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Investigation of Physicochemical Properties of Tabin Mud Volcano

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ABSTRACT

Volcano mud is a rare phenomenon found in specific areas, such as Lipad, Sabah, Malaysia, characterized by superficial vents that expel mud and gas flows. This process influences topography, soil properties, ecosystems, and landscapes. Understanding the chemical composition and physical properties of this mud is crucial for assessing rare-earth elements, fluid characteristics, and environmental impacts. In this study, the mud's physicochemical properties were analyzed, revealing a pH of 7, moisture content of 25.17%, and a particle size distribution of 6368 d.nm. Geochemical analysis via Energy Dispersive X-Ray (EDX) identified elements like Oxygen, Silica, Aluminum, Iron, and others, with O and Si being dominant. Rare clinochlore minerals were also detected using X-Ray Diffraction (XRD). The mud exhibited a negative surface charge of -26.5 mV and a unique morphology described as flakes and brittle, differing from typical soil structures as observed by Field Emission Scanning Electron Microscopy (FESEM). Additionally, a high nitrogen compound content of 2.31% was detected, indicating potential gas release of nitrogen and carbon dioxide.

1. Introduction

Tabin Wildlife Reserve is a protected area located in Lahad Datu, Sabah, Malaysia on the island of Borneo. It is known for its diverse wildlife, including elephants, Sumatran rhinoceroses, tigers, and various species of birds and insects. The reserve also contains several mud volcanoes, which are unique geological features formed by the eruption of mud instead of lava. It is also an important location for conservation and research efforts for many endangered species. The Global Positioning System (GPS) coordinates for the reserve are 4.834° N, 118.062° E. It covers an area of approximately 870 square kilometers and is home to a wide variety of plant and animal species. Some of the notable

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species found in the reserve include the Bornean elephant, Sumatran rhinoceros, clouded leopard, and many species of birds and primates.

Tabin Wildlife Reserve is indeed a forest reserve and classified as the Class VII Forest Reserve. It is a protected area that is dedicated to preserving the natural forest and wildlife within its boundaries. The species, many of which are found only in Borneo. It is also an important area for conservation and research, with many studies being conducted on the plants and animals that live within the reserve. The reserve is also a popular destination for ecotourism, as it offers visitors the opportunity to experience the natural beauty of the Bornean rainforest and see some of the unique species that call it home. The remaining of an area of 8,616 hectares of 10% has been retained as Core Area for the reserve and has never been licensed for logging [1].

Mud volcanoes are geological features that can be found on land or under the sea. They are formed when pressurized mud and fluids are forced to the surface through a vent. The chemical composition of the mud and fluids can vary depending on the location of the volcano and the source of the material. Generally, mud volcano fluids are composed of a mixture of water, clay minerals, dissolved gases (such as methane and carbon dioxide), and dissolved salts (such as sodium, potassium, and magnesium). The mud itself is primarily composed of clay minerals, such as illite and smectite, along with small amounts of silt, sand, and organic matter. Trace elements such as sulfur, boron, and lithium may also be present in the mud. It is worth noting that the composition of the mud and fluid can be influenced by the tectonic activity, subsurface fluid chemistry and the local geology of the area. Mud volcano that flows out from beneath the surface of the land are therefore a mineral rich source and consist of a mound of mud and clay containing very high concentrations of calcium, potassium and sodium [2]. Correspondingly, it is found that a mineral rich source forming important natural-licks for animals as a source of salt [3].

This study deepens efforts to find out the contents of chemicals in the Tabin volcanic mud. It is worth noting that the composition of the mud and fluid can be influenced by the tectonic activity, subsurface fluid chemistry and the local geology of the area. The mud volcano fluids can also contain different minerals that are formed due to the alteration of the original rock. The fluids can be acidic, neutral or kaline, depending on the rock formation and the subsurface fluid chemistry. In any event, mud volcano has often been considered as a descriptive term and generically a surface discharge of mud, water and gas [4]. It is also independent of the geological processes, and settings that drive and control the fluid manifestation [4]. In essence, the interaction between fluids with different chemical and isotopic composition, and the properties of the erupted mud (including changes in the density) response to changes of pressure and temperature [4]. Thus, with a naturally challenging development and huge eruption process, this study carries out to inspect the potential of the rare-earth elements present in Lipad mud volcano. In another research study, mud volcanic has relatively elevated Na and Cl concentration compared with other elements [5].

A previous study showed that, Lipad mud volcano has the concentration of Fe and Mn between the inner zone and outer zone were relatively similar while, the concentrations of Mg, Na, Ca and K were higher in the inner zone [1]. The purpose of this research exploration is to understand the chemical content that lead to their formation in inspecting rare-earth elements, the fluids and gases that they release, and the impact they have on the environment.

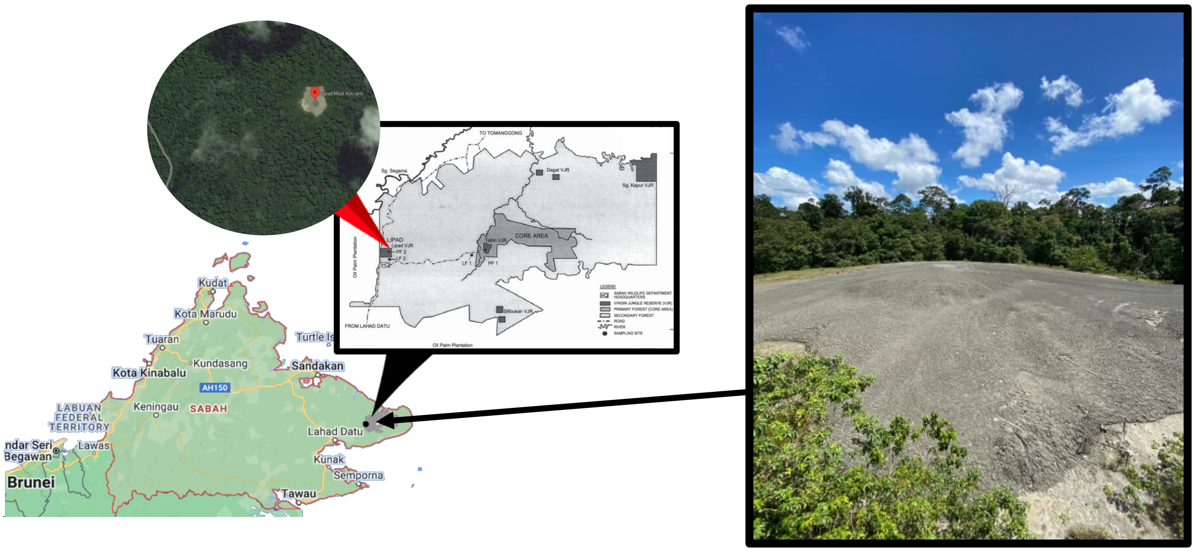


Fig. 1. Tabin Wildlife Reserve and Lipad mud volcano in Lahad Datu, Sabah

2. Methodology

2.1 Sampling Site and Geochemical Analysis Method

Mud from the Lipad Mud Volcano was then transferred to a bottle and sent to the University Malaysia Sabah laboratory in Kota Kinabalu. During sampling, the volcano was observed to be a stable geological formation, constantly bubbling with gas and occasionally erupting with small explosions. The mud pool, surrounded by a small crater filled with water, served as a habitat for various bird species and other wildlife. The mud's physical characteristics were soft and wet, composed of clay, silt, and water, giving it a smooth, slippery texture. When dry, it became hard and crumbly, but when wet, it was soft and malleable, making walking difficult. The research flow is shown in Figure 2.

Three chemical components of the Lipad Mud Volcano were determined. X-Ray Diffraction (XRD) analysis, following BS EN 13925-1:2003, examined the crystal structure by analyzing diffraction patterns. CHNS analysis quantified Carbon (C), Hydrogen (H), Nitrogen (N), Sulfur (S), and Oxygen (O). Zeta potential and particle size distribution were measured using a Zetasizer at Universiti Malaysia Sabah. Moisture content was tested per standard soil methods.

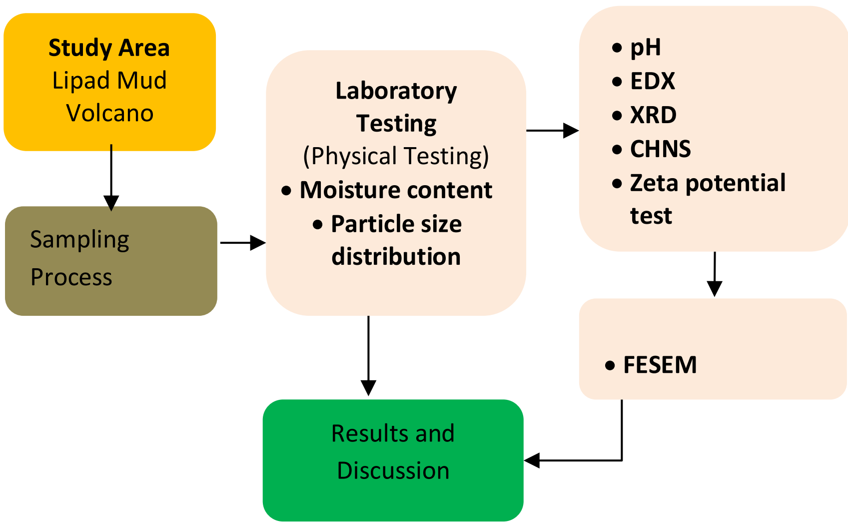


Fig. 2. Sampling details and processing

3. Results

Field Emission Scanning Electron Microscopy (FESEM) used to obtain high-resolution images of a Lipad mud volcano sample's surface. FESEM test results provide detailed information about the sample's morphology, topography, and composition. Based on Figure 3, FESEM images for Lipad mud volcano shows the particle morphology in micron size ranges from 1 ɥm to 10 ɥm with magnification from x500 to x10000. The surface morphology was discovered and revealed the mud surface structure features like flakes, brittle, flat and different from common soil morphological structure.

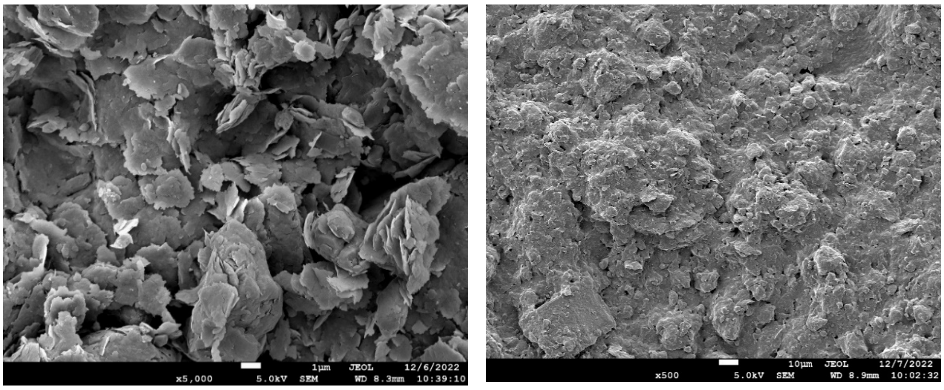
In terms of color, the mud volcano shows grayish fossil colour and the texture are smooth, powdery, superfine and seen pulverized. In natural conditions, Lipad mud volcano is odourless. Furthermore, surface topography described from Figure 3 shows that the surface topography of Lipad mud volcano is smooth, thin and angular. Compared to soil characteristic, Lipad mud volcano was observed as having high ability to hold water and nutrients like salt. Correspondingly, the independent particle structure as seen in Figure 3 in superfine form of non-cohesive soil is believed to be the main factor in contributing to the ability of holding water as nutrients.

Salt is found in Lipad mud volcano in the form of Sodium chloride (NaCl) as depicted in Table 1 which represents small amount of organic composition in Lipad mud volcano. Similarly, the images show the uniformity of particle structure of Kaolin clay soil [8,9]. Thus, soil horizons which are distinct layers in the soil that can vary in thickness, color, and texture observed during this study. Fortunately, the properties and soil classification test showed that the Lipad mud volcano mainly are classified as clay and silty clay loam. Identically, mud volcano from various location in other countries also classified as clay form [10]. The shape noticed are flaky and thin particles. Compared to the organic soil structure [11,12], the horizon structure is contradicted with Lipad mud volcano. As a result, the crystal image of Lipad mud volcano shows independent soil structure and hardly comparable with other soil structure. It has a unique representation which is believed to be governed by minerals form as presented in Figure 3.

Energy Dispersive X-Ray Analysis (EDX) is used to identify the elemental composition of a Lipad

Energy Dispersive X-Ray Analysis (EDX) test employed in this study to determine the elemental composition of a Lipad mud volcano sample. In the case of Lipad mud volcano sample, EDX analysis used to identify and quantify the elements present in the soil. Table 1 presents the elemental that was discovered in Lipad mud volcano. Concentration of trace elements in Lipad mud volcano presented in percent, % where, Oxygen are the largest component found that made up the mud with almost 57.7% and followed with Silica, Si 22.9%. Aluminum is 9.9%, Ferum, Fe and Potassium, K are 3.3% and 2.2% respectively. The component detected to be consists of 4 lowest content of Magnesium, Natrium, Chloride and Titanium which are 1.5%, 1.5% 0.6 and 0.3% respectively. The O content was found to be slightly higher than recommended value of 46.6% [14]. While, O found up to 62.02% for clay soil [15].

Consequently, Lipad mud volcano has weakly alkaline pH ranges from 7.0 to 7.7. Furthermore, Lipad mud volcano is classified as silty clay and compared to other silt loam, the pH is same with weak alkaline or 7.5 [15] while the same elements of Al, Si, Fe, K, P and S are the major elements detected in the soil [16]. This study has also discovered the Lipad mud volcano contains a high concentration of Silica, Si 22.9% which contributes to the hardiness of mud when it is in a dried form.



(a) x50000; 1ɥm (b) x500; 10ɥm

Fig. 3. FESEM images for Lipad mud volcano

Table 1
EDX - Chemical composition of Lipad mud volcano

Spectrums	Layer 1, %	Layer 2, %	Layer 3, %
Oxygen, O	57.7	57.2	48.5
Silica, Si	22.9	23.9	17.6
Aluminum, Al	9.9	9.5	6.9
Ferum, Fe	3.3	2.4	2.5
Potassium, K	2.2	2.1	1.7
Magnesium, Mg	1.5	1.6	1.1
Natrium, Na	1.5	2.1	0.7
Chlorine, Cl	0.6	1.1	-
Titanium, Ti	0.3	-	-

Table 2
CHNS – Analysis for Lipad mud volcano

Spectrums	Carbon (in %)	Hydrogen (in %)	Nitrogen (in %)	Sulphur (in %)	Weight (mg)
Lipad mud volcano	0.74	1.149	2.31	0.367	103.3
Sulfanilamide	41.81	4.65	16.26	18.62	101

The CHNS test used to determine the relative amounts of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) present in Lipad mud volcano sample. Table 2 shows the results from CHNS test where Lipad mud volcano has 0.74% in Carbon (C) and Hydrogen (H) is about 1.149%. In addition to the CHNS test, other types of elemental analysis included Nitrogen and Sulphur which are about 2.31% and 0.367%, respectively, while Nitrogen amount is overweight 103.3% consist of 2.31% and it is the largest element. Expressly, in natural conditions Lipad mud volcano will release gases as known as nitrogen and carbon dioxide. In particular, mud volcano investigated reducing sulfate to bisulfide and probably dissolved nitrogen to ammonia [17].

Additionally, Sulfanilamide was found in Lipad mud volcanos, as explained, and observed previously on site and laboratory testing. Lipad mud volcano is also defined as odourless, even wrapped, and stored for more than 6 months and remained odourless. Sulfonamide antibiotics consist of a sulfanilamide pharmacophore with a functional group comprised of a five- or six-membered ring with N, S, and/or O substitutions [18]. Sulfanilamide is an organic sulfur compound structurally similar to p-aminobenzoic acid (PABA) with antibacterial property. Sulfanilamide competes with PABA for the bacterial enzyme dihydropteroate synthase [19]. In this study, the Lipad mud volcano consists of organic sulfur, which has antibacterial properties, and is enriched with minerals. Animals were also observed using it naturally as a source of drinking water, licking salt and for wallowing. Sulfanilamide molecular formula is $C_6H_8N_2O_2S$.

X-ray diffraction (XRD) used as analytical technique to analyze the crystal structure of Lipad mud volcano materials. XRD is a valuable tool for soil scientists and geotechnical engineers to gain a better understanding of the mineralogical composition of soils and how this composition affects the behavior of soils in various applications. Thus, XRD used for analyzing Lipad mud volcano contain minerals such as clays, which have complex crystal structures that can affect the behavior of the mud itself. By identifying the specific minerals present in the Lipad mud volcano, the properties such as soil texture, plasticity, and shear strength can be observed. Lipad mud volcano has Quartz which is mineral composed of, Silicon Dioxide (SiO_2) or known as silica mineral. Silicon dioxide or layered inorganic clay composite powder comprises layered inorganic clay [20]. Silica Fume is a highly effective pozzolanic material containing silicon dioxide, SiO_2, reacts with clay minerals (aluminium oxide, Al_2O_3) and produces Aluminium silicate hydrate (A-S-H) [21] which are suitable as soil stabilizer. Therefore, with the present of Silicon Dioxide, it can be concluded that, in its natural form the mud is wet and unsorted liquid form, while in its natural drained and dried, the mud physically hardens due to the present of Silicon Dioxide. Generally, the behaviour of Lipad mud volcano can be concluded as soft and weak in wet natural condition and tend to naturally stabilize when drained and dried.

Cis-(cyclohexane-1,2-diamine-N,N') di(thiocyanate-S) platinum(II) with molecular formula $C_6H_{14}N_2Pt^{+2}$ [22] is a coordination compound with the chemical formula $[Pt(C_6H_{12}N_2)(NCS)_2]$. It is a type of platinum complex, which is a type of coordination compound that contains a central platinum ion bonded to other atoms or molecules, called ligands, through coordinate covalent bonds. In this particular compound, the platinum ion is coordinated to two thiocyanate ligands, which are bonded to the platinum through the sulfur atoms. The platinum ion is also coordinated to a bidentate ligand called cyclohexane-1,2-diamine, which is a type of chelating ligand that forms a ring structure around the platinum ion. The complex has a cis configuration, meaning that the two thiocyanate ligands are bonded to the same side of the platinum ion. Cis-(cyclohexane-1,2-diamine-N,N') di(thiocyanate-S) platinum(II) is a well-known coordination compound that has been extensively studied for its biological and pharmacological properties where clay been used.

Lipad mud volcano also consists of clinochlore, syn. Clinochlore is a mineral that belongs to the chlorite group, which is a group of phyllosilicate minerals. It has the chemical formula $(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$ and is also known as magnesium iron aluminum silicate hydroxide. Clinochlore is a green mineral that typically occurs in metamorphic rocks such as schists and phyllites. It is a member of the solid solution series that includes the minerals chamosite, clinochlore, cookeite, diabantite, donbassite, nimite, pennantite, prochlorite, ripidolite, sudoite, and thuringite. These minerals have similar crystal structures and chemistries but differ in the relative proportions of magnesium, iron, and aluminum in their crystal lattice.

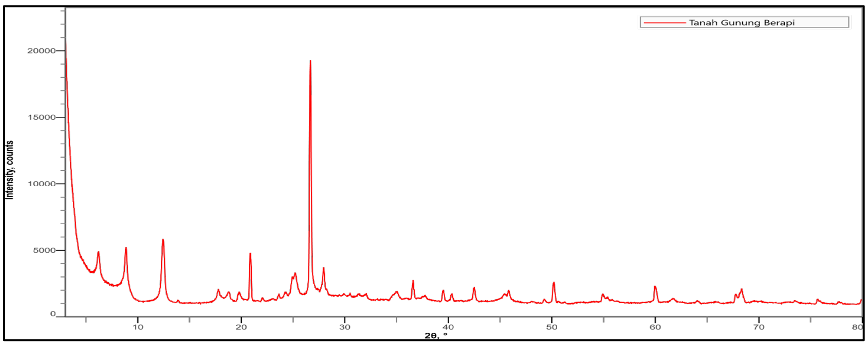


Fig. 4. X-Ray diffraction particle analysis for Lipad mud volcano

This shows that the Lipad mud volcano is significant and unique compared to other soils because it contains the rare clinochlore minerals, which are a sub-variety of the large family of chlorite minerals. Where, the crystallization of chromian clinochlore is less abundant found in other places. Additionally, the electrical profile of the sample was tested using Particle Size Analyzer (Zeta sizer) and the result shows that the sample contains a negative charge - 26.5 mV as depicted in Figure 5. According to [26], the polarity charge of volcano soil or mud depends on the types of minerals present in the soil. Based on the prior data, silica (negative charge) has dominated the composition, therefore, the surface charge of the mud might be inhibited by this element. The particle size distribution for the mud is also tested using Zeta sizer and recorded as 6368 d.nm which is in concurrent with the previous researchers who classified the particle size below than 0.002 mm as mixture composition of sand, silt, clay particles and soil aggregates [27,28]. Also, the particle distribution size of volcano mud is recorded as dominated by fine grain (84.47%) and mostly is clay sized particle (55.4%) and silt size particle around 30% [29]. The final characteristic tested for this sample is moisture content as 25.17%.

			Mean (mV)	Area (%)	Width (mV)
Zeta Potential (mV):	-26.5	Peak 1:	-33.0	62.7	8.26
Zeta Deviation (mV):	12.5	Peak 2:	-14.3	37.3	6.83
Conductivity (mS/cm):	0.238	Peak 3:	0.00	0.0	0.00
Result quality :	Good				

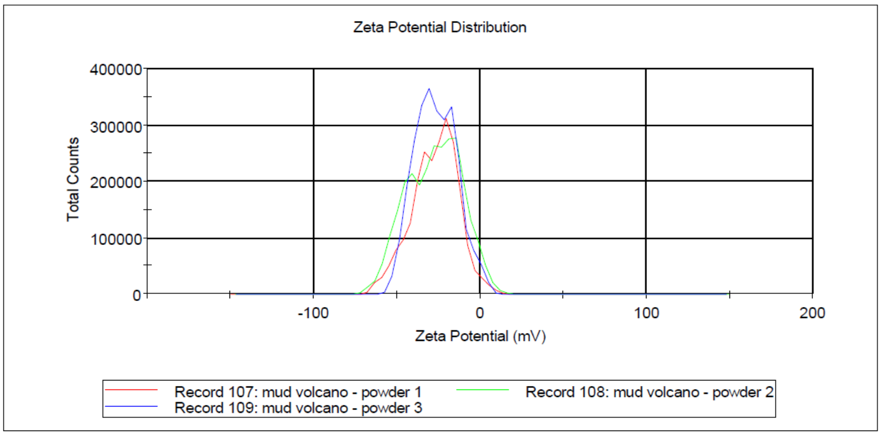


Fig. 5. Zeta potential of volcano mud Lipad, Sabah

4. Conclusions

The physiochemical characteristics of Lipad volcano mud is determined in this study including physical properties and geochemical characteristics of the mud. The pH of the sample was recorded as pH 7 and the moisture content of it is 25.17% while the particle distribution size recorded as 6368 d.nm. This property defines the composition Lipad volcano mud particle as clay, silt and fine soil. The elements detected inside the mud are O, Si, Al, Fe, P, K, Mg, Na, Cl) and Ti includes the rare clinochlore mineral. This element also reflects on the composition that occurs below the earth. High concentration of Si inside the mud positively inhibited the negative surface charge of the mud as -26.5 mV. Nitrogen compound which is 2.31% also noted in this study and this amount potentially initiates the release of nitrogen and carbon dioxide gases during the vent expel of mud.

The morphology of the mud recorded as flakes, brittle, flat are different from common soil morphological structure using Field Emission Scanning Electron Microscopy (FESEM). The study of characteristic and properties of volcano mud in Lipad, Sabah is important to understand and define the mud, the element present at underlying strata, the gasses release, and the effect toward the surrounding. In this study, those characteristics and properties of the mud were measured and the data was discussed in details in order to provide and give a platform or based line knowledge to the researchers.

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