The potential of lithium enrichment in Lapindo Brantas, Mount Anyar, and Buncitan Mud Volcanoes, Sidoarjo District, East Java Province

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Abstract. Lithium is an alkaline, metallic element found primarily in the earth's crust and seawater. Recently, the industry's need, especially lithium batteries, has been increasing. Lithium exploration is directed to various geological environments that have the potential to contain lithium. Based on previous research, mud products from mud volcanoes can contain lithium. We conducted this research to determine the potential for lithium enrichment found in mud produced by mud volcanoes in Lapindo, Mount Anyar, and Buncitan. Samples were prepared to analyze petrography, X-ray diffraction (XRD), ICP-MS, and ICP-AES. Mineralogically, the mud sample comprises smectite, kaolinite, quartz, plagioclase, clinopyroxene, calcite, pyrite, and dolomite. Lithium in the mud sample has an average concentration of 92.5 ppm with the highest concentration of 130 ppm from the Lapindo Mud volcano. The lowest concentration of 70 ppm comes from the Buncitan Mud Volcano sample. Based on its mineralogy and structure, the dominant of smectite and kaolinite clay minerals can bind the lithium. Lithium in the study area is thought to come from altered rocks below the surface, which migrate and are bound to clay minerals predominantly found in subsurface mud.

Keywords: lithium enrichment, mud volcano, Lapindo Brantas, Mount Anyar, Buncitan.

1. Introduction

Elemental lithium is the lightest metal element and the densest of all the non-gaseous elements at 20°C and can float in water [1]. This element is not found freely in nature but is found in compounds with other minerals. Lithium is found in igneous rocks such as pegmatite, brine water, and clay minerals from hydrothermal alteration. The use of lithium in the industry is quite diverse. Lithium is an essential component in digital device and electric car batteries. Apart from the battery industry, lithium is also used in the metallurgical, ceramic, and glass industries, polymers, and health [2].

The potential for lithium sources in Indonesia is still open. One of the previous studies was carried out at BledugKuwu Mud Volcano by Rohmah et al. [3] by testing the mud's lithium content. Lithium content is found in montmorillonite clay minerals with a concentration of 29 ppm in wet conditions. Based on the research of Rohmah et al. [3], lithium has the potential to be found in mud from the natural phenomenon of mud volcanoes. Mud volcanoes are the appearances of a cone-shaped topography that occurs naturally from the materials below the earth's surface and consists of fine mud, liquid, and gas [4]. Lapindo mud is one of the largest mud sources that emerged in 2006 in the Kendeng Zone and the North Coast Alluvial Plains Zone [5]. Apart from Lapindo mud volcano, several other mud volcanoes are found, such as Mount Buncitan and Mount Anyar. This phenomenon
produces mud products that can be utilized. The waste materials in the form of mud from mud volcanoes in the future can be a potential source of lithium.

Based on Tanikawa study [6], he concluded that Lapindo mud can contain lithium. The type of lithium-bearing clay minerals, the lithium concentration, and lithium enrichment in the mud have not been studied yet. Therefore, this research will test the lithium content in the mud in 3 locations that have never been carried out in previous research, namely in Lapindo Mud, Mount Anyar, and Buncitan, Sidoarjo, East Java. By knowing the lithium concentration and the mud mineralogy, we will know the possible factors controlling the lithium enrichment in the Lapindo mud volcano. With this research, it is hoped that lithium in volcanic mud in the Sidoarjo region can be identified and used in industry.

2. Geological setting

According to van Bemmelen [5], the research area belongs to the eastern Kendeng Zone and the North Coast Alluvial Plain Zone based on the physiographic division of eastern Java. The Kendeng Zone is characterized by a series of low hills with undulating morphology, with an altitude of 50–200 meters. The North Coast Alluvial Plain Zone is straight with 0–100 m with a relatively flat slope.

The research area's stratigraphy is based on the Regional Geological Map of the eastern part of the Surabaya and Sapulu sheets [7] and the northern part of the Malang sheet [8] (Figure 1). It is composed of the Lidah Formation from the Late Pliocene, which extends to the Pucangan Formation area. The Kabuh Formation is found in the north of the research area with sea facies and gradually changing to land facies, which is thought to be in conformity with the Jombang formation, and an unconformity with Quaternary volcanic rocks. Volcanic activity is located on the southern side of the study area. It is known to originate from the Lower Quaternary Volcano Formation, namely from Gendis Volcano rocks, Jombang Volcano rocks, and Anjasma Muda volcanic rocks from the Middle Pleistocene. The Tuf Rabano Formation, namely from the rocks of Tengger Volcano, Arjuna Welirang Volcano, and Ringgit Volcano come from the Late Pleistocene-Holocene Period. The Upper Quaternary Volcano Formation, namely from the Penanggungan Volcano and Panderman Volcano, come from the Late Pleistocene-Holocene Period.

The research area is belong to the Java Island Central Depression Zone, which was formed due to the Eurasian plate's collision with the Indo-Australian plate. According to van Bemmelen [5], geological data show that the stratigraphy and tectonics of the eastern Kendeng Zone are still in an evolving state (tectonic processes are still ongoing). Duyfjes (1938, in Waluyo et al. [9]) concluded that the Gujangan anticline in the Porong area was intersected by a transversion fault with a descending eastern part. The Gujangan Fault is a sign of a transition between the tip of the Kendeng Zone, which falls in the Porong Delta, and the Madura Strait, which is still decreasing and filled with sediment, has not been folded. Along the central depression zone, the mud volcano phenomenon can be found in the Sidoarjo area, namely Lapindo Mud, Mount Anyar, and Buncitan mud volcanoes. Based on Putrohadi's research in Setiadi et al. [10], Sidoarjo mud originates from the Kujung Formation, the oldest formation in the Rembang mandala. The mud from the Kujung Formation under high pressure flowed upward by grinding the Pucangan Formation's claystone. This mudflow then penetrates the Watukosek fault zone, which passes through the Sidoarjo area.
3. Methods
The study consisted of 8 samples of mud, with 5 mud samples collected from the Lapindo Mud Field, 1 mud sample from the Mount Anyar Field, and 2 mud samples from the mud volcano field in Buncitan Village. The analysis carried out in the study consisted of mineralogical analysis in the form of petrography and XRD and geochemical analysis in the form of ICP-MS, and ICP-AES. The petrographic analysis was carried out on 4 samples, divided into 2 fractions, namely the fraction <63 μm with a centrifuge and the fraction 63–125 μm. XRD, ICP-MS, and ICP-AES analyzes were performed on all samples. XRD analysis was carried out at the Central Laboratory, Geological Engineering Department UGM, while ICP-MS and ICP-AES were carried out at ALS Chemex, Canada. The analytical results were used to assess the mud’s mineralogical and chemical
characteristics, the concentration of lithium in the mud, and the factors causing the enrichment of lithium in the mud at Lapindo Mud Field, Mount Anyar, and Buncitan Village.

4. Results and Discussion
4.1. Mineralogical characteristics
Based on petrographic observations of thin slices of fraction <63 μm, it was found that the mineralogical composition of the mud samples included clay minerals, carbonate materials, plagioclase, quartz, opaque minerals, and pyrite. In the 63–125 μm fraction, the mineralogical composition was found, including clay minerals, carbonate materials, quartz, opaque minerals, plagioclase, and clinopyroxene (Table 1).

| Sample code | Fraction <63 μm                                                                 | Fraction 63–125 μm                                                                 |
|-------------|--------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| L-3B        | Clay minerals, carbonate material, quartz, opaque mineral                      | Clay minerals, clinopyroxene, quartz, plagioclase, opaque mineral, carbonate material |
| L-5B        | Clay minerals, plagioclase, carbonate material, opaque mineral                 | Clay minerals, carbonate material, quartz, opaque mineral                          |
| L-6B        | Clay minerals, pyrite, plagioclase, carbonate material, opaque mineral         | Clay minerals, carbonate material, quartz, opaque mineral                          |
| L-BA        | Clay minerals, carbonate material, plagioclase, opaque mineral                 | Clay minerals, carbonate material, quartz, opaque mineral                          |

In the sample fraction <63 μm, the dominant clay minerals compose with a percentage of 57–75%, followed by 7–13% carbonate material, 7–10% opaque minerals, and 7–20% plagioclase. In one sample, quartz minerals with a percentage of 8.33% and pyrite with a percentage of 22% were found. In the 63–125 μm fraction of the sample, clay minerals continued to dominate with a percentage of 40–50%, followed by 11–14% quartz, and 9–14% opaque minerals. Also, in one sample, plagioclase minerals were found with a percentage of 11% and pyroxene 23%. Carbonate material in the form of foraminifera fossils were found with a percentage of 6–29%.

Based on XRD analysis, the mud sample's mineralogy consists of smectite, kaolinite, quartz, plagioclase, calcite, dolomite, and pyrite minerals (Figure 2). Smectite mineral is a clay mineral that dominates the sample, followed by kaolinite. The smectite clay minerals in the study area were formed by the feldspar diagenesis [11]. Kaolinite minerals were formed by weathering or hydrothermal alteration of aluminosilicate minerals [12].

The carbonate material, namely calcite, dolomite, and foraminifera fossils, is thought to have originated from the lithology of carbonate sedimentary rocks around the study area (Putrohadi in Setiadi et al. [10]). Meanwhile, the research sample's volcanic material is thought to come from volcanic activity around the research area [8].

4.2. Geochemical characteristics
Based on the results of the analysis using the ICP-MS and ICP-AES methods, the dominant mud samples were enriched by the main oxide compounds SiO₂, Al₂O₃, and Fe₂O₃, with a concentration range of SiO₂ 47.1–60.8 wt.%, Al₂O₃ 13.35–20 wt.%, and Fe₂O₃ 6.63–12.9 wt.%. CaO were found with a concentration range of 1.64–3.12 wt.%, MgO 1.55–2.33 wt.%, Na₂O 1.92–2.85 wt.%, K₂O 1.06–1.6%, Cr₂O₃ 0.006–0.014 wt.%, TiO₂ 0.7–1.22 wt.%, MnO 0.09–0.15 wt.%, P₂O₅ 0.09–0.16 wt.%, SrO 0.03–0.12 wt.%, and BaO 0.02–0.05 wt.%. 
The dominant content of $\text{SiO}_2$ in the mud samples comes from quartz, feldspar, and clay minerals [13]. The high levels of $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, and $\text{K}_2\text{O}$ are thought to be related to the abundance of clay minerals present in the sample. Besides, the $\text{Na}_2\text{O}$ content is principally related to the presence of plagioclase feldspar. The opaque minerals present in the sample are related to $\text{TiO}_2$, dolomite minerals are related to the abundance of $\text{MgO}$, and calcite minerals are related to the abundance of $\text{CaO}$ in the sample [13]. The highest concentration of trace elements in the sample, namely $\text{Sr}$ reached 1065 ppm, element $\text{Ba}$ reached 425 ppm, element $\text{V}$ reached 360 ppm, and $\text{Zr}$ reached 248 ppm.

![Mineral identification from XRD results for all samples based on random oriented measurement.](image)

**Figure 2.** Mineral identification from XRD results for all samples based on random oriented measurement.

### 4.3. Lithium concentration

The lithium concentration in the mud sample can be seen in Table 2. The average concentration of lithium in the study area sample reached 92.5 ppm. The average concentration of lithium in the sample is above the average concentration of lithium in the earth's crust, which is 17–20 ppm [14].

| Sample code | Li (ppm) |
|-------------|----------|
| L-1B        | 90       |
| L-2B        | 80       |
| L-3B        | 130      |
| L-4B        | 90       |
| L-5B        | 100      |
| L-6B        | 90       |
| L-BA        | 90       |
| L-BB        | 70       |
| **Average** | **92.5** |
The average concentration of lithium in the study sample, compared to the lithium concentration from several world brine water sources (Figure 2), is still classified as low. The economical range of lithium-containing brine sources in the world is 200–4000 mg/l [15].

![Figure 3](image)

**Figure 3.** Bar diagram of comparison of lithium concentrations from mud samples in the study area with several sources of lithium in the world (Houston and Gunn [16]; Anson Resources [17]; Tang *et al.* [18]; Starkey [19]; Evans [14]; Sari *et al.* [this study]).

Based on its distribution, the highest lithium concentrations in the Lapindo mud are found on the eastern and northern sides of the mudflow center, while those on the south side tend to be further from the center of the eruption, have lower concentrations (Figure 4). In the mud samples from Mount Anyar and Buncitan, the lithium concentrations were found to be the same (Figure 5).

### 4.4. Lithium enrichment

Lithium is not found freely in nature but is found in compounds with other minerals. Weathering causes lithium to be released from its binding minerals. Lithium results from the weathering process can form sediment or bond in clay minerals, such as smectite, kaolinite, illite, and fibrous clay minerals. Lithium in clay minerals appears as impurities, inclusion materials, trapped in lattice structures, adheres to the surface of clay minerals, or become the isomorphic substitution of an element [20].

In research samples, lithium can be found in all mud samples containing kaolinite and smectite clay minerals. The dominant clay minerals compose the mud with a percentage based on petrography and XRD. Sample L-3B is a mud with the highest lithium concentration at 130 ppm. This sample is dominated by clay minerals smectite and kaolinite. The smectite mineral in the L-3B sample based on XRD has a relative percentage based on the semi-quantitative calculation of 27.3%, and kaolinite is 9.1%. The L-BB sample was a mud sample with the lowest lithium concentration at 70 ppm. The mineral content of smectite and kaolinite in the L-BB sample has a relative percentage based on semi-
quantitative calculations, which tend to be lower than the other samples, namely 20% smectite 13.3% kaolinite.

Figure 4. Map of the distribution of lithium concentrations in mud samples at Lapindo Mud Volcano. The sampling location is marked with a yellow circle symbol (○).

Figure 5. Lithium concentration distribution map in mud samples in a) Mount Anyar Mud Volcano and b) Buncitan Mud Volcano. The sampling location is marked with a yellow circle symbol (○).
According to Güven [20], smectite with lithium content is formed due to ion substitution. Ion substitution can occur between lithium and Al, Mg, and Fe. Lithium content is also found in the form of oxide compounds bound to the surface of kaolinite through an adsorption process [21]. Based on plotting between lithium and oxides of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, Na$_2$O, CaO, MgO, K$_2$O, and TiO$_2$ from all mud samples, it is known that the correlation between lithium concentration and the percentage of oxide in the sample is known.

4.5. Model of lithium enrichment

The source of lithium in the study area is thought to come from rocks altered beneath the surface, which cause the release of lithium from its binding minerals. Lithium released from bound rock undergoes migration and is bound to clay minerals predominantly found in subsurface diapir. In the research area, which is included in the depression zone of East Java, mud diapir is easily found beneath the surface due to an overpressure process that causes the rock layers to bury and form mud.

Subsurface mud migrates to the surface of the ground through fault zones. The mud that has appeared on the surface over time gets a new supply of mud from within the surface and causes lithium to become increasingly enriched in the minerals in the mud, one of which is bound to or undergoes ion substitution with clay minerals found in the sample. The study area's lithium enrichment model is illustrated and shown in Figure 6.

**Figure 6.** Lithium enrichment model for mud volcanoes in the study area.
5. Conclusions
Mineralogical characteristics of the mud consist of smectite, kaolinite, quartz, opaque minerals, calcite, plagioclase, dolomite, pyroxene, and pyrite. Chemically, the mud comprises dominant oxide compounds SiO$_2$ 59.47%, Al$_2$O$_3$ 20.24%, and Fe$_2$O$_3$ 9.32%. The highest concentration of trace elements was found in Sr 1065 ppm, Ba 425 ppm, V 360 ppm, and Zr 248 ppm. Morphologically, the mud sample has an irregular-agglomeration appearance with few pores, cubic, and flaky.

The lithium concentration in the mud samples of the study area reached an average of 92.5 ppm with the highest concentration in the Lapindo mud sample, namely 130 ppm, and the lowest in the Buncitan mud sample, which was 70 ppm. The dominant smectite and kaolinite clay minerals in the mud act to bind lithium. Lithium in the study area is thought to come from altered rocks below the surface, which migrate and are bound to clay minerals predominantly found in subsurface mud.

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