Sains Malaysiana 52(9)(2023): 2529-2543
http://doi.org/10.17576/jsm-2023-5209-05

Rare Earth Element Characterization of Bledug Kuwu Mud Volcano, Central Java, Indonesia, Based on Geochemical Analyzes (Susceptibility, XRF, XRD, SEM-EDS and ICP-EOS)

(Pencirian Unsur Nadir Bumi Gunung Berapi Lumpur Bledug Kuwu, Jawa Tengah, Indonesia, Berdasarkan Analisis Geokimia (Kerentanan, XRF, XRD, SEM-EDS dan ICP-EOS))

RINA DWI INDRIANA[1,*], HIJRAH SAPUTRA[2], MARIYANTO MARIYANTO[3], ELEONORA AGUSTIN[4], MIMIN IRYANTI[5] & CAHYO AJI HAPSORO[6]

[1]Department of Physics, Faculty of Science and Mathematics, Diponegoro University, Indonesia
[2]Postgraduate School, Universitas Airlangga, Surabaya, Indonesia
[3]Department of Geophysical Engineering, Faculty of Civil, Planning and Geo-Engineering, Institut Teknologi Sepuluh Nopember, Indonesia
[4]Department of Geophysics, Faculty of Mathematics and Natural Science, Padjadjaran University, Bandung, Indonesia
[5]Department of Physics, Faculty of Education of Mathematics and Natural Science, Universitas Pendidikan Indonesia, Bandung, Indonesia
[6]Department of Physics, Faculty of Mathematics and Natural Science, Universitas Negeri Malang, Malang, Indonesia

Received: 8 March 2023/Accepted: 22 August 2023

ABSTRACT

Mud volcano material is generally rich in oxides, while oxides are the main compounds forming rare earth elements. Bledug Kuwu, Central Java, Indonesia, is one of the active mud volcanoes, so there may be rare earth elements. This research is the characterization of rare earth elements (REE) in the Bledug Kuwu mud using magnetic and geochemical methods. Magnetic characterization uses magnetic susceptibility measurements. The geochemical characterization of the mud samples consisted of the XRF (X-Ray Fluorescence), XRD (X-Ray Diffraction), ICP-EOS (inductively coupled plasma) test, and the SEM-EDS (Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy) test. The results of the geochemical analysis of the Bledug Kuwu mud sample were the content of quartz, kaolinite, and calcite with an average concentration of 42.26%, 23.67%, and 33.96%. The susceptibility of Kuwu's mud is 0 because the concentration of metal elements is low; according to the results of XRF, XRD, and SEM tests identified the main mud elements as C, O, Si, Ca, and Al. The rare earth elements in Kuwu's mud are Ce, Dy, Eu, Gd, Ho, La, Nd, Pr, Sm, Tb, Y, and Sc. The highest concentrations were Ce 52.22 ppm and La 47.95 ppm.

Keywords: Geochemical; mud volcano; petromagnetic; rare earth elements

ABSTRAK

Bahan gunung berapi lumpur umumnya kaya dengan oksida, manakala oksida adalah sebatian utama yang membentuk unsur nadir bumi. Bledug Kuwu, Jawa Tengah, Indonesia ialah salah sebuah gunung berapi lumpur aktif, jadi mungkin ada unsur nadir bumi. Kajian ini adalah pencirian unsur nadir bumi (REE) dalam lumpur Bledug Kuwu menggunakan kaedah magnetik dan geokimia. Pencirian magnet menggunakan ukuran kerentanan magnetik. Pencirian geokimia bagi sampel lumpur terdiri daripada XRF (Pendarfluor Sinar-X), XRD (Belauan Sinar-X), ujian ICP-EOS (plasma berganding induktif) dan SEM-EDS (Mikroskop Elektron Imbasan-Spektroskopi sinar-X serakan tenaga). Hasil analisis geokimia sampel lumpur Bledug Kuwu adalah kandungan kuarza, kaolinit dan kalsit dengan purata kepekatan 42.26%, 23.67% dan 33.96%. Kecenderungan lumpur Kuwu ialah 0 kerana kepekatan unsur logam adalah rendah; mengikut keputusan ujian XRF, XRD dan SEM mengenal pasti unsur lumpur utama sebagai C, O, Si, Ca dan Al. Unsur nadir bumi dalam lumpur Kuwu ialah Ce, Dy, Eu, Gd, Ho, La, Nd, Pr, Sm, Tb, Y dan Sc. Kepekatan tertinggi ialah Ce 52.22 ppm dan La 47.95 ppm.

Kata kunci: Geokimia; gunung berapi lumpur; petromagnet; unsur nadir bumi

Introduction

A *mud volcano* is a geological phenomenon appearing on the surface, where mud material comes from the earth. Mud material comprises various mineral elements and gases moving out of eruptive material (Barber, Tjokrosapoetro & Charlton 1986; Brown 1990; Deville & Guerlais 2009; Dimitrov 2002). Some minerals in the mud are essential and needed by the latest technology. Several unique minerals in the mud element are called rare earth elements (REE). The REE comprise of Lanthanide, Yttrium, and Scandium groups which are irreplaceable and unique. They are available to explore. The REE can produce neo-magnets with a better magnetic field than ordinary magnets. REE can also increase a material's strength, hardness, and resistance to heat (Zhang et al. 2012).

In Indonesia, there are several mud volcanoes scattered on the island of Java, located in Sangiran, Bangkalan (Madura), Ciuyah (West Java), Kesongo (Central Java), Semolowaru, Gunung Anyar, Sedati, Porong, and Sidoarjo (East Java). Geologically, the existence of mud volcanoes in Java forms a straight line. Mud volcanoes in Java are part of the active Mud Volcano route, which stretches from Purwodadi – Cepu – Bojonegoro – Porong (Ibrahim, Subardjo & Sendjaja 2010). Bledug Kuwu is a mud volcano from a group of mud volcanoes in Central Java. A group of mud volcanoes in Central Java is related to the oil and gas deposits beneath it (Bambang et al. 2012).

Around Bledug Kuwu there are Bledug Cangkring, Bleduk Crewek, Bledug Medang, Bledug Kesongo and Bledug Anak Kesongo. Bledug Kuwu is the most active mud volcano compared to the others (Satyana & Asnidar 2007). Bledug Kuwu is in the Randublatung zone. The Randublatung zone is part of the Rembang and Kendeng zones' confluence (Rugayya & Suryanto 2019). The Randublatung Zone extends from Semarang to Surabaya, ±250 km long and ±10 km wide. The triangle zone indicates the subsurface structure of the Randublatung zone (Bambang et al. 2012; Bemmelen 1949). Bledug Kuwu is a mud volcano formed due to natural gas rising to the surface through the medium of subsurface structures and carrying mud whose density is lighter than the surrounding sediment. The eruption process is due to pressure from below, which can push up the rock in its path. Claystone, marl, and sandstone dominate the lithology of Bledug Kuwu (Husein 2015; Nurhandoko et al. 2019). The geological structure that controls the emergence of the Bledug Kuwu mud volcano is a fold structure and a fault structure (Bambang et al. 2012). The anomaly in the Bledug Kuwu area originates from fractured rocks extended from the southwest to the northeast (Indriana, Nurwidyanto & Haryono 2007) (Figure 1).

Bledug Kuwu water is salty as a presence of a salt dome under the surface (Indriana, Nurwidyanto & Haryono 2007). Mineral exploitation that is already done in Bledug Kuwu is salt. The processing of salt from brine is done traditionally and is still going until today. The amount of brine water produced is small, so it is considered uneconomical and only used locally by the local community. Other minerals contained in the mud and brine water besides salt have yet to be utilized. Several mud volcanoes have REE in the mud material with different compositions, and the compounds in the mud consist of SiO_2, Al_2O_3, and $CaCO_3$ (Carretero 2020; Delisle et al. 2002; Lina et al. 2019; Maslov, Shevchenko & Bychkov 2021; Queiber et al. 2017; Talas et al. 2015; Vignesh et al. 2016).

The rare earth elements characterization in the Kuwu mud uses ICP-EOS to be the novelty of this research. The previous mineral characterization in Bledug Kuwu uses brine water. The result of ICP–EOS and geochemical tests of the Kuwu are Si, Na, K, Mg, Li, and B (Sulistiyono et al. 2018). The geothermal activity causes forming of these mineral elements (Rizqiya 2014; Rohmah et al. 2018). Mud volcano activity occurs due to geothermal sources. This geothermal source supplies thermal energy, producing mud containing sulfur and salt minerals. Sulfur and salt concentrations in Bledug Kuwu were 62.883 × 102 mg/ and 57.15 mg/L (Sa'diyah, Syarwani & Hadiantoro 2017; Sabdaningsih 2018; Siregar & Siregar 2016). Geochemical analysis of the Bledug Kuwu mud used the XRD method with three samples. The distance of the point sample from the source is 200 m. The results of the XRD test are elements of sulfur (SO_2 and SO_3) as much as 10.9 ppm - 73.83 ppm. Analysis of rare earth elements also used brine water samples (Arienzo et al. 2022). It is essential to use ICP-EOS and magnetic tests on Bledug Kuwu mud samples because it is necessary to carry out characterization tests of rare earth elements contained in Bledug Kuwu mud samples with different viscosity levels.

REE are generally not found as free elements in the earth's crust except in complex compounds. Separating process of REE from these compounds uses some methods. This research novelty is characterizing REE of Bledug Kuwu's mud using magnetic and geochemical methods. The petromagnetic characterization uses magnetic susceptibility measurements. The geochemical characterization of the mud samples consisted of the XRF (X-Ray Fluorescence), XRD (X-Ray Diffraction), ICP-EOS (inductively coupled plasma) test, and the SEM-EDS (Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy) test.

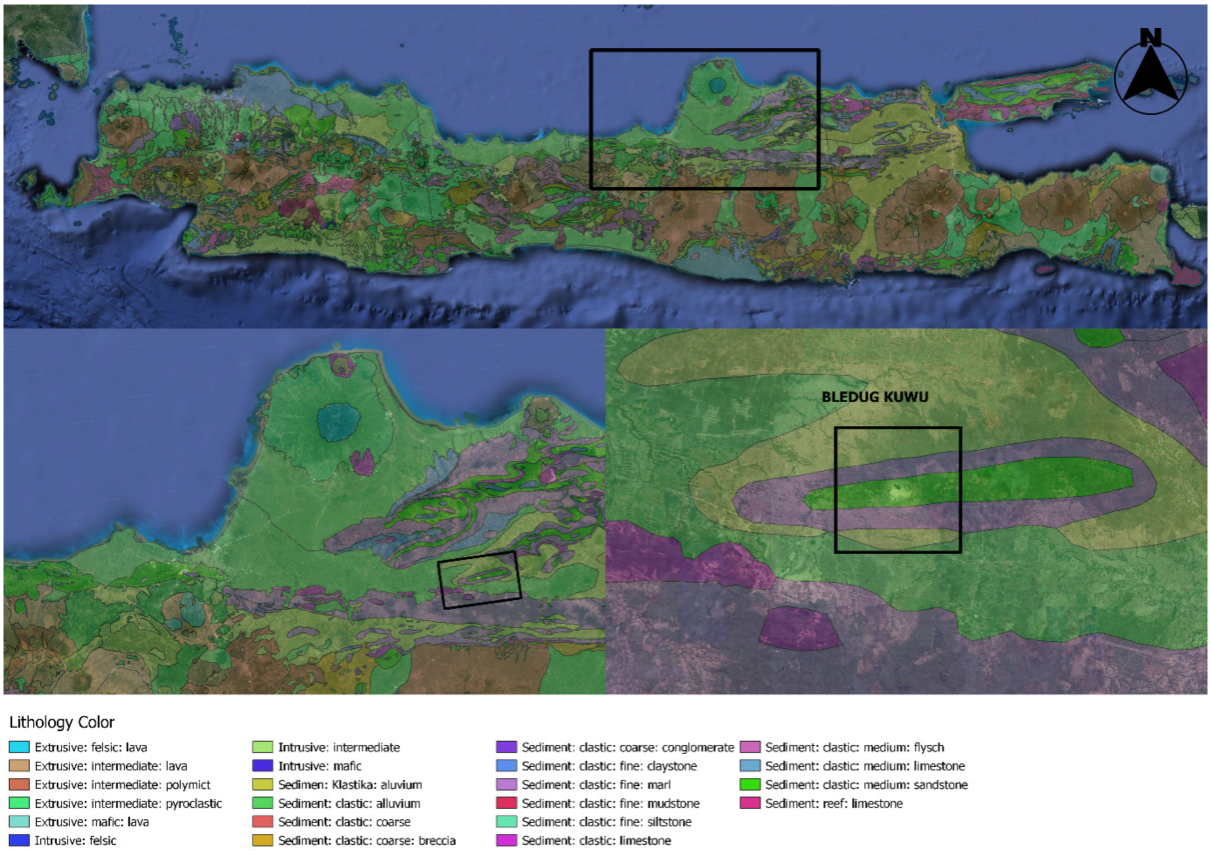


FIGURE 1. Bledug Kuwu Mud Volcano location and lithology map

MATERIALS AND METHODS

Bledug Kuwu is one of the mud volcanoes in Central Java and the most active among the other mud volcanoes, located in Kuwu Village, Kradenan District, Purwodadi Regency, Central Java Province. Bledug Kuwu mud eruptions occur almost continuously. The diameter of Beldug Kuwu is ± 650 meters. The location of Bledug Kuwu can be at coordinates 7°07'03.90″S, 111°07'17.61″E. Bledug Kuwu has two large Bledugs, which are active and surrounded by small Bledugs (Figure 2).

Bledug Kuwu has two large Bledugs that are active and surrounded by small Bledug. The Bledug Kuwu mud eruption contains gas that triggers an explosion with a frequency of 0.1 – 2 explosions/minute with an explosion height of up to 5 m. Currently, 5 m explosions are rare, presumably because the amount of gas below the surface of Bledug Kuwu has decreased. Bledug Kuwu is a pie-type mud volcano with two large pies and several small pies. Bledug Besar (big pie) in the east is smaller in diameter than in the west but surrounded by many small pies and unstable conditions.

The mud samples used surface samples, there were 10 points, and each sample weight or volume was 1000 mL. Sample points were around Bledug Kuwu, especially big Beldug 1 (Figure 3). Sample conditions are solid surface samples, soft surface samples, and surface samples that tend to be liquid. Sample picking used non-metallic equipment. Point selection is aware of safety during sampling, so taking samples with regular grids and traversing mud volcanoes is impossible. The location of the sample points encircled big Bledug 1, while the surface conditions were unstable and dangerous around Bleduk 2, so we could not take a mud sample. Samples taken from small Bledug are soft to liquid samples, while the mud from large Bledug is denser to soft. The map of the sampling position is in Figure 2. The solid samples are at points T1, T2, T3, and soft samples are at T4, T5, and T10, while the more liquid samples are at points T6, T7, T8, and T9.

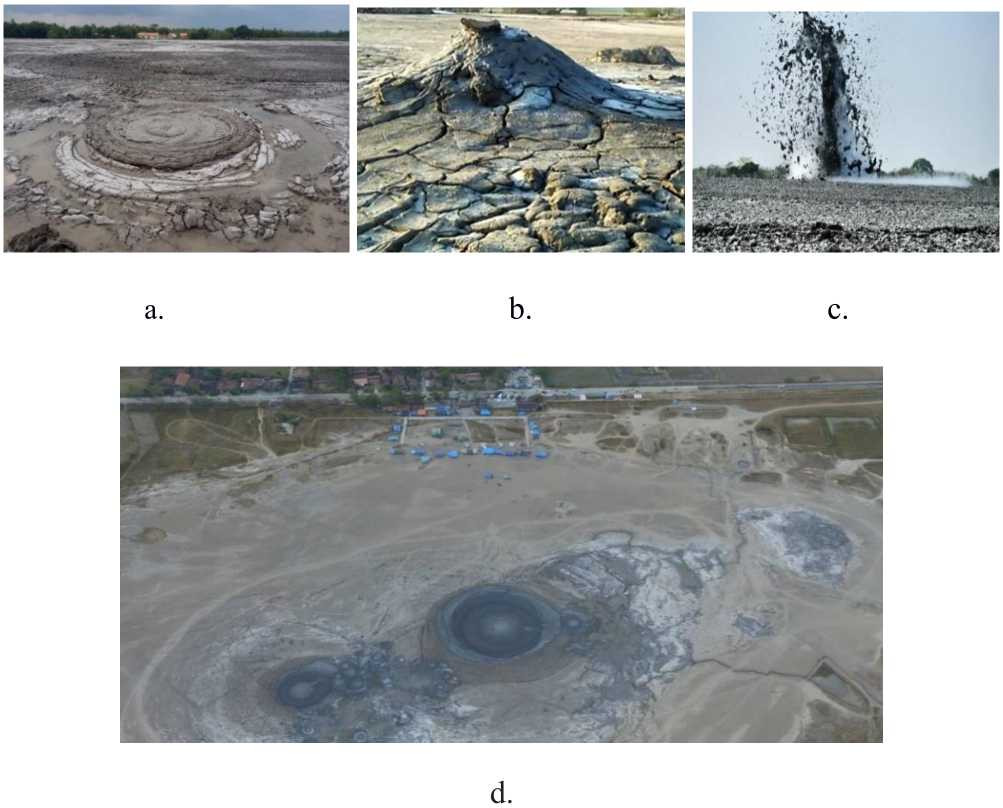


FIGURE 2. Bledug Kuwu mud volcano a). small pie b). small gryphone c). Kuwu explotion, and d). Bledug Kuwu pie (https://www.idntimes.com/travel/destination)

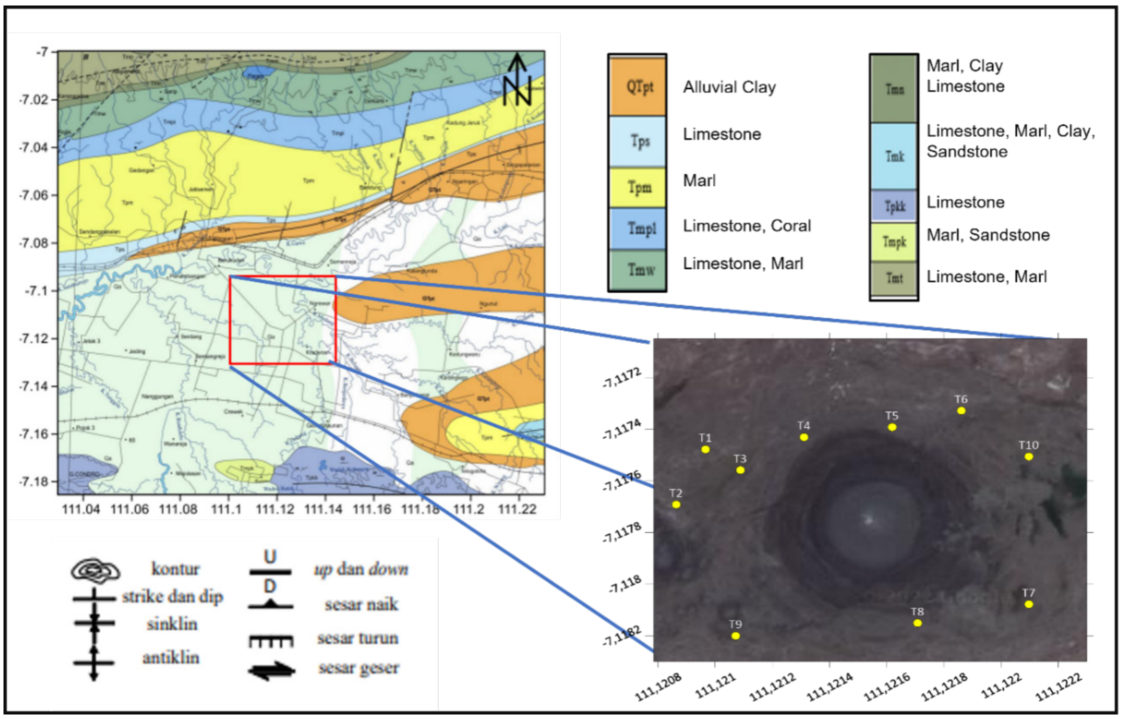


FIGURE 3. Geology map of Ngawi Region and Sample position in Bledug Kuwu

The preparation process in the laboratory used natural drying. After drying, the mud sample was sieving by using a sieve to obtain homogeneous clay particles. Sample preparation is carried out according to the test and prepared for various measurements/tests consisting of susceptibility, XRD, XRF, SEM-EDS, and ICP-EOS.

The susceptibility test or measurement of low-frequency magnetic susceptibility based on mass (χLF) depends on the frequency (χFD %). A susceptibility test determines the natural metal content. The number of samples tested was ten samples. The magnetic test used Barrington MS2. The value of LF (m^3/kg) was used to determine the concentration of magnetic minerals (Davies et al. 2011, 2007; Milkov 2000). The value of FD is used to determine the portion of superparamagnetic refined grains (SP) contained in the mud sample. A low value of FD % (<2%) indicates that there are no SP items in the sample, while a very high value of FD % (>14%) contains only SP items. If the value of FD % is 2-14%, then the sample contains a mixture of SP and non-SP granules (Milkov 2000).

XRF (X-Ray Fluorescence) measurements were carried out to determine the composition of elements in a material/sample. XRF is a non-destructive technique for identifying and calculating the concentration of each element in the sample. XRF measures the wavelength of each element in the material from the fluorescence emission the sample produces when irradiated by X-rays (PanAnalytical 2009). The tool used was Thermo Scientific ARL. The number of samples tested was 10.

X-ray Diffraction (XRD) testing was carried out to identify the phases of crystalline materials and can provide information about the dimensions of the unit cell. The type of element is identified from the analysis of elemental diffraction patterns. The XRD method is known as the powder fingerprint method because XRD produces the shape of the powder diffraction patterns. Diffraction patterns depend on the size and shape cell, the atomic number, and the position of the atoms in the cell (Smallman & Bishop 2000). Analysis used XRD X'Pert Pro PanAnalytical, conducted at ITS Indonesia (Institution Technology Sepuluh November, Surabaya). The number of samples tested was 3.

Morphological, topographical, and elemental analysis of the samples using SEM results – EDX (Scanning electron microscope). Scanning Electron Microscopy (SEM) is an electron microscope that creates images by concentrating a beam of high-energy electrons on the surface of a sample and the detection signal from electron interactions with the sample surface. Collected signal type in an SEM varies and can include secondary electrons, x-rays characteristics, and electron backscattering. An electron microscope is a beam of light that concentrates on the electrons to gain much higher magnification than a conventional light microscope. SEM can observe both structures and form the finer-scaled surface, furnished with EDX (Electron Dispersive X-ray), and detect elements in the sample as the observed surface through the conductor electron (Scimeca et al. 2018). SEM analysis used Hitachi FlexSem 1000 at ITS Indonesia (Institutaon Technology Sepuluh November, Surabaya). The number of samples tested is 3, and the sample number used is the same as the sample used in the XRD test.

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP -EOS) was performed for multi-element metal assay, which uses a plasma source to excite the atoms in the sample. The number of samples tested was 10. The mud samples tested have a filtering process (minimum size pore 2.5 µm uses Whatman quantitative ashless filter paper 42), the maximum TDS of Aquos is 2%, the mud samples have a dilution process, and sample treatment only uses pro-analysis chemical reagents (pa). Measuring REE concentrations used Inductively Coupled Plasma Atomic-Optical Emission Spectrometry (ICP-OES) analysis using PerkinElmer Optima 8300 ICP-EOS Spectrometer, conducted at BRIN Indonesia (Institution Research and National Innovation).

Results and Discussion

The Bledug Kuwu mud's color is light brown on a dry surface, while on a soft and liquid condition, it is dark brown-black to black and gray. Dried mud forms cracks on the surface, and its texture becomes hard and sticky when exposed to water. Mud close to the source of the eruption is black and becomes light brown as it gets farther away. Around the center, the mud color on the surface is brown, but beneath, it is still black and soft, making it easy to sink. The closer to the point of eruption, the mud water content increases and its color is gray to black. In the processing of rock formation, chemical decomposition occurs and produces secondary minerals (Rohmah et al. 2018). One of the secondary minerals is clay. Clay minerals consist of kaolinite, illite, and montmorillonite (Sari & Warmada 2021). The elements of kaolinite are silica and alumina, and both element compositions are arranged alternately. The surface layer of kaolinite is more robust and taught than montmorillonite and illite, so less water enters the rock layer (Brindley & Brown 1980; Mori & Kano 2009). Based on previous research, the types of mud found in

Bledug Kuwu have the same characteristics as mud in other mud volcanoes in Java and contain montmorillonite. Montmorillonite is a mud whose water content affects its phase (Agustawijaya & Krisnayanti 2013; Brand & Brenner 1981; Bowles 1984; Chen 1975; Grim 1968; Ibrahim, Subardjo & Sendjaja 2010; Mazzini & Etiope 2017; Zainudin et al. 2010). Samples were prepared and tested for susceptibility, XRF, XRD, SEM-EDS, and ICP-EOS. The results of the sample test are as follows:

Susceptibility Measurement of sample susceptibility used low frequency (χLF) 47 kHz and high frequency (χHF) 470 kHz. This processing produces a frequency-dependent magnetic susceptibility FD(%) (Sudarningsih et al. 2017). The susceptibility results can provide information on the ability of the Kuwu mud material to be magnetized. Table 1 shows the result of sample susceptibility. The χFD is an indicator of mineral superparamagnetic (SP) content. If the value of χFD (%) < 2% indicates that the magnetic minerals contained in the sample are not superparamagnetic (Milkov 2000). In Table 1, the χFD value (%) is 0%. Based on the theory, the mud sample does not contain superparamagnetic minerals (SP). The amount of superparamagnetic minerals is less, except for sample 1, which has a χFD value of 12.5%.

All samples are surface samples, and samples 1 to 10 are in different locations around Bleduk Kuwu. Sample 1 is the densest surface sample compared to the others. The position of sample 1 is between large Bledug 1 and 2. Samples 2 and 3 are solid but soft, while other samples are liquid. Liquid sample collects from small Bledug that appears around the large Bledug. Liquid or soft samples do not significantly affect the results of χFD. This result explains that the sample phase does not affect the susceptibility value. The high value of χFD in sample 1 may be due to chemical and physical reactions that have occurred previously or due to environmental exposure. Sample T4 is near Bledug 1, and sample T2 is near Bledug 2. The values of χLH and χLF are the highest, but no susceptibility appears from the Bledug Kuwu mud. Fresh samples taken directly from small Bledug have higher χLH and χLF values than the others. Metal elements in the mud material cause the presence of susceptibility. The presence or absence of metal elements Fe, Mg, and others needs further testing to analyze the susceptibility value in the Kuwu mud volcano material. The next element test is the XRF test.

X-Ray Fluorescence (*XRF*) The analysis of mud composition used XRF. The χFD result cannot identify the metal element, so the XRF test obtained the results of any elements contained in the sample. Table 2 is a table of elements and compounds of Bledug Kuwu mud. Table 2 shows the main elements Si, Ca, Fe, Al, and Cl. The other elements are Sx, K, Ti, Sr, Zr, Br, Nb,

TABLE 1. Susceptibility magnetic of Bledug Kuwu mud

No	Sample	LF	LH	FD%
1	T1	8.8	7.7	12.5
2	T2	9.3	9.3	0
3	T3	8.3	8.3	0
4	T4	9.6	9.6	0
5	T5	8.6	8.6	0
6	T6	9	9	0
7	T7	9	9	0
8	T8	8.9	8.9	0
9	T9	8.9	8.9	0
10	T10	8.7	8.7	0
Mean	-	8.91	8.8	1.25
Maximum	-	9.6	9.6	12.5
Minimum	-	8.3	7.7	0

Rb, Mo, In, Sb, Sn, Ru, and As. The dominant elements are Si = 20.34 % - 23.01 %, Ca = 13.67 % - 15.49 %, Fe = 7.63 % - 8.77 %, Al = 2.9 % - 9.11 %, and Cl = 4.39 % - 9.53%, and the other have lower element concentrations. The oxide compounds formed are SiO_2, Ca O, Fe_2O_3, Al_2O_3, and Cl. The average concentration values of the dominant oxide compounds were SiO_2 = 45.363%, Ca O = 20.518%, Fe_2O_3 = 11.661 %, Al_2O_3 = 8.149%, and Cl = 8.255%, and the other have lower oxide compound concentrations. XRF results identified Quartz as the main compound with a 43.6% - 49.23 % concentration. The presence of oxide compounds allows the formation of rare earth elements in the Bledug Kuwu mud.

Elements that appeared due to the XRF test did not present REE. The lantana element was not obtained in the Bledug Kuwu mud by XRF test. In a previous study, the XRF results of Kuwu brine water yielded 49.30% calcium, lithium, boron, and other components. Salt, a sodium carbonate compound of as much as 31.29%, is thought to contain lithium and boron (Sulistiyono et al. 2018; Sumarno, Ratnawati & Nugroho 2012; Tran et al. 2013). Mud and brine water samples produced the same element, calcium. The calcium concentration in the mud is lower than in the brine water. The Si element dominates Kuwu's mud element. Other elements in common are aluminum and chloride. The XRF method detected the element Fe but at a small concentration of 8.159%. The small concentration of Fe probably caused the low χFD value. The XRF test has not been able to show the expected REE elements. The presence of oxide compounds allows rare REE, according to the characteristics of REE present in the oxide material. The next test is the XRD test to determine the crystalline material contained in the sample.

TABLE 2. XRF Element and compound concentration of Kuwu mud sample

Element	Mean (%)	deviation	Oxide compound	Mean (%)	deviation
Si	21.208	0.3100	SiO_2	45.363	0.6600
Ca	14.672	0.2100	CaO	20.518	0.2900
Fe	8.159	0.1200	Fe_2O_3	11.661	0.1700
Al	5.205	0.5700	Al_2O_3	8.149	1.0700
Cl	7.335	0.1700	Cl	8.255	0.1700
Sx	1.453	0.3700	SO_3	3.066	0.9100
K	1.390	0.1000	K_2O	1.701	0.1200
Ti	0.584	0.0730	TiO_2	0.966	0.1200
Sr	0.130	0.0400	SrO	0.155	0.0470
Zr	0.048	0.0150	ZrO_2	0.063	0.0200
Br	0.036	0.0068	Br	0.033	0.0068
Nb	0.021	0.0025	Nb_2O_5	0.030	0.0035
Rb	0.026	0.0086	Rb_2O	0.029	0.0094
Mo	0.013	0.0031	MoO_3	0.019	0.0047
In	0.007	0.0009	In_2O_3	0.008	0.0011
As	0.029	0.0011	As_2O_3	0.008	0.0140
Sb	0.014	0.0012	Sb_2O_3	0.008	0.0015
Sn	0.006	0.0012	SnO_2	0.008	0.0015
Ru	0.005	0.0019	RuO_4	0.006	0.0026

X-ray Diffraction (XRD) The XRD test results selected for analysis were samples T1, T5, and T9. Sample T1 is a sample with different susceptibility test results and is the densest sample, sample T5 is a soft sample, and sample T9 is a sample from a small Bledug near Bledug 2. The XRD results of the T1, T5, and T9 mud samples contained 29.6% - 36.5% Quartz (SiO_2), 19.5% - 29.0% Kaolinite ($Al_2 H_4O_9Si_2$), 40.7% - 44.7% Calcite ($Ca CO_3$). The density value is 2,599 g/cc - 2,707 g/cc. The percentage by weight of the elements in the mud is O = 51 .8%, Si = 20.1%, Ca = 16.6%, Al = 6.1%, C = 5.1%, and H= 0.5%. The concentration of each compound in each sample is in Table 3.

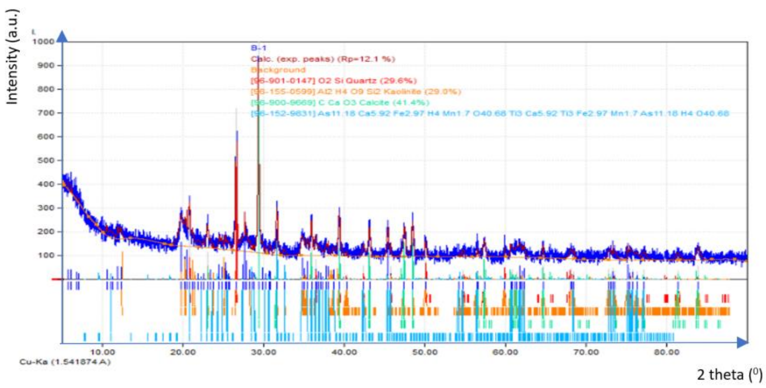
The concentrations of compounds in samples T1, T5, and T9 are Calcite, Quartz, and Kaolinite. Sample T1 has the highest concentration of kaolinite. Sample T5 has the highest concentration of calcite, while sample T9 has the highest quartz concentration. The T1 sample has other results, although not dominant. The susceptibility results showed the value of FD 0% in the T1 sample, while the T2 - T10 samples were 0%. The XRD results identify the presence of Fe, Li, Mn, and Sn elements but are not dominant. Fe, Mg, and others, known as solid metal elements, did not appear in the XRD test of samples T5 and T9. The absence of metal elements is a condition that produces zero susceptibility (χ FD = 0%) in the mud sample.

The results of the XRD test are in the graph in Figure 4. The highest intensities are Calcite ($Ca CO_3$) in a trigonal crystal phase, Kaolinite ($Al_2 H_4O_9Si_2$) in a triclinic crystal phase, and Quartz ($Si O_2$) in a trigonal crystal phase. In Figure 4(a), which represents the T1 sample, other compounds are not dominant. The T5 sample did not show a non-dominant peak (Figure 4(b)). The T9 sample had one non-dominant peak, while sample T1 had several non-dominant peaks $As_{11.18} Ca_{5.92} Fe_{2.97} H_{4,} Mn_{1.7} O_{40.68} Ti_3 Ca_{5.92}$, $Ti_3 Fe_{2.97} Mn_{1.7} As_{11.8} H_4 O_{40.68}$.

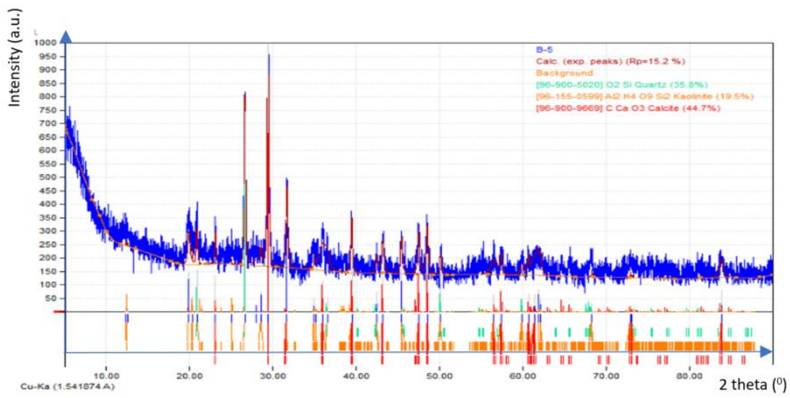
The dry mud sample of Bledug Kuwu tested produced a composition of quartz, kaolinite, and calcite. Mud samples in various mud volcanoes around the world are generally composed of SiO_2 and Al_2O_3 and contain elements of REE (Lina et al. 2019; Maslov, Shevchenko & Bychkov 2021; Talas et al. 2015; Vignesh et al. 2016). Indonesia has a very abundant source of oxide material contained in quartz sand. Quartz oxide (SiO_2) dominates quartz sand, with a purity of SiO_2 up to 95-97%. Kaolinite is also dominant in clay. The kaolinite is an alumina (Al_2O_3) source with up to 40% purity. Limestone or calcite ($CaCO_3$), with a purity of up to 98%, also dominates the compound in mud (Munasir et al. 2012). Nanotechnology requires intelligent materials, namely oxide materials/nanomaterial oxides such as Zn O, SiO_2, MgO, Al_2O_3, TiO_2, Fe_2O_3, Y_2O_3, Ce O, and Mn O. The concentration of quartz, kaolinite, and calcite in the dry mud of Bledug Kuwu is below 50%, so no one is the most dominant. In general, kaolinite dominates up to 40% of clay concentration, but in the Kuwu sample, the kaolinite concentration value is lower the 40%. Based on the geology map of the Kuwu, the limestone is dominant; the calcite concentration in the samples tested only reached 44.7%. Previous studies have shown that brine water and Bledug Kuwu mud are dominated by aluminum silica, clay, and Lithium in the Li-Montmorillonite clays. The wet mud samples treated in the experiment contained 0.0029% lithium (Rohmah et al. 2018). The results of the XRD test for the Bledug Kuwu mud sample did not reveal the presence of Lithium in the dry mud sample.

TABLE 3. Compound concentration of Kuwu mud sample

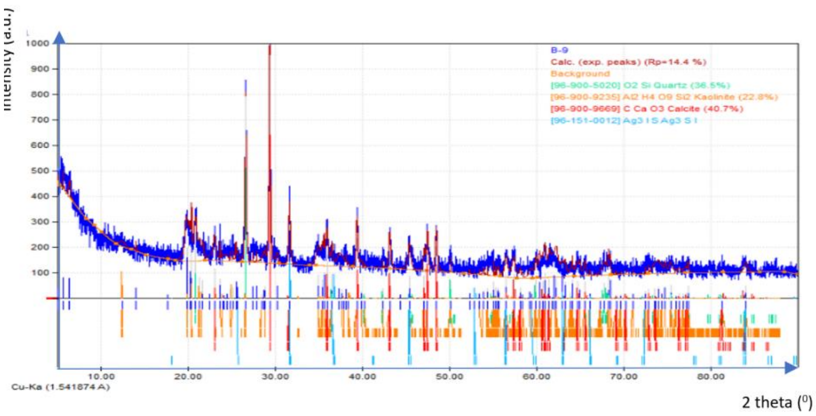
Concentration (%)	T1	T5	T9	Min	Max	Mean	Density (g/cm^3)
Calcite	41.40	44.7	40.7	40.7	44.7	42,26	2.707
Kaolinite	29.0	19.2	22.8	19.2	29.0	23,67	2.599
Quartz	29.6	35.8	36.5	29.6	36.5	33.96	2.626
Other	Ti	-	Ag	Reference:			
	Fe	-	-	Quartz : Kihara (1990)			
	Mn	-	-	Kaolinite : Bish (1993)			
	As	-	-	Calcite : Sitepu (2005)			



a.



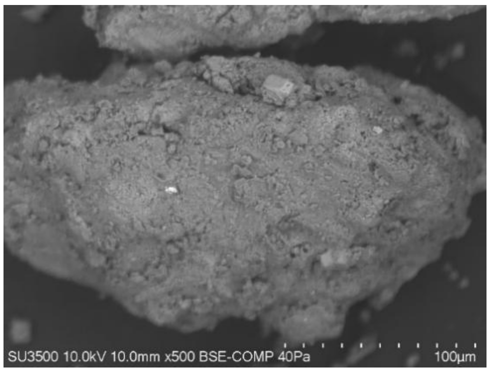
b.



c.

FIGURE 4. XRD, a) Sample T1 b) Sample T5 c) Sample T9

SEM-EDS (Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy) Rock morphology study focuses on the rock's shape, structure, and form. Rock morphology analysis uses to identify rock constituent elements. SEM is the newest method for nanoscale materials because shape influences physicochemical characteristics. SEM is an efficient scanning technique, useful in current materials research, microanalysis, investigative applications, and high-resolution imaging. Element identification is easy using an energy-dispersive X-ray spectrometer (EDS) connected to a scanning electron microscope (SEM). SEM-EDS produces the image and energy intensity. The SEM identifies element response as element energy response. The SEM image surface of the mud contains a variety of mineral crystal particles such as kaolinite, calcite, and quartz, with a large number of intergranular pores and microcracks, mainly distributed around the mineral crystals. At a 500× magnification, the voids and calcite mineral grains are uniformly distributed over the entire sample surface. At a 500× magnification, a large number of calcite and kaolinite flakes can be clearly observed on the surface of the quartz, with a relatively large amount of voids formed between these flakes (Figure 5(a)). The SEM-EDS test identifies C, O, Fe, Na, Mg, Al, Cl, Si, K, and C. The most weight is O at 40.98% and C at 31.35%. The lighter metal element Al is 7.05%, Si = 9.48%. Calcium, the main component in the Kuwu area, has a weight percentage of 4.54%. Other elements weigh less than 2%. These results indicate the consistency of the oxide content in the mud as a medium for the formation of REE. SEM-EDS spectrum observed that the major elemental constituents are C and O with smaller concentrations of Al, Si, Ca, and Cl, and minor concentrations of Mg and K (Figure 5).

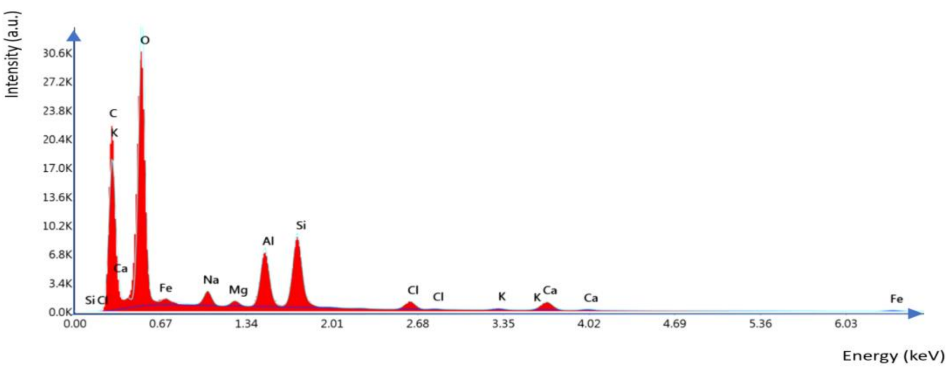


a.

Smart Quant Results

Element	Weight %	Atomic %	Error %
C K	31.35	42.83	8.54
O K	40.98	42.04	7.92
FeL	1.28	0.38	16.38
NaK	2.01	1.43	7.67
MgK	0.62	0.42	7.34
AlK	7.05	4.29	3.93
SiK	9.48	5.54	3.66
ClK	2.08	0.96	5.53
K K	0.62	0.26	15.76
CaK	4.54	1.86	5.45

b.



c.

FIGURE 5. a) SEM-EDS image illustrating the mud morphology (500 x), b) quantifying the spectral data, and c) Corresponding EDS spectrum illustrating the elemental composition

Inductively Coupled Plasma-Optical Emission Spectroscopy (*ICP-EOS*) Kuwu mud ICP-EOS test results showed the presence of REE Ce, Dy, Eu, Gd, Ho, La, Nd, Pr, Sm, Tb, Y, and Sc, while Lu, Yb, and Tm were not detected. The most content is Ce 52.22 ppm and La 47.95 ppm, with a deviation of 0.06 and 0.22. Table 4 shows the results of the ICP -EOS test.

The seventeen REE consist of heavy REE and light REE. Heavy REE difine as lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm). REE concentrations in the earth's crust range from 130 µg/g to 240 µg/g. REE concentration is higher than other commonly exploited elements and much higher than the respective chondritic abundances. Bledug Kuwu mud contains heavy and light rare earth elements. The heavy REE in the Kuwu mud is La, Ce, Nd, Pr, and Sm, while Pm and Lu are undetected. The results of the ICP-EOS analysis show that the REE content in each sample is different but has a range of values that is not too large except for Gd. The difference concentration between the maximum and minimum element values is six ppm and 0.7 ppm. The difference is not much, therefore, the concentration of each sample is almost the same. The sample phase was solid, soft, and liquid, which did not affect the REE concentration obtained. Gd element was undetected in all samples because the concentration was less than others. In mud samples that tend to be a denser phase, Gd is unidentified, but in soft mud samples, Gd is present. The T10 sample has a different Gd value of -81 ppm.

Lutetium (Lu) is the hardest and densest metal. The percentage of lutetium in a mineral was less, as in the mineral monazite, lutetium found at 0.003% (Dia et al. 1999; Naimi & Ayoubi 2013). Lu does not identify by ICP -EOS in the mud sample of Kuwu. Thulium is not free but is identified in monazite, gadolinite, xenotime, and euxenite. Thulium can be isolated by reducing anhydrous fluoride with calcium metal or by reducing its oxide with lanthanum metal (Davisson, Presser & Criss 1994; Higgins & Saunders 1974; Kopf et al. 2003). Thulium is one of the least abundant elements on earth (Aslan et al. 2001; Lepichon et al. 1990; Martin et al. 1996). The calcite compound dominated the Kuwu 's mud, but Thulium was not in the Kuwu case. Figure 6 shows the average value of each rare earth element's concentration in the Bledug Kuwu mud. Graph 5 does not include extreme values in Gd.

TABLE 4. Rare Earth Element of Bledug Kuwu in mud sample

Sample	Rare Earth Element Concentration (ppm)														
	Ce	Dy	Eu	Gd	Ho	La	Lu	Nd	Pr	Sm	Tb	Tm	Yb	Y	Sc
T1	56.7	13.3	10.6	10.7	2.7	49.4	<IDL	26	27.4	17.9	16.5	<IDL	<IDL	3.3	8.3
T2	49.6	8	10.5	<IDL	2.3	46.3	<IDL	23.6	20	16.9	16.1	<IDL	<IDL	3	7.8
T3	59.4	9.5	10.9	<IDL	1.9	51	<IDL	26.4	23.5	18.1	16.4	<IDL	<IDL	4.8	8.9
T4	49	13.3	10.8	9.8	2.7	46.5	<IDL	23.6	26.3	18.3	16.5	<IDL	<IDL	3.4	8.2
T5	49.4	13.6	10.2	15.4	2.5	46.6	<IDL	23.7	27.3	18.2	16.1	<IDL	<IDL	3	7.5
T6	55.1	10.5	10.3	<IDL	1.7	49.3	<IDL	24.6	23.8	17.2	15.8	<IDL	<IDL	4.9	7.8
T7	50.9	11.9	10.3	6.6	1.2	47	<IDL	22.2	25.8	17.3	15.8	<IDL	<IDL	3.4	7.9
T8	46.3	12.7	10.2	11.9	1.7	46.6	<IDL	24.9	26.5	17.5	15.9	<IDL	<IDL	4.2	7.9
T9	57.7	14.1	10.2	15	1.8	50.1	<IDL	24.6	27.7	18.1	15.6	<IDL	<IDL	5.5	8.3
T10	48.1	<IDL	10.6	-81	1.3	46.7	<IDL	22.6	8.2	15.4	16	<IDL	<IDL	3.7	7.8
Min	48.1	8	10.2	-81	1.2	46.3	-	22.2	8.2	15.4	15.6	-	-	3	7.5
Max	59.4	14.1	10.9	15.4	2.7	51	-	26.4	27.7	18.3	16.5	-	-	5.5	8.9

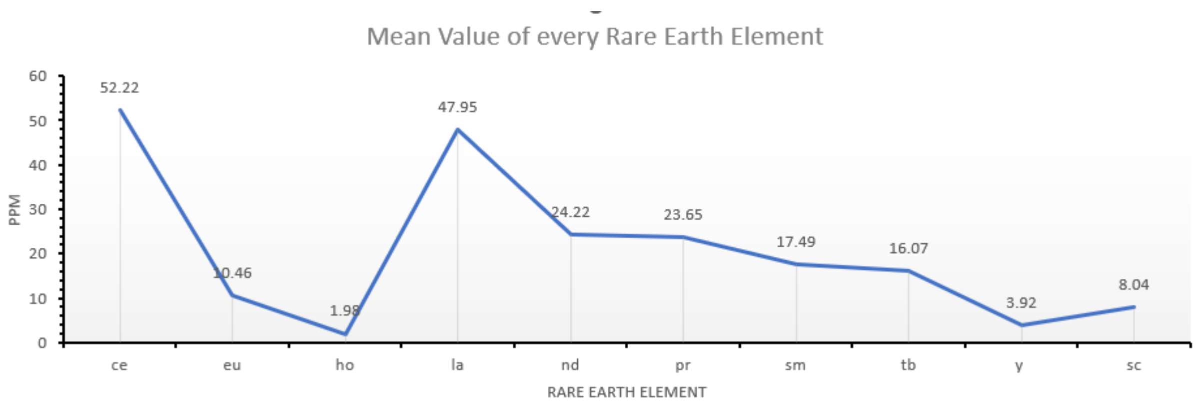


FIGURE 6. Average value of rare earth element's concentration in Bledug Kuwu mud

Gadolinium (Gd) is a lanthanide having very similar chemical and physical properties, the electron configuration of gadolinium results in a 3+ oxidation state. The characteristics of the 3+ oxide are very stable. Gadolinium is a rare REE. The amount of REE is around 60 parts per million (ppm), and Cerium is the most abundant REE element. The amount of Ce in nature exceeds Nickel (56 ppm) and Copper (25 ppm) (McGill 1993). Gadolinium occurs as oxides, carbonates, silicates, and phosphates. Gd is present in minerals such as monazite, bastnaesite, and apatite. The concentration of Gadolinium oxide in REE is around 0.7-4.0%, while the amount of REE in minerals is only 4%, so Gd is rare (Garret 2004; Srodon 1999). There are oxide compounds in Bledug Kuwu mud, producing Gd but in low concentrations (Attia et al. 2012; Kopf 2002; Kopf et al. 2003; Rizqiya 2014).

The graph shows that the highest concentration is Ce. As is well known, Ce is the most abundant REE component. Other REEs have an average concentration value of 1.95 ppm to 24.22 ppm. The significant elements are Ce 52.22 ppm and La 47.95 ppm, while the minor REE are Ho and Y. Holmium is a minor component of the mineral monazite and bastnaesite. Monazite and Bastnaesite. It extraction process produces Yttrium. The ion exchange and solvent extraction obtains Yttrium elements. Holmium can absorb neutrons, so it is used in nuclear reactors to keep a chain reaction under control. Some magnets on alloys also use Holium.

The Bledug Kuwu geochemical analysis results, explain the presence of REE content in the Bledug Kuwu mud. The number of REE elements in the Kuwu mud is 10 of 17 types. The formation of REE in the Kuwu mud is related to the tectonic activity of the Kuwu area. The availability of REE is generally associated with volcanic activity. High temperature and pressure affect the chemical activity that causes the formation of REE in a compound. Kuwu Mud Volcano is a mud volcano that is far from volcanism but is associated with oil and gas deposits. Even though it is far from volcanic activity, Kuwu mud still contains REE elements. The REE concentration in the Kuwu mud is lower than in the Lapindo mud. Lapindo mud is also an oil and gas deposit area in the East Java region close to Mount Penaggungan, thus enabling the formation of REE more optimally. The tectonic activity in the Rembang and Randublatung depression zones increases chemical activity in the Kuwu area, producing several REEs.

CONCLUSION

The results of the geochemical analysis of the Bledug Kuwu mud sample were the content of quartz, kaolinite, and calcite with an average concentration of 42.26%, 23.67%, and 33.96%. The susceptibility of Kuwu's mud is 0 because there is less metal element. According to the results, XRF, XRD, and SEM tests identified the main mud elements as C, O, Si, Ca, and Al. The REE in Kuwu's mud are Ce, Dy, Eu, Gd, Ho, La, Nd, Pr, Sm, Tb, Y, and Sc. The highest concentrations were Ce 52.22 ppm and La 47.95 ppm.

ACKNOWLEDGMENTS

The RKI (Riset Kolaborasi Indonesia) was granted by Diponegoro University, Semarang, no: 434-10/UN7.D2/PP/VI/2022.

REFERENCES

Agustawijaya, D. & Krisnayanti, B.D. 2013. Evaluasi kebolehjadian sistem panas bumi berdasarkan aspek geokimia dan deformasi geologi untuk Gunung Lumpur Sidoarjo-Jawa Timur. *Seminar Nasional III Teknik Sipil 2013*. Universitas Muhammadiyah Surakarta. G-347-G-352.

Arienzo, M., Ferrara, L., Trifuoggi, M. & Toscanesi, M. 2022. Advances in the fate of rare earth elements, REE, in transitional environments: Coasts and estuaries. *Water* 14(3): 401. https://doi.org/10.3390/w14030401

Aslan, A., Warne, A.G., White, W.A., Guevara, E.H., Smyth, R.C., Raney, J.A. & Gibeaut, J.C. 2001. Mud volcanoes of the Orinoco delta, eastern Venezuela. *Geomorphology* 41(4): 323-336.

Attia, O.E.A., Ab Khadra, A.M., Nawwar, A.H. & Radwan, G. 2012. Impacts of human activities on the sedimentological and geochemical characteristics of Mabahiss Bay, North Hurghada, Red Sea, Egypt. *Arab. J. Geosci.* 5: 481-499.

Bambang, P., Handoko, T., Sunardi, E., Hadi, S. & Sawolo, N. 2012. Mud volcano and its evolution. *Earth Sciences*. InTech. doi:10.5772/24944

Barber, A.J., Tjokrosapoetro, S. & Charlton, T.R. 1986. Mud volcanoes, and shale diapirs, wrench faults and melanges in accretionary complex, Eastern Indonesia. *Am. Assoc. Petrol. Geol. Bull.* 70: 1729-1741.

Bemmelen, R.W. 1949. *The Geology of Indonesia. Vol IA*. Netherland: The Haque Martinus Nijhoff, Government Printing Office.

Bowles, J.E. 1984. *Physical and Geotechnical Properties of Soils*. McGraw Hill, Inc.

Brand, E.W. & Brenner, R.F. 1981. *Soft Clay Engineering*. Elsevier Scientific Publishing Company.

Brindley, G.W. & Brown, G. 1980. *Crystal Structures of Clay Minerals and Their X-Ray Identification.* Mineralogical Society of Great Britain and Ireland. Vol. 5. https://doi.org/10.1180/mono-5

Brown, K. 1990. The nature and hydrogeologic significance of mud diapirs and diatremes for accretionary systems. *J. Geophys. Res.* 95: 8969-8982.

Carretero, M.I. 2020. Clays in pelotherapy. A review. Part I: Mineralogy, chemistry, physical and physicochemical properties. *Applied Clay Science* 189: 105526.

Chen, F.H. 1975. *Foundation on Expansive Soil, Development in Geotechnical Engineering* Vol. 12. Amsterdam: Elsevier Scientific Publishing Company.

Davies, R.J., Mathias, S.A., Swarbrick, R.E. & Tingay, M.J. 2011. Probabilistic longevity estimate for the LUSI mud volcano, East Java. *Journal of Geological Society* 168: 517- 523.

Davies, R.J., Swarbrick, R.E., Evans, R.J. & Huuse, M. 2007. Birth of a mud volcano: East Java. *GSA Today* 17(2): 4-9.

Davisson, M.L., Presser, T.S. & Criss, R.E. 1994. Geochemistry of tectonically expelled fluids from the Northern Coast Ranges: Rumsey Hills, California. *Geochima et Cosmochima Acta* 58(7): 1687-1699.

Delisle, G., Von Rad, U., Andruleit, H., Von Daniels, C., Tabrez, A. & Inam, A. 2002. Active mud volcanoes on-and offshore eastern Makran, Pakistan. *Int. J. Earth Sci*. 91(1): 93-110.

Deville, E. & Guerlais, S-H. 2009. Cyclic activity of mud volcanoes: evidence from Trinidad (SE Caribbean) *Mar. Pet. Geol*. 26(9): 1681-1691.

Dia, A.N., Castrec-Rouelle, M., Boulègue, J. & Comeau, P. 1999. Trinidad mud volcanoes: where do the expelled fluids come from? Ge*ochimica et Cosmochimica Acta* 63(7-8): 1023-1038.

Dimitrov, L.I. 2002. Mud volcanoes - the most important pathway for degassing deeply buried sediments. *Earth Sci. Rev.* 59(1-4): 49-76.

Garrett, D.E. 2004. *Handbook of Lithium and Natural Calcium Chloride: Their Deposits, Processing, Uses and Properties.* Amsterdam: Academic Press.

Grim, R.E. 1968. *Clay Mineralogy.* 2nd ed. New York: McGraw-Hill. p. 596.

Higgins, G.E. & Saunders, J.B. 1974. Mud volcanoes-their nature and origin. Contribution to geology and palaeobiology of the Caribbean and adjacent areas. *Verh. Naturfosch. Ges.* 84: 101-152.

https://www.idntimes.com/travel/destination. Accessed on 27 July 2022.

Husein, S. 2015. *The International Geology Course Programme*. *Petroleum and Regional Geology of Northeast Java Basin, Indonesia*. 7-11 December 2015. 10.13140/RG.2.1.2408.3280

Ibrahim, G., Subardjo & Sendjaja, P. 2010. *Tektonik dan Mineral di Indonesia.* Jakarta: Badan Meteorologi Klimatologi dan Geofisika.

Indriana, R.D., Nurwidyanto, M.I. & Haryono, K.W. 2007. Interpretasi bawah permukaan dengan metode *self potential* daerah Bledug Kuwu Kradenan Grobogan. *Berkala Fisika* 10(3): 155-167.

Kopf, A. & Deyhle, A. 2002. Back to the roots: Boron geochemistry of mud volcanoes and its implications for mobilization depth and the global B cycling. *Chem. Geol.* 192(3-4): 195-210.

Kopf, A., Deyhle, A., Lavrushin, V.Y., Polyak, B.G., Gieskes, J.M., Buadnidze, G.I., Wallmann, K. & Eisenhauer, A. 2003. Isotopic evidence (He, B, C) for deep fluid and mud mobilization from mud volcanoes in the Caucasus continental collision zone. *Int. J. Earth Sci.* 92: 407-425. doi.10.1007/S00531-003- 0326-y

Le Pichon, X., Foucher, J.P., Boulégue, J., Henry, P., Lallemant, S., Benedetti, M., Avedik, F. & Mariotti, A. 1990. Mud volcano field seaward of the Barbados accretionary complex: A submersible survey. *J. Geophys. Res***.** 95(B6): 8931-8943.

Lina, C., Rui, M., Paula, F., Claudia, M., Eduarda, P., Vitor, M., Luis, P. & Carlos, V. 2019. Rare earth elements in mud volcano sediments from the Gulf of Cadiz, South Iberian Peninsula. *Sci. of the Total Environment* 652: 869-879.

Maslov, A.V., Shevchenko, V.P. & Bychkov, A.Y. 2021. The distribution of trace elements in mud volcano sediments: Searching for features of a juvenile component impact. *Moscow Univ. Geol. Bull.* 76: 436-444. https://doi.org/10.3103/S0145875221040086

Martin, J.B., Kastner, M., Henry, P., Le Pichon, X. & Lallsment, S. 1996. Chemical and isotopic evidence for sources of fluids in a mud volcano field seaward of the Barbados accretionary wedge. J. *Geophys. Res*. 101: 20325-20345.

Mazzini, A. & Etiope, G. 2017. Mud volcanism: An updated review. *Earth Sci. Rev.* 168: 81-112.

McGill, I.J. 1993. Mathey rare earth elements. *Ullmann´s Encyclopedia of Industrial Chemistry.* Weinheim: Wiley-VCH. pp. 607-649.

Milkov, A.V. 2000. Worldwide distribution of submarine mud volcanoes and associated gas hydrates. *Marine Geology* 167: 29-42.

Mori, J. & Kano, Y. 2009. Is the 2006 Yogyakarta earthquake related to the triggering of the Sidoardjo, Indonesia mud volcano? *Journal of Geography* 118(3): 492-498.

Munasir, M., Triwikantoro, T., Zainuri, M. & Darminto, D. 2012. Uji XRD dan XRF pada bahan meneral (batuan dan pasir) sebagai sumber material cerdas ($CaCO_3$ dan SiO_2). *Jurnal Penelitian Fisika dan Aplikasinya (JPFA)* 2(1): 20-29.

Naimi, S. & Ayoubi, S. 2013. Vertical and horizontal distribution of magnetic susceptibility and metal contents in an industrial district of Central Iran. *J. Appl. Geophys*. 96: 55-66.

Nurhandoko, B.E.B., Kurniadi, R., Susilowati, Triyoso, K., Sri Widowati, Asmara Hadi, M.R., Rizal Abda, M., Martha, R.K., Elfa Fatiah & Rizal Komara, I. 2019. Integrated subsurface temperature modeling beneath Mt. Lawu and Mt. Muriah in The Northeast Java Basin, Indonesia. *Open Geosciences* 11(1): 341-351. https://doi.org/10.1515/geo-20190027

PANalytical B.V. 2009. *X-ray Fluorescence Spectrometry*. http://www.panalytical.com/index.cfm?pid=130. Accessed on 30 September 2009.

Queiber, M., Burton, M., Arzilli, F., Chiarugi, A., Marliyani, G.I., Anggara, F. & Harijoko, A. 2017. CO_2 flux from Javanese mud volcanism. *Journal of Geophysical Research: Solid Earth* 122(6): 4191-4207.

Rugayya, S. & Suryanto, W. 2019. Characterization of seismic signals at Bledug Kuwu using goodness-of-fit criteria analysis. *Journal of Physics: Conference Series.* 1242: 012050. 10.1088/1742-6596/1242/1/012050

Rizqiya, F. 2014. Analisis struktur fraksi fasa kristal natrium klorida dari *Brine Water* Bledug Kuwu sebagai fungsi waktu kristalisasi berdasarkan pola difraksi sinar X (X Ray Diffraction). Sarjana. Universitas Islam Negeri Sunan Kalijaga, Yogyakarta (Unpublished).

Rohmah, M., Lalasari, L.H., Wahyuadi, J. & Natasha, N.C. 2018. Lithium recovery from Bledug Kuwu mud volcano using water leaching method. *2018 IEEE International Conference on Innovative Research and Development* (ICIRD). 11-12 May.

Sabdaningsih, A. 2018. MITOLOGI DAN SAINS: Bledug Kuwu di Kabupaten Grobogan. *Sabda: Jurnal Kajian Kebudayaan* 13(1): 7-17. doi.org.10.14710/sabda.13.1.7-17

Sari, I.G.A.A.S. & Warmada, I.W. 2021. *IOP Conf. Ser.: Earth Environ. Sci.* 851: 012042. doi.10.1088/1755-1315/851/1/012042

Satyana, A.H. & Asnidar. 2007. Mud diapirs and mud volcanoes in depression of Java to Madura: Origins nature and implications to petroleum system. *Annual Convention & Exhibition Indonesia: Indonesian Petroleum Association* 32: 139.

Sa'diyah, K., Syarwani, M. & Hadiantoro, S. 2017. Adsorption of nickel in nickel sulphate solution (NiSO4) by Lapindo mud. *Jurnal Bahan Alam Terbarukan* 6(1): 39-44.

Scimeca, M., Bischetti, S., Lamsira, H.K., Bonfiglio, R. & Bonanno, E. 2018. Energy dispersive X-ray (EDX) microanalysis: A powerful tool in biomedical research and diagnosis. *European Journal of Histochemistry: EJH* 62(1): 2841. https://doi.org/10.4081/ejh.2018.2841

Siregar, S. & Siregar, N.I. 2016. Analisis dan pemanfaatan unsur belerang dan salinitas lumpur Bledug Kuwu di Desa Kuwu, Kecamatan Kradenan, Kabupaten Grobongan, Jawa Tengah. *POSITRON: Berkala Ilmiah Fisika* 6(1): 40-42.

Smallman, R.E. & Bishop, R.J. 2000. *Modern Physical Metallurgy and Materials Engineering.* New York: Hill International Book Company.

Srodon, J. 1999. Nature of mixed-layer clays and mechanisms of their formation and alteration. *Annu. Rev. Earth Planet Sci.* 27: 19-53.

Sudarningsih, S., Bijaksana, S., Ramdani, R., Hafidz, A., Pratama, A., Widodo, W., Iskandar, I., Dahrin, D., Fajar, S.J. & Santoso, N.A. 2017. Variation in the concentration of magnetic minerals and heavy metals in suspended sediments from Citarum River and tributaries, West Java, Indonesia. *Geosciences* 7: 66.

Sulistiyono, E., Lalasari, L. H., Mayangsari, W. & Prasetyo, A. 2018. Study of lithium extraction from brine water, Bledug Kuwu, Indonesia by the precipitation series of oxalic acid and carbonate sodium. *AIP Conference Proceedings* 1964: 020007.

Sumarno, S., Ratnawati, R. & Nugroho, A.N.A. 2012. Recovery garam lithium dari air asin (Brine) dengan metoda presipitasi. *Teknik* 33(2): 67-69.

Talas, E., Duman, M., Küçüksezgin, F., Brennan, M.L. & Raineault, N.A. 2015. Sedimentology and geochemistry of mud volcanoes in the Anaximander Mountain Region from the Eastern Mediterranean Sea. *Marine Pollution Bulletin* 95(1): 63-71. https://doi.org/10.1016/j.marpolbul.2015.04.042

Tran, K.T., Van Luong, T., An, J.W., Kang, D.J., Kim, M.J. & Tran, T. 2013. Recovery of magnesium from Uyuni Salar brine as high purity magnesium oxalate. *Hydrometallurgy* 138: 93-99.

Vignesh, A., Ramanujam, N., Rasool, Q. & Swapan, K.B. 2016. Geochemical evidence for provenance, tectonic settings, and presence of gas hydrate in mud volcano sediments of Andaman Islands. *Oil Gas Res.* 2: 111. doi:10.4172/2472-0518.1000111

Zainudin, A., Badri, I., Padmawijaya, T., Humaida, H. & Sutaningsih, E. 2010. *Fenomena Geologi Semburan Lumpur Sidoarjo*. Bandung: Badan Geologi, Kementerian Energi dan Sumber Daya Mineral.

Zhang, C., Qiao, Q., Appel, E. & Huang, B. 2012. Discriminating sources of anthropogenic heavy metals in urban street dust using magnetic and chemical methods. *Journal of Geochemical Exploration* 119-120: 60-75.

*Corresponding author; email: rinadwiindriana@lecturer.undip.ac.id