Geochemical Approach to Reveal The Genetic Occurrence of Gibbsite, Relative to The Parent Rock Type in Lateritic Bauxites

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Abstract. Situating in a tropical climate, will be favourable for Indonesia and Malaysia to have an intensive weathering and a concentration of lateritic bauxite. The study area takes place in Kuantan, Pahang State, Malaysia and Landak area, West Kalimantan, Indonesia. The study area has different type of parent rock, topography and drainage condition, which will also cause the different characteristics of alumina minerals in bauxite. One of the common form of alumina minerals is known as Gibbsite [Al(OH)₃]. The objective of this research is to investigate the genesis of gibbsite from two different parent rocks. Samples were taken and collected from pitting, analyzed for Al₂O₃, Fe₂O₃, SiO₂ and TiO₂ using XRF and XRD examination. The parent rock of bauxite in Kuantan is basalt, meanwhile, in Landak, ranges from granodiorite to andesite. Petrography and XRD analyses of Kuantan bauxite shows predominant gibbsite, with minor amount of goethite, hematite, kaolinite, illite, quartz and feldspar, while in Landak, minerallogically consists of variant amount of gibbsite, goethite, hematite, kaolinite, illite and quartz. In Kuantan, the amount of Al₂O₃ varies from 23.6% - 51.01%, nearly similar than that in Landak that varies from 31.35% - 55.03%. Gibbsite in Kuantan is assumed as a transformation of Ca-rich plagioclase and Ferromagnesian- silicate minerals, on the other hand, gibbsite in Landak was produced from direct weathering of primary Al- silicate minerals (Na- plagioclase and K-feldspar). From study, it can be inferred that gibbsite formed from a layer of silicaties and will concentrated in finer clay as a weathering product. Moreover, the different types of parent rock will produce different types and amount of alumina minerals. The study will be beneficial to predict the existence of potential alumina minerals in lateritic bauxite.

1. Introduction
About 90% of the bauxite has often been mined to fulfill the needs of aluminium industry. As a raw material for aluminium industry, bauxite consists chiefly of aluminium hydrate or hydroxide minerals. The bauxite exploration in Indonesia has had a long history, where it first started in 1924 and experienced in Kijang, Bintan Island, Riau Province [1]. Thirteen years later, in 1937, the existence of bauxite in Kuantan, Pahang State, Malaysia was first discovered by the Geological Survey [2]. The bauxite occurrence in Kuantan area is underlain by basalt.
In Malaysia, research area lies in the neighbourhood of Kuantan, between Pahang and Terengganu States. The study area in Kuantan is allocated around Bukit Tanah Merah at Tanjung Gelang; Jabor in the Kemaman district of Terengganu and Bukit Goh Estate (Figure 1). The studied bauxite deposit in West Kalimantan, Indonesia, is located in Landak area (Figure 2). Lateritic bauxite in West Kalimantan extends in Northwest – Southeast direction along the Ketapang, Sanggau, Landak, Kubu Raya, Pontianak, Bengkayang and Singkawang areas. The elongated existence of lateritic bauxite is termed as laterite belt.

Figure 1. Regional geological map of Kuantan area and geological cross section of the Kuantan basalt. Study area is plotted as circle number in the map. Figure has modified from [2].
The discovery of bauxite in Malaysia and Indonesia brings up numerous investigations to identify the parent material and tracing the genetic history of bauxite ore (gibbsite – $\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}$). Few studies concern on the genesis of gibbsite that commonly observed in lateritic bauxite. This paper will discuss about the genesis of gibbsite using petrography and geochemical approach.

2. Method
Field investigation was carried out through pitting, auger drilling as well as quarry and road-cuts examination. The total depth of holes are ranging from 5 to 10 m in Kuantan, Pahang State and a constant depths of 10m in Landak, West Kalimantan. The width and length of pit hole is 1m x 1m. Channel sampling method was applied, where samples were collected at 2 m intervals and vertically logged. Samples were washed to removed silica content, analyzed petrographically, as well as XRD and XRF examination. To determine the name of parent rock, texture and mineralogical composition, 44 samples were analyzed petrographically. Approximately 66 samples were analyzed using XRF to identify some major oxide (i.e. $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{TiO}_2$, $\text{R-SiO}_2$ and $\text{T-SiO}_2$) and 44 samples were analyzed using XRD, in order to led the discovery of a complex minerals.

3. Regional Geological Setting

3.1. Regional Geology
Granitoids occupy the North and Northwest of Kuantan, Pahang State, Malaysia, with characteristics of grey in color, comprising of porphyritic and non-porphyritic granite. Diabase/dolerite is present as an intrusion formed in Early Cretaceous age (Bignell & Snelling, 1977). Dolerite rock is assumed as the assimilation result of granitic material by the basic magma. The parent rock of bauxite in Kuantan, Pahang State, Malaysia refers to the volcanic series of basalt flows formed in Pleistocene (Quaternary). Basalt outcrops surrounds the granitic hills. The basalt shows black to greenish black in color, vesicular and augite to olivine bearing. According to K-Ar radiometric dating, Kuantan basalt has an age [3]. The younger alluvial deposit widely covers the basalt along Sungai Kuantan and coastal areas (Figure 1).

Volcanic series of Gunungapi Raya Formation belongs to the oldest rock of lithostratigraphic unit in Landak area, West Kalimantan, Indonesia (Figure 2). The oldest volcanic series had been formed in Jura to Trias and consisted of altered andesite, dasite, basalt which is enriched by chlorite and epidote, with additional conglomerate as thin intercalation, sandstone and mudstone. Greater part of Landak area is belonging to Mensibau Granodiorite Formation (Cretaceous – Jura) and also known as part of
Singkawang batholith. The Mensibau Granodiorite Formation demonstrates I-type granitoid and consisted of granite, quartz diorite, adamelite and tonalite as an intrusion rocks. The Mensibau Formation is overlaid by Hamisan Formation (Oligocene in age) and comprised of quartz arenite, lithic arenite and coglomerate. The younger aluvial deposits consist of loose materials of mud, sand, pebble and organic remnants.

4. Result and Discussion

4.1. Topography, Vegetation and Climate

The study areas in Kuantan, Pahang State and Landak, West Kalimantan Province are flat to undulating. In Kuantan, the undulating hills have flat tops and low ridges between 30 to 60 m in altitude. The highest point is a basalt outcrop that lies in Bukit Tinggi (136 m), meanwhile, the nearby area is relatively below 15 m and swampy. Most of the study area in Kuantan, Pahang State, Malaysia occupies a low-lying areas with altitude of below 15 m, such as in Bukit Goh Estate, Bukit Tanah Merah (more than 70%) and Jabor (more than 40%). The low lying areas (below 15 m) have successfully produce a fairly intensive lateritic type weathering (with bauxite thickness ranges from 1 to 2m). A large area of Kuantan is cultivated with oil palm and rubber. It is characterized by high tree. In Kuantan area, West Malaysia, rainfall against dry season occurs in a short period, about 4-5 months with annual rainfall average ranges from 2.540 mm to 3750 mm and annual mean temperature of 27 °C.

In Landak area, undulating hills cover a large area and have altitude of 25 m to 140 m with relative slopes of 15% - 40%. The highest point (>140 m) is a mountainous complex of Bala, Ambalan, Loncet, Kepayang, etc. with relatively steep sloping of higher than 40%. Along the river, swamp and valley are belonging to low lying areas and have altitude of 10 m to 25 m. Undulating hills are covered by numerous high tree, such as eaglewood tree, timber, rattan, etc, meanwhile, the low lying areas are occupied by cocoa, fruit plants and paddy. The climate is characterized by an annual mean temperature of about 24 – 33°C with annual rainfall average is up to 2460 - 4907 mm. The period of rainfall against dry season distributed over 4-8 rain months and 4-6 dry months.

4.2. Vertical Weathering Profile

The vertical weathering profile of bauxite in Kuantan view illustrates overburden consists of dark brown clayey soil with organic litter commonly varies from 0.5 m up to 1.5 m depths (Figure 3). The middle horizon is occupied by reddish to brownish lateritic material with thickness about 1 to 7.6 m. The upper part of middle horizon belongs to lateritic iron crust and bauxite zone (with thickness up to 2 m measured from the bottom of overburden horizon). The bauxite zone consists of abundant amount of concretions, pisolithic and nodules, meanwhile the lower section of middle horizon consists of granular to earthy materials. The concretion varies from 0.5 to 10 cm with average size of less than 3.2 cm. Nodules and concretions are embedded in a porous clear matrix. The lower section of middle horizon exhibits brownish residual clay of kaolinite and termed as saprolith. The lateral distribution of bauxite zone differs from the overburden horizon, most of bauxite zone is found restricted or not continuous laterally, while overburden horizon covers a lateral extent.

A vertical weathering profile in Landak area is relatively different in the middle zone. The top zone of middle horizon (below the organic clayey soil) is occupied by yellowish brown to red brick of detrital weathered sediments or named as Laterite Paleosol. The lighter color of yellow is caused by the existence of felsic minerals. Bauxite zone consists of an intense concretion and nodule of red brick bauxite, surrounded by smaller granular bauxite and clay. In a lower horizon of saprolith, whitish kaolinite occupies the top followed by residual fragment of weathering rock as performed by boulder size (≥25cm).
4.3. Geochemical Data
Quantitative results for geochemical analysis indicate high alumina content and were performed in Bukit Goh Estate, Jabor and Bukit Tanah Merah of Kuantan areas, Pahang – Terengganu States, Malaysia, respectively from greater content of bauxite. A fairly high alumina values range from 40 – 51.01%, moderate alumina Al$_2$O$_3$ values range from 30 – 39% and low values from 23.6 to 29%, as performed by samples taken from respective areas of Bukit Goh and Jabor, meanwhile the alumina content in Bukit Tanah Merah ranges from 33% to 44% (Figure 4). All the samples had relatively high iron oxide (Fe$_2$O$_3$) content, varying from 16.59 % - 30%. The highest percentage of iron oxide was performed by samples taken from Bukit Tanah Merah, on the contrary, lesser value was performed by Bukit Goh’s samples. The value of silica (SiO$_2$) ranges from 1.44% (in those derived from basic igneous rocks) to 25% (in the profiles derived from more acid rocks) and it seems decrease as found in the Bukit Tanah Merah (from 1% to 17%). The titanium (TiO$_2$) content in most of representative samples varied from 2.83 % to 5%. All of oxide compound taken from 1 sampling point is performed on Figure 5. A vertical plot of geochemical data through depth (Figure 5) shows negative correlation between Fe$_2$O$_3$ and Al$_2$O$_3$. The increase of Al$_2$O$_3$ (gibbsite) is followed by the decrease of Fe$_2$O$_3$.

Silica (SiO$_2$) is preserved as relict quartz or combined with alumina and termed as Reactive Silica (i.e. kaolinite and halloysite) [4]. Alumina (Al$_2$O$_3$) in saprolith and bauxite zone becomes enriched respectively in kaolinite and gibbsite. The free alumina content rely on the grain size of quartz and kaolinite. The iron content reflects the type of parent rocks. Titanium (TiO$_2$) presents incorporated with amphiboles and biotite as well as additional primary Ti-minerals (ilmenite, rutile, sphene).

Bauxite in Kuantan, which is characterized by high ferric oxide content is termed as ferruginous bauxite [5]. The study area in Bukit Goh Estate is present as the most promising location for ferruginous bauxite. Quartz and kaolinite are abundant in low-grade bauxites or having high SiO$_2$. 

Figure 3. The vertical weathering section of bauxite profile in Kuantan area, Pahang – Terengganu States, Malaysia.
Figure 4. Distribution map of alumina (Al$_2$O$_3$) in neighbourhood Kuantan, between Pahang and Terengganu States, Malaysia. Courtesy of PT. ANTAM, Tbk., Unit Geomin.

Figure 5. Distribution map of alumina (Al$_2$O$_3$) in neighbourhood Kuantan, between Pahang and Terengganu States, Malaysia. Courtesy of PT. ANTAM, Tbk., Unit Geomin.

In Landak area, West Kalimantan, Indonesia, samples were taken from middle horizon, in every 2 meters from the top of middle horizon and downward. Quantitative results from total 90 samples show a fairly high alumina values range from 40.12% - 55.03% and moderate alumina with Al$_2$O$_3$ values range
from 31.35 – 39.73%. Since most of granitoids occurred as parent rock, silica content is relatively higher than iron oxide. The value of silica (SiO$_2$) ranges from 5.67% (in those derived from Andesite) to 49.34%. The low content of iron oxide (Fe$_2$O$_3$) ranges from 4.19 to 17.69%. The value of TiO$_2$ is following the number of biotite and most of the samples have value <1.17% (Figure 6). Based on figure 5 and 6, the decreasing of TiO$_2$ from bottom to top is always followed by the increasing of Al$_2$O$_3$ or bauxite formation as supported by negative correlation between TiO$_2$ and Al$_2$O$_3$.

4.4. Mineralogical Evolution

Petrography and XRD analyses confirm that resistant/ relict minerals occurred together with neogenetic minerals. The relict minerals comprise of quartz, magnetite, trace of ilmenite and sphene, meanwhile the neogenetic minerals are represented by kaolinite, gibbsite, goethite, hematite, etc (Table 1). The neoformed kaolinite is often shows tiny size and fills voids in the matrix of laterite [6]. Ferruninous bauxite layer as found in Kelantan is constituted mainly of gibbsite, hematite, goethite and minor amount of quartz. On the contrary, bauxite in Landak area comprises of gibbsite, quartz, kaolinite, anatase and illite.

The mafic parent minerals (such as Ca- rich Plagioclase, Amphibole, Pyroxene and Olivine) contain rich in Ca, Fe and Mg elements, meanwhile, felsic parent minerals (such as Quartz, Orthoclase, Na- rich Plagioclase and Muscovite) contain Si, K and Na elements. The stage of mineral transformation into the weathering products is illustrated in Figure 7. The early stage of weathering is initiated with cracking of parent minerals. At the time of cracks are getting large, gibbsite nucleation occurred along the cracks, simultaneously growth in coincided with breakdown and dissolution of unstable minerals. Goethitization can occur in the inner part of pyroxene, biotite and felty amphibole. Gibbsite nucleation still continuous progressively as well as geothitization. Progressive dissolution of unstable minerals have produced neoformed veinlets. At the end, the structure of gibbsite boxwork pseudomorphs was produced, while most of unstable minerals dissolved (as shown by black color, geothite pseudomorphs after pyroxene and felty amphibole were formed and the occurrence of neoformed veinlets. The end product of bauxitization is also well seen under the thin section observation (Figure 8).
Figure 7. The illustration of parent minerals transformation with progressive bauxitization as visible in thin section. In basalt, a: Olivin, b: Pyroxene, c: Plagioclase; in Granitoids, a: K-feldspar, b: Muscovite, c: Plagioclase, d: Quartz. Modified from (Valenton, et al., 1997)

Figure 8. Cross nicol microphotograph of boxwork pseudomorph of bauxite is shown as scatter fibrous. Opaque mineral (MO) is suspected as gibbsite and Fe – oxide as goethite [FeO(OH)] and/ or hematite. Sample is taken from Landak area, West Kalimantan.
Table 1. XRD results of bauxite concretion taken from various parent rock

| Sample No | Mineral Composition | %   | Parent Rock   |
|-----------|---------------------|-----|---------------|
| 1         | Quartz              | 24.8| Syeno granite |
|           | Gibbsite            | 65.46|               |
|           | Goethite            | 0.52|               |
|           | Kaolinite           | 8.5 |               |
|           | Anatase             | 0.73|               |
| 2         | Quartz              | 16.89| Quartz syenite|
|           | Gibbsite            | 72.96|               |
|           | Goethite            | 4.73|               |
|           | Kaolinite           | 5.42|               |
| 3         | Gibbsite            | 71.83| Syeno granite |
|           | Quartz              | 23.38|               |
|           | Kaolinite           | 2.11|               |
|           | Goethite            | 2.68|               |
| 4         | Quartz              | 46.11| Granodiorite  |
|           | Gibbsite            | 21.94|               |
|           | Kaolinite           | 15.66|               |
|           | Muscovite           | 1.01|               |
|           | Anatase             | 1.44|               |
|           | Illite              | 13.84|               |

4.5. Genesis

Feldspar presents as the source of Al in the parent rock. Feldspar is a kind of mineral that easily altered as affected by weathering. In the saprolith zone of middle horizon, feldspar is pseudomorphically replaced by kaolinite. They tend to be dissolved, partly leached and followed by forming amorphous or poorly crystallized compounds of clarkite. During dissolution, the primary mineral of Albite and/or K-feldspar is easily transformed to kaolinite through following chemical reaction:

\[
\begin{align*}
\text{NaAlSi}_3\text{O}_8 (\text{Albite}) + 4\frac{1}{2}\text{H}_2\text{O} + \text{H}^+ &\rightarrow \text{Na}^+ + 2\text{Si(OH)}_4 + \frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{Kaolinite}) \\
2\text{KAlSi}_3\text{O}_8 (\text{K-feldspar}) + 2\text{H}^+ + 9\text{H}_2\text{O} &\rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{Kaolinite}) + 4\text{H}_4\text{SiO}_4 + 2\text{K}^+ 
\end{align*}
\]

The weathering process still continued through dissolution, releasing Na\(^+\) and soluble silica downward and will produce gibbsite as an alteration end-product at bauxite zone, as shown by following reaction:

\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{Kaolinite}) + 5\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 (\text{Gibbsite}) + 2\text{H}_4\text{SiO}_4 (\text{Soluble Silica})
\]

The ratio of Si : Al in feldspar is 3 : 1, and through weathering process, this ratio will be reduced to 1 : 1. Nearly similar to K-feldspar, muscovite has a short chemical reaction to produce gibbsite due to
its weaker chemical bond. Based on the reaction above, gibbsite preserved as the highly insoluble aluminum hydroxide that typically found in highly weathered of tropical soils. The element of Si (derived from Quartz and other silicate minerals) still remains in relict minerals, whereas other elements are washed out rapidly and leached easily (such as Ca, K, Na and Mg). The element ability to be washed out and leached easily depends on its mobility and soluble character. The pH factor is also controlled bauxite formation, normally bauxitization needs pH higher than 4 and Eh of lower than 4 [8].

Basic igneous parent rock will composed predominant Ca- rich Feldspar and Ferromagnesian minerals (such as amphibole, pyroxene and olivin as found in the Kuantan area). Ferromagnesian minerals as well as volcanic glass have devitrified chiefly to montmorillonite (or smectite, in general) [9]. Smectite which is saturated with H$^+$ will decomposes respectively to kaolinite, gibbsite and hematite as the end- product. Detail transformation process of each parent mineral to the end-product of gibbsite, goethite and or hematite is illustrated in Figure 9.

A condition of free, unimpeded, rapid drainage and desilication beyond kaolinite is suspected formed the gibbsite. Al- goethite and gibbsite are the main Al- bearing mineral of alteration product.

5. Conclusions
The comparison study of bauxite derived from basic and acid igneous parent rock, respectively from Kuantan, Pahang State, Malaysia and Landak, West Kalimantan Province, Indonesia has improved the understanding about the quality of bauxite from different parent rock. Bauxite in Kuantan is formed as a result of weathering of the basalt, whereas bauxite in Landak is derived from various granitoid rocks. Most of the bauxite deposit exhibits horizontal beds or blanket- like deposits. The high-grade bauxite in the study areas is defined somewhat arbitrarily. Kuantan bauxite consists of the hydrous aluminum oxides in forms of gibbsite as much as 23.6% - 51.01%, meanwhile Landak’s bauxite contains 31.35% - 55.03%. Alumina content in granitoids, derived from Na- rich feldspar, feldspathoid, muscovite and/or biotite minerals, contributes to the development of gibbsite earlier than gibbsite formation from mafic minerals (such as Ca- rich feldspar, pyroxene, amphibole and olivine). Felsic parent minerals are undergone dissolution, formed kaolinite and subsequent gibbsite through hydrolysis of kaolinite. On the other hand, mafic parent minerals (including Ca- feldspar) are undergone dissolution, transformed to smectite – kaolinite and produced gibbsite and goethite as end products of bauxitization. The most important control on the genesis and distribution of lateritic bauxite in the
study area is subsurface drainage. Water percolation through the faulted and fractured parent rocks is extremely efficient in leaching silicate and concentrating the aluminium in the form of gibbsite.

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