fe and Mg [6]. Low intensity of chlorite indicates Fe rich chlorite, while high intensity chlorite indicates Mg rich chlorite [5]. The percentage abundance of chlorite in the core showed a fairly dynamic variation in the range of 20-30%. The lowest abundance can be seen in the top of core (Fig. 3).

5.2 Evolution of climatic conditions
Chemical weathering rate in the watershed can be determined by the relative abundance of clay minerals, mechanism of weathering represents climate conditions [2]. Relative abundance of chlorite and illite were considered to relatively dry periods, whereas the humid condition lead more intensive of chemical weathering therefore kaolinite will dominance [11,14]. Moreover, kaolinite/illite (Ka/Il) ratio can also be used as a chemical weathering indicator, high Ka/Il ratio indicate strengthened chemical weathering and weak physical erosion, and contrary when the ratio is low [12].
Crystallinity and chemistry of illite can provide information related to weathering conditions, which are very sensitive to climate changes [16]. Illite chemistry ratio below 0.5 represents the rich illite of Fe and Mg, which is characteristic of the physical process of erosion, whereas a value above 0.5 indicates Al rich illite that formed in strong hydrolysis process [2,3,11]. Illite crystallinity is mainly controlled by crystal thickness that generally showed a weathering mechanism, low illite crystallinity associate with poor chemical weathering, which is formed at low temperature and rainfall [17]. Based on those factors, three zone could be distinguished (Fig. 4).

Figure 4. Down core variations of illite crystallinity, illite chemistry, and kaolinite/illite (Ka/Il) ratio.

The illite chemical ratio in all zone showed a low average value of 0.43 (Fig. 4). The lowest illite chemistry found in zones A and B (Fig. 4). Zone A has a range of illite chemistry 0.37-0.41, and zone B has a range of 0.35-0.46. Further, illite crystallinity revealed similar condition that Zone A has a low illite crystallinity, where the average was the lowest compared to other units (0.19°Δ2θ). It demonstrated that the climate of its formation at that time was low temperature and rainfall, which will cause weak chemical weathering, but increased in physical weathering. In zone A was also indicated by upward trend of chlorite, vice versa downward trend of kaolinite up to boundary of Zone B, this showed the climate were very dry and arid among other units. Previous research was conducted [9], through analysis of pollen abundance in Lake Pemerak one of parts of the Lake Sentarum, revealed similar conditions that the climatic at that time were dry and arid caused of last glaciation maximum.

Illite chemical in Zone B shows a low value ranging from 0.35 to 0.46. The climatic conditions of this zone were still arid and dry. Although, there were slight increase of illite chemical and kaolinite at the top of this zone, indicating that chemical weathering was beginning to increase slightly to Zone C. Zone C was characterized by significant rates of illite chemistry with a range of 0.43-0.56. Particularly at the top of this zone was > 0.5, where Al rich illite formed due to strong hydrolysis. Strong hydrolysis is caused by high rainfall and warm climate. In addition, Ka/Il ratio and kaolinite abundance are quite significant increased up to the top of this zone, while the abundance of chlorite tends to decrease, it would be related to the current warm climate triggering an efficient hydrolysis.

6. Conclusion
Lake Sentarum sedimentary record showed abundance of clay minerals that consists of illite, chlorite, and kaolinite. The changes in their relative abundance, illite chemistry, and illite crystallinity reflect changes in forming mechanism, and climate conditions particularly in Lake Sentarum watershed. Strong physical erosion occurred in the bottom of core sediment that reflect arid and dry climate. Another conditions take place in the top of core sediments, climate were dominated by high rainfall and humid conditions, thus generated strong chemical weathering.
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