The Rare Earth Elements in Grobogan Mud Volcanoes, Indonesia: Alternative Mineral Resources for Advancing the Green Energy Technology

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The Rare Earth Elements in Grobogan Mud Volcanoes, Indonesia: Alternative Mineral Resources for Advancing the Green Energy Technology

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Abstract: The Indonesia is one of the prospective countries for rare earth element (REE) exploration. The study of rare earth elements in Indonesia is growing enormously. Currently the exploration is focused on the granitoid rock that widely distributed in Sumatera, Sulawesi, Kalimantan and Papua. The famous one is potential sources of REE come from residual tin mining in Bangka Island, Sumatera. Meanwhile the potential of REE abundance in mud volcano area is rarely studied and analyzed. The objective of this paper is to present the potential of REE in the Grobogan mud volcano, which has not been done before. As REE is one of the very important materials in green energy technology. Mud volcano is still considered as the sources of disaster with less impact compared to traditional volcanoes. Mud volcano is believed to have no benefits for human life. This study was done to show the REE contents from the mud sample in study area. The sample was taken from the fresh mud of eight mud volcanoes in study area. These mud volcanoes appear on the surface due to Rembang-Madura-Kangean fold and thrust belt activity. Among the 17 rare earth elements, 16 of them recorded in mud sample, only Promethium (Pm) was not recorded in this study. The 5 most common rare earth elements that present in the mud sample are Scandium (Sc), Cerium (Ce), Lanthanum (La), Neodymium (Nd), and Yttrium (Y). SEM analysis was done to the mud samples show that the mud samples are dominated by Smectite-Illite clay mineral. Clay mineral can be the sources of the REE abundances in the mud volcanoes.

Keywords: Rare earth elements; mud volcano; fold and thrust belt; green technology

1. Introduction

The rare earth elements (REE) are a group of metallic elements in periodic table that consist of 15 elements of Lanthanides (Lanthanum, Cerium, Praseodymium, Neodymium, Promethium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, and Lutetium), Yttrium (Y) and Scandium (Sc). The first rare earth element was found by Carl Axel Arrhenius, who was a thirty-year-old Swedish artillery officer and an amateur mineralogist, stumbled on a black heavy stone at a Ytterby mine in 1787[1-3]. The sample was then sent to Johan Gadolin, a Finnish chemist in University of Abo. Gadolin was able to do chemical analysis in 1794 that concluded 38% of the material was unknown earth material, which then he named it as Yttrium (Yt). In 1907, George Urbain, a French chemist, discovered the last rare earth element, Lutetium, from the Ytterby sample. Ytterby is an important village for rare earth element discovery as at least 8 elements were found in Yttrby, they are Yttrium, Erbium, Terbium, Ytterbium, Scandium, Thulium, Holmium, Dysprosium, and Lutetium[3].

REE becomes very important nowadays due to its application in green technologies and high-tech applications[64-68]. The critical role of REE in the transition to low carbon energy and high technology industries, motivate the increasing of global REE demand to an approximate annual growth rate of 5% by the end of 2020[52] (Fig. 1). In general, the most common geological environments that host REE are divided into two major groups. They are magmatic rare earth deposits and sedimentary rare earth deposits. The magmatic REE

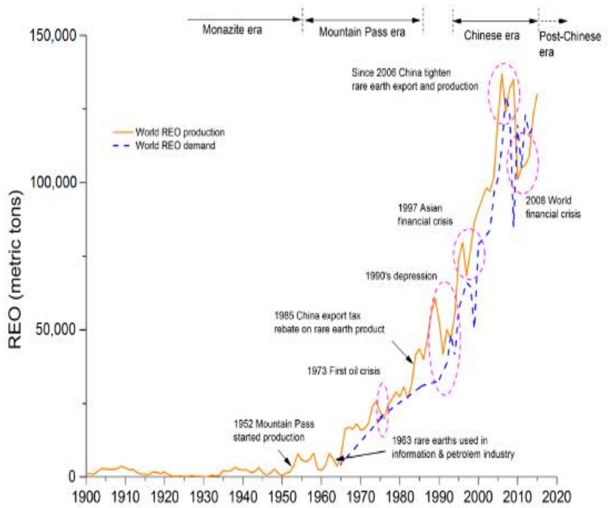


Fig. 1: Global REE production and demand in 1900-2020[52].

related to the magmatic mineralization that enrich the rocks with REE. It is the most common abundant REE and mineable on earth. Hydrothermal process also contributes to the enrichment of REE through metasomatic events after the primary magmatic mineralization. Combination of both also suspected the main process in magmatic REE generation[4-6]. The examples of magmatic REE are carbonatite deposits (China's Bayan Obo in China, Mountain pass in California), Peralkine deposits (Bokan mountain in Alaska) and Pegmatitic apatite (Mineville in New York). Carbonite deposits can be divided into three types: i) primary magmatic type, ii) hydrothermal type, and iii) carbonatite weathering crust. Primary REE deposits are found in Carbonatite and Peralkine igneous rock[7,8]. Exploration projects normally target carbonate igneous rock (carbonatite) or their weathering products[9].

The sedimentary REE deposits are the rare earth elements that are concentrated within sedimentary rocks. The sedimentary REE can be divided into four types: i) residual/placer deposits (paleo placer in Witwatersrand in South Africa, Elliot Lake Mining District in Canada, Bangka-Belitung in Indonesia), ii) phosphorite deposits (Florida/Idaho in USA), iii) ion adsorption clays (China Clay deposits in China), iv) REE bearing coals

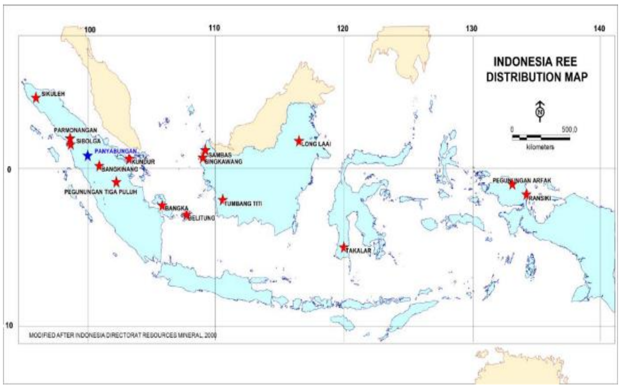


Fig. 2: Occurrence of manganese nodules, cobalt crusts, marine mud and phosphorites at the ocean basins, seamounts and continental margins in the oceans[8].

(Pennsylvania in USA). The residual REE deposits can be formed from deep intense weathering of igneous rock, pegmatites or iron-oxide copper gold deposits[8]. Placer deposits come from tertiary or quaternary deposits and also can come from Precambrian deposits. Monazite is the common REE bearing mineral in igneous, metamorphic and sedimentary rocks that maybe concentrated in placer deposits. Phosphorite deposits is sedimentary rock that contains high level of phosphate minerals that often linked to marine environments (Fig. 2). Phosphorus comes from weathering of rocks on land which transported by rivers to the ocean and then concentrated in marine sediments[10].

Ion adsorption clays-type REE deposits are the type of REE deposits that accumulated in clay minerals due to adsorption process or weathering process in tropical environment. The REE adsorbed to the surface of clay minerals (illite), kaolinite or halloysite[11]. Southern China is the world's main source for heavy rare earth elements (HREE). The REE bearing coals-REE type deposits are the REE that accumulated in coal due to the physical or chemical erosion from source material. According to recent studies, explorationists also start working on exploiting extraterrestrial REE resources, with the Earth's Moon becomes the logical first target. Current and future missions to the Moon, Mars, or other nearby planets will be incorporated the possibility to explore the REE resources in our Solar System[8,9]. It also concludes that rare earth metals are present in all kinds of geology setting, stretching from mountains range all the way down to marine sediments in the oceanic crust. Unfortunately, very little research has been done on the potential of REE in mud volcanoes and the study of their geology. This may be another potential REE resource that is completely different from any other documented REE resource.

The REE in Indonesia normally presents as by-products from alluvial gold and tin mining activity. Indonesia has several alluvial gold mining but the REE deposits in tin mining are more economics. The famous tin mining normally presents in the Southeast Asian Tin Belt stretching from Karimun islands-Singkep-Bangka-Belitung in Sumatera[12,13]. In general, there are five types of REE main exploration targets in Indonesia, they are: i) REE deposits associated with alkaline-peralkaline igneous rock (South Kalimantan province), ii) REE deposits associated with secondary lateritic deposits (West Kalimantan province), iii) REE deposits associated with placer monazite (xenotime) as by-products of placer tin mining (Bangka-Belitung, Kampar and Riau islands in Riau province), iv) REE deposits associated with coal bearing sedimentary rock (lapangan batubara Air Laya in South Sumatera), v) REE deposits associated with ion adsorption (Granit Sibolga in North Sumatera). There are at least 15 locations of REE potential in Indonesia that associated with granitoid rock and its weathered crusts as Fig. 3 shown below[13-16]. The challenging exploration of REE in Indonesia comes from the complex of the geology, REE deposits that associated with the presence of radioactive minerals, and the difficulties in separating and extracting the REE from the tin mineralization[14].

Among all the REE exploration targets in Indonesia, none of them consider mud volcano deposits as one of the potentials of REE resources. REE resources from mud volcanoes began to be discussed after the eruption of Lumpur Sidoarjo (LUSI) mud volcano and the development of REE needs worldwide. The earliest documentation of REE resources in LUSI mud volcano was supplied by the Plumlee, et al. (2008). It was then continued by Agustawijaya et al. (2017). Then the last updated measurement was done by Wibowo et al. (2022). From these documented results, there are at least 7 major rare earth elements dominated the mud of LUSI mud volcano (Fig. 4). They are Cerium (Ce), Lanthanum (La), Neodymium (Nd), Yttrium (Y), Praseodymium (Pr), Scandium (Sc), and Samarium (Sm).

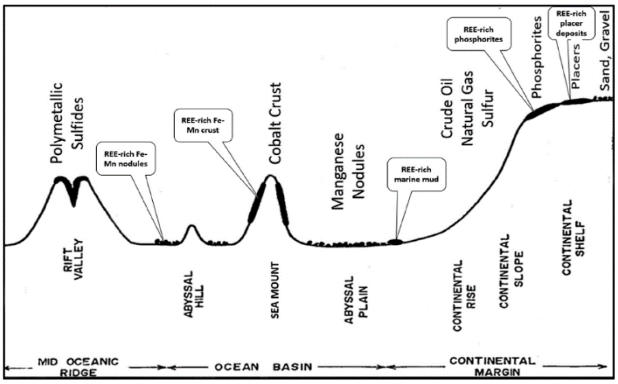


Fig. 3: Distribution of REE potential in Indonesia[14].

The importance of mud volcano REE resources study becomes renowned since the last 6-7 years[20-24]. In Indonesia, the mud volcano REE study was only focused in LUSI mud volcano whereas there are many other active mud volcanoes in Indonesia. One of them is in the research area, the Grobogan district, Central Java Province. One of the objectives of this research is to explore the potential of REE resources in other active mud volcanoes in Indonesia.

The emergence of mud volcanoes on the earth's surface cannot be separated from the control of geological structures which are tensional stress. This is due to the tensional stress allows fluids from subsurface to emerge to the earth's surface. Likewise, magma from below the earth's surface emerges to the earth's surface through normal faults[25-27]. Grobogan mud volcanoes are influenced by the a left-hand horizontal fault geological structures, known as Rembang-Madura-Kangean-Sakala (RMKS) Fault Zone, and Fold thrust Kendeng Fault Zone, that are most likely to control the appearance of mud volcanoes on the earth's surface (Fig. 5). Basically, strike-slip faults and thrust faults are compressional faults, divided the zone into fault segments. It is common to find mud volcano associated with faults and anticlines. The RMKS Fault Zone is a zone of tectonic disturbance as long as 650 km long and 15-40 km wide situated at the

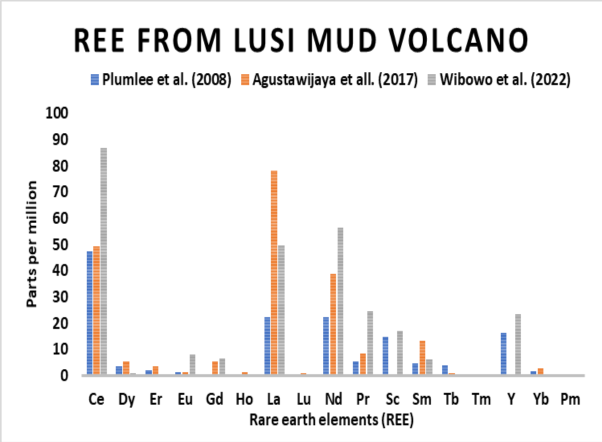


Fig. 4: Comparison of REE content from mud sample of LUSI mud volcano from 2008 to 2022[17-19].

northern side of East Java from Rembang through Madura and Kangean Islands to Sakala offshore areas. The fault zone trends west-east[28]. The Kendeng Thrust Fault zone that has disturbance as long as 200 km long with east – west trend present in the southern side of the Grobogan mud volcanoes.

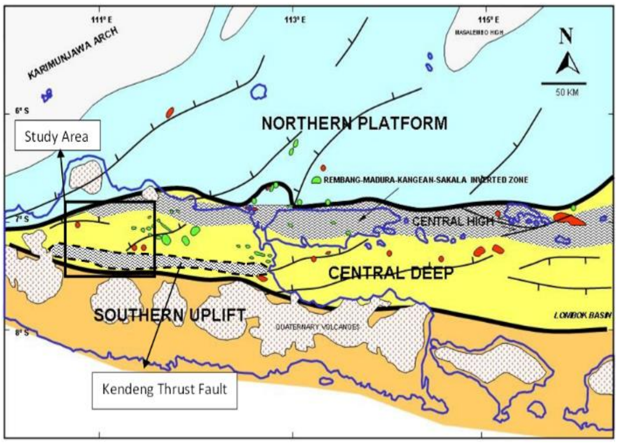


Fig. 5: Geologic setting of East Java Basin and study area (modified from Satyana et al., 2004).

REE are needed for green technologies and high-tech applications, besides many other uses in manufacturing or daily needs of human equipment. Certain kind of rechargeable batteries that use Cadmium (Ca) or Lead (Pb) have been replaced with rechargeable battery from Lanthanum-Nickel-Hydride (La-Ni-H). The increasing use of electric cars and motorcycles causes increasing of REE consumption. The group of REE contains Nd, Pr, Dy, and Tb is important materials for electric car manufacturing and hybrid car generator. Whereas the La, Nd and Ce are the important material in hybrid car battery manufacturing. REE is also used as catalysts to purify the crude oil (La, Nd, Pr)[13,16]. REE is used as fertilizer in agriculture to improve crop growth and production. In medical, Gd has beed used in a chelated form as a contrast agent in magnetic resonance imaging (MRI)

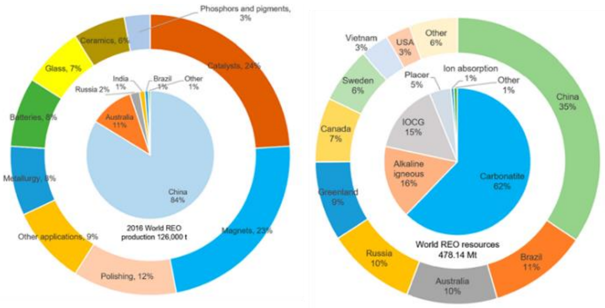


Fig. 6: Global distribution of REE production and consumption in 2015 (right); Global distribution of REE by principal deposit (left).

measurements[8]. Fig. 6 is the global REE production and REE consumption in 2015.

2. Methodology of Research

The REE is divided into two major groups among all 17 rare earth elements, light rare earth element (LREE) and heavy rare earth element (HREE). The LREE consists of Scandium (Sc), Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), and Europium (Eu). The HREE consists of Yttrium (Y), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), and Lutetium (Lu). The methodology in this paper was done by doing geological field mapping (visiting each mud volcanoes and taking the mud samples), laboratory measurement with ICP-MS method, and followed by regression analysis, Sun and McDonough (1989)[29] normalization display on spider diagram, and hierarchical clustering.

The mud samples from each of mud volcanoes in Grobogan district were sent to the Laboratory facilities in Center for Geological Survey in Bandung (Fig. 6). Analysis of rare earth metals or often known as Rare Earth Elements (REE) is carried out using ICP-MS (Inductively

Fig. 7: ICP-MS laboratory in Centre for Geological Survey in Bandung (picture was provided by Laboratory of Geological Survey Centre in Bandung).

Coupled Plasma Mass Spectrometry) technology (Fig. 7). This technology is a combination of induction plasma and plasma spectrometer which measures elements based on mass number and has a low detection limit. The use of this technology is increasingly popular for measuring low or even very low concentrations of radioactive elements. ICP-MS is used to analyze samples that are liquids (such as water) or that can be dissolved, or acid digested. ICP-MS can detect many elements at levels below 0.1 part per trillion (ppt), elements at concentrations up to 100s or even 1000s of parts per million (ppm). One thousand ppm is 0.1%, and the concentration range from 0.1 ppt to 0.1% covers 10 orders of magnitude. There are at least 8 mud samples were analyzed that came from 8 mud volcanoes in Grobogan District.

Beside the REE analysis, we also conducted the Scanning Electron Microscope (SEM) analysis in the same laboratory to the mud samples of the Grobogan mud volcanoes. The main equipment used in SEM analysis is JEOL JSM-6360LA Scanning Electron Microscope equipment, equipped with an Energy Dispersive System (EDS), made in Japan.

3. Result and Discussion

The REE measurement results from the mud samples in Grobogan mud volcanoes were compared with Lusi mud volcano REE measurements. After plotting the result from all 8 mud volcanoes in Grobogan district, the major REE domination is still the same as previously shown in Lusi mud volcano. The most dominant REE in order are Sc, Ce, La, Nd, and Y, whereas Pr and Sm present in smaller amount compared to the first 5 elements (Fig. 8). This trend result aligns with the result of REE measurement from mud sample in Lusi mud volcano. Sc become the most dominant REE in Grobogan mud volcanoes. Anak Kesongo and Medang mud volcanoes have the highest content of Sc. Sc is famous for its use in aerospace industry. The Al-Sc alloys are strong and very light, it is suitable for airplane or car manufacturing. The small amount of Sc is sufficient to create lighter aircraft or cars[30].

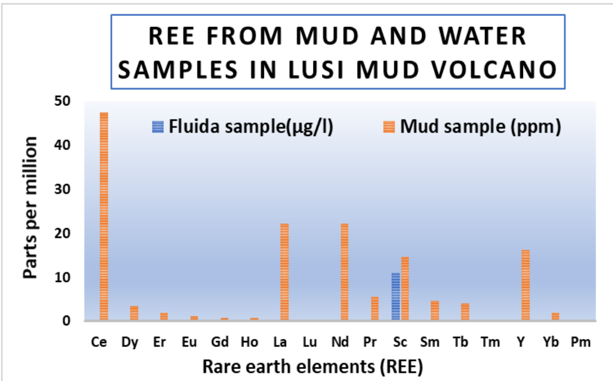


Fig. 8: Mud sample REE measurement from Grobogan mud volcanoes and Lusi mud volcanoes.

Burhannudinnur (2019) stated that based on foraminifera analysis in the mud sample from each mud volcanoes in Rembang Zone or Grobogan district, the origin of the mud came from the Early Miocene to Pliocene formation, which is Tawun formation. Tawun formation is foraminifera rich mudstone dominated lithology that was deposited in middle Neritic (60-140 mwd) to upper Bathyal (1000-4000 mwd) marine environment. Meanwhile, the mud source in Lusi mud volcano and neighboring mud volcanoes, is suspected originally came from younger formation, which is Pleistocene Kalibeng formation. Kalibeng (Upper) formation is dominated laminated argillaceous mudstone lithology with foraminifera enrichment[31,32].

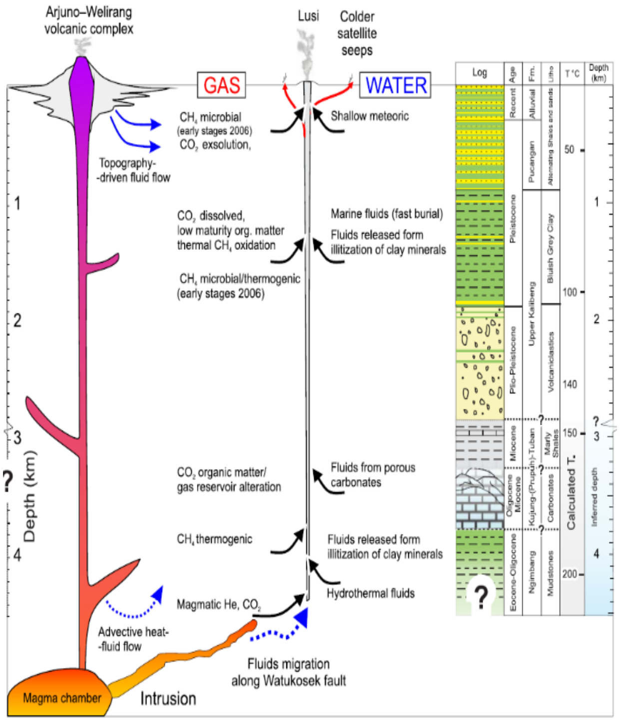


Fig. 9: Cartoon summarizing the various sources of water at the Lusi site[32].

Most of the water samples in Grobogan mud volcanoes are salty and hot or warm. The water may possibly come from the trapped water during the burial of marine sediments with the combination of water influx from the hydrothermal system (Fig. 9). This water can also bring the REE and enrich the REE content of the material erupted from mud volcanoes. The mud may also have REE content from other process like weathering and erosion enrichment processing.

Plumlee et al. (2008) shared the result of the REE measurement from the mud and water sample of Lusi mud volcano (Fig. 10). It is clearly seen that the REE content from mud sample is much higher than REE content in water sample. This result can be used as reference that REE content in Grobogan mud volcano most likely comes from the mud itself. The mineralogy of mud in Lusi mud volcano is dominated by silicate mineral, like kaolinite

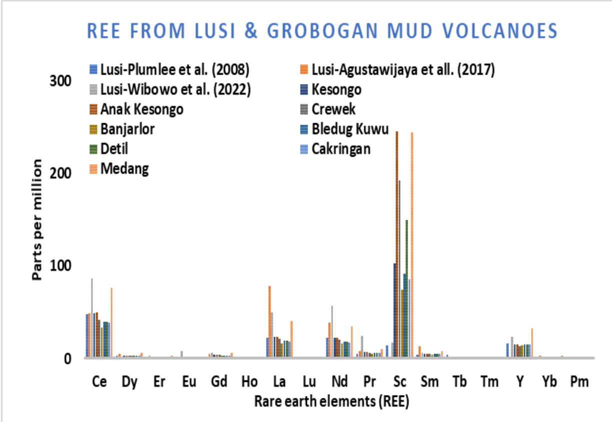
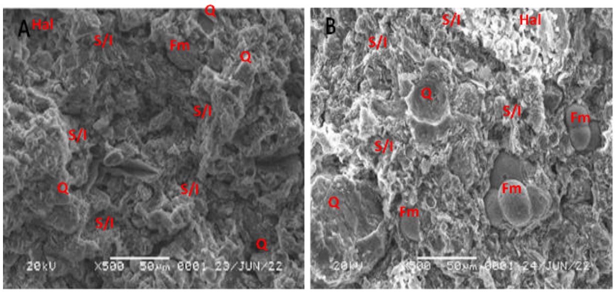


Fig. 10: REE from mud and water sample of Lusi mud volcano[17].

and muscovite. Clay mineral in the mud sample has the ability to adsorb the REE through ion substitution[33]. Agustawijaya et al. (2017) mentioned that the porous clay mineral like smectite-illite is ideal for trapping the REE.

SEM analysis was done for the mud sample of mud volcano in Grobogan district. The result showed the domination of smectite-illite mineral in the mud sample (Fig. 11). The SEM analysis clearly shows indication of silica and alumina sheets of the clay mineral (smectite-illite) of the mud samples. Foraminifera fossils is also present abundantly.



(a) (b)

Fig. 11: SEM analysis from mud samples in (a) Crewek and (b) Anak Kesongo mud volcanoes. It shows the alumina sheets of the smectite/illite structure from the mud samples. Q = quartz; S=smectite; I=Illite; Hal=Halite.

The geochemical data of mud volcanoes from different locations indicate variations in the content of Rare Earth Elements (REE), grouped into light-REE (LREE) and heavy-REE (HREE), as well as Scandium + Yttrium (Sc+Y). In this study, these geochemical groups were variables in the statistical analysis. The average LREE content across Grobogan zone mud volcanoes is approximately 101.22 ppm. Besides, HREE has an average of 13.39 ppm, while Sc+Y has an average of 158.36 ppm. The data and comparisons of geochemical characteristics were presented in the form of a scatterplot with regression analysis to comprehend the relationship between the variables (Fig. 12).

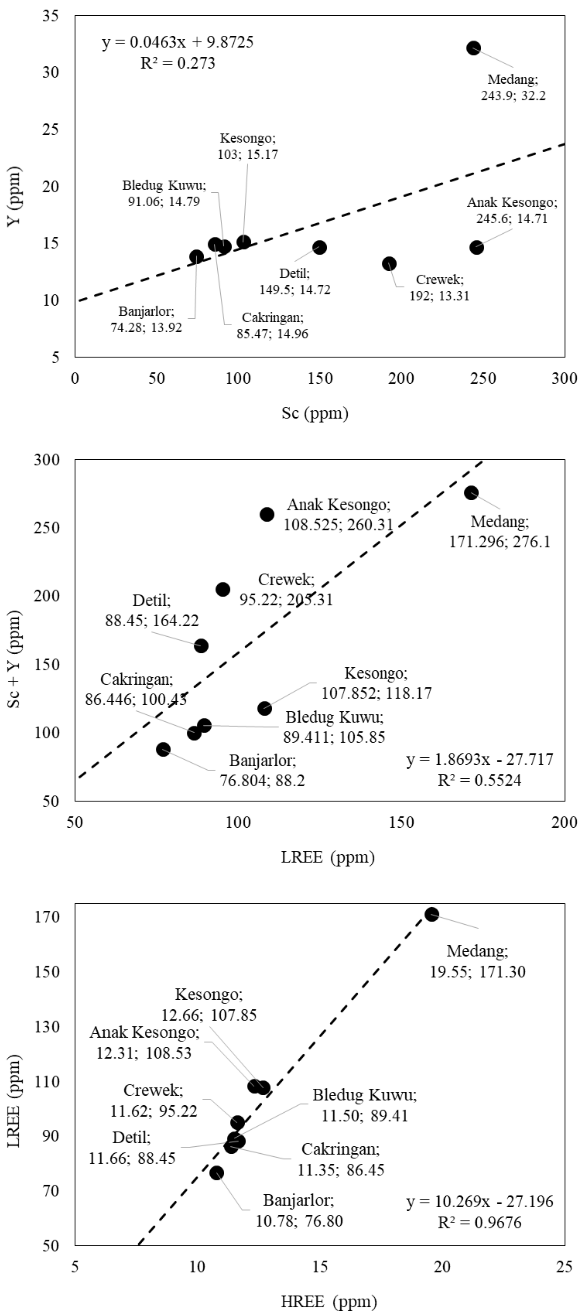


Fig. 12: Scatterplot of Sc+Y, HREE, and LREE for each geochemical data of observed mud volcanoes in the Rembang Zone, along with the regression analysis. Each geochemical value data of every mud volcano sites represented in (*x*;*y*); LREE: La, Ce, Pr, Nd, Sm, Eu; HREE: Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

The Medang mud volcano has the highest geochemical value among the mud volcanoes in the Grobogan. Medang mud volcano demonstrates LREE content of 171.29 ppm, HREE content of 19.55 ppm, and Sc+Y content of 276.1 ppm. In contrast, the mud volcano with the lowest geochemical values is Banjarlor, with LREE content of 76.8 ppm, HREE content of 10.78 ppm, and Sc+Y content of 88.2 ppm. The R^2 value (coefficient of determination) in the linear regression in this study serves as a statistical measure that reflects the ability of the model to explain the variation in the observed geochemical variables. This plays a key role in understanding the relationship between these variables. A value closer to 1.0 indicates a stronger and more consistent relationship, while a value closer to 0.0 suggests the data are more randomly scattered and tend to be non-linear. The regression analysis results revealed a strong relationship between LREE and HREE for each mud volcano, as evidenced by a high R^2 value of 0.9676 and a gradient value of 10.3. This implies that for every 1.0 ppm increase in HREE, there is a 10.3 times increase in LREE concentration. The analysis also showed that the geochemical characteristics of Medang mud volcano were significantly different from those of the other mud volcanoes. PCA was conducted to gain a deeper understanding of these characteristics, Principal Component Analysis (PCA) was conducted (Fig. 13). This analysis illustrates the relationships between the abundance of earth elements in the geochemical data of mud volcanoes based on the PCA vectors generated by each variable.

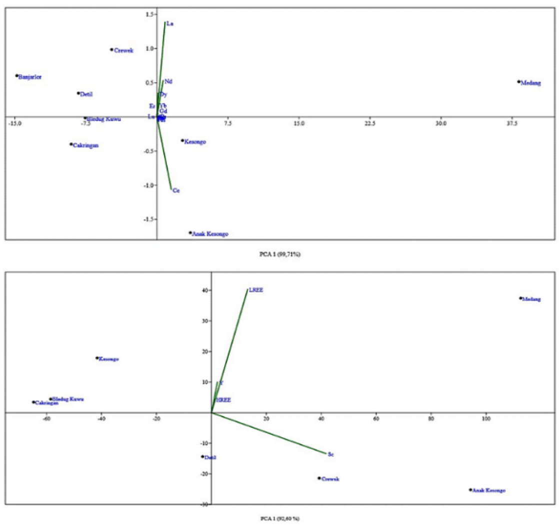


Fig. 13: PCA analysis on the variable data of Rare Earth Elements (REE) La to Ce in mud volcanoes (upper), LREE vs. HREE vs. Sc+Y (lower). The vectors (green line) illustrate the relationships between the compared variables.

The PCA results for all REEs indicated a significant relationship between La and Ce. Higher concentrations of La corresponded to lower abundances of Ce, as demonstrated by the opposing direction of the vectors for the La and Ce variables. Similar vector directions indicate a positive correlation observed in elements La, Nd, Dy, Yb, and Gd. It shows an increase in La concentration, followed by an increase in Nd, Dy, Yb, and Gd. The PCA results also confirmed a proportional relationship between the LREE and HREE. Interestingly, LREE and HREE also showed a proportional relationship with Y (Yttrium). These elements did not show a significant relationship with the Sc abundance. Based on the vector lengths for each variable, it can be concluded that La, Ce, LREE, and Sc played significant differentiating roles in each mud volcano.

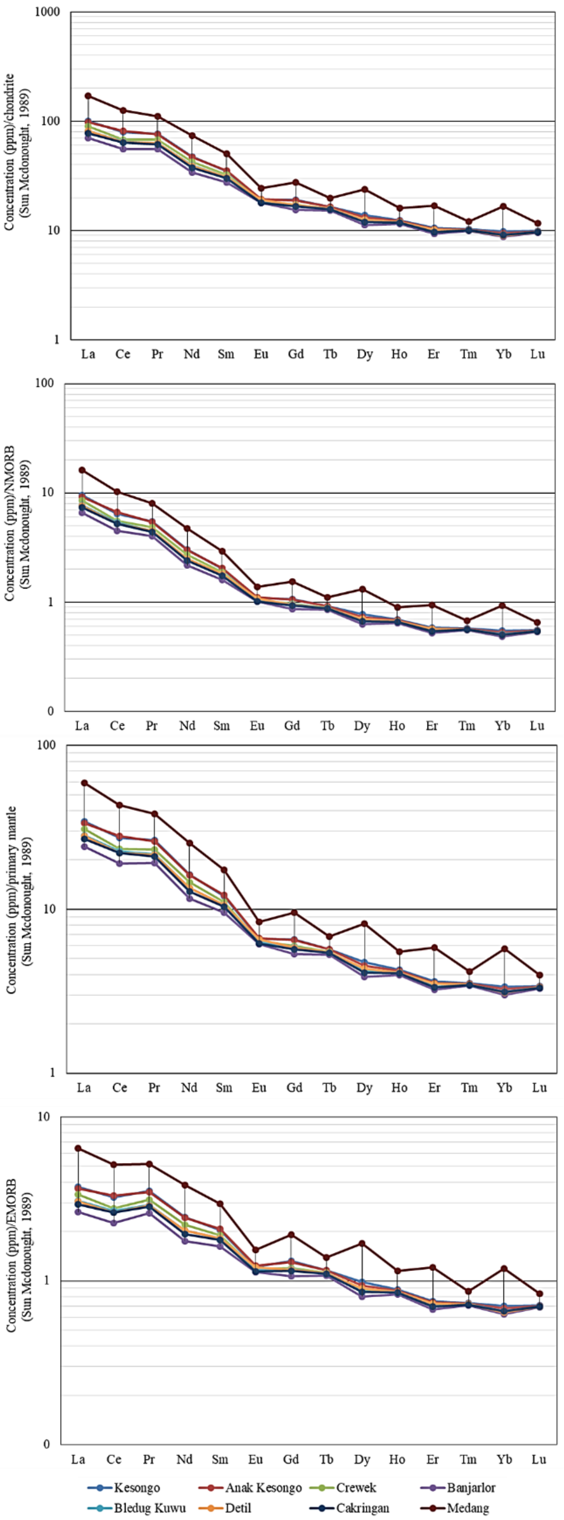


Fig. 14: Spider Diagram of mud volcanoes in the Grobogan, based on normalization results compared to Chondrite, Primary mantle, Enriched Mid-Ocean Ridge Basalt (EMORB), and Normal Mid- Ocean Ridge Basalts (NMORB).

Rare earth elements (REE) can be highly significant in determining the characteristics of mud volcanoes because these elements originate from different sources and exhibit diverse element mobility characteristics. The mobility of REEs is greatly influenced by their atomic mass, with lanthanide elements, such as La, having a lighter atomic mass than Ce. This mobility affects the availability of REEs in the source rocks into mud of the mud volcano. In geochemistry, rare-earth elements are typically presented as normalized spider diagrams, where the concentrations of rare-earth elements are normalized to reference standards refer to Sun and McDonough (1989). Common reference standards include Chondrite, Primary mantle, Enriched Mid-Ocean Ridge Basalt (EMORB), and Normal Mid-Ocean Ridge Basalts (NMORB). Naturally, the abundance of REEs in the Earth's crust exhibits the Oddo-Harkin's effect, a general zigzag pattern formed due to differences in atomic size[34]. The results of REE normalization from La to Ce can be observed in Fig. 14.

The Normalized REE spider diagram indicates the relative abundance of mud volcano materials compared with the reference standard materials. Values above 1.0 indicate relative enrichment based on the comparison material, while values below 1.0 indicate conditions of lower abundance. It can be observed in the diagram that all LREE in the mud volcano show higher abundance compared to standard references, such as Chondrite, Primary mantle, Enriched Mid-Ocean Ridge Basalt (EMORB), and normal mid-ocean ridge basalts (NMORB). In contrast, the HREE from the mud volcano tended to be less abundant than EMORB and NMORB. This result suggests that mud volcanoes in the Grobogan originate more from continental crust than oceanic crust. From this analysis, it is clear that the geochemical characteristics of the mud volcanoes are strongly influenced by their formation. Rare earth elements are formed through geological processes related to geochemical enrichment and are influenced by the characteristics of source rocks, pressure, and subsurface temperature[18,35,36]. Hierarchical clustering was performed to identify the similarities in characteristics among the analyzed mud volcanoes based on Euclidean index distance values presented in the dendrogram (Fig. 15).

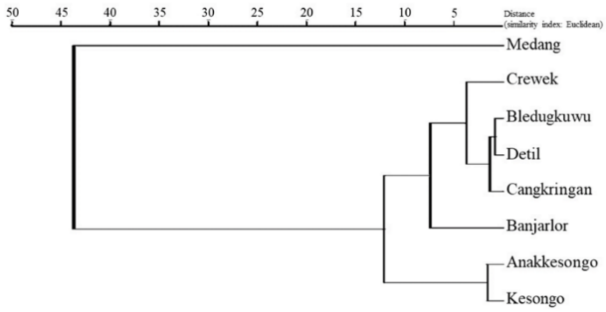


Fig. 15: Dendrogram of hierarchical clustering of mud volcanoes in the Grobogan. This graph illustrates the level of similarity between the mud volcanoes based on the Euclidean distance, similarity index.

The dendrogram indicates the level of similarity in the characteristics of the analyzed mud volcanoes. Some neighboring mud volcanoes, like the Kesongo and Anak Kesongo mud volcanoes, share similar characteristics.

The similarity between Detil and Bledug Kuwu is also noticeable, which appears to be more similar than others. Interestingly, Medang is a mud volcano that is relatively distinct from all analyzed mud volcanoes. This result suggests that the Medang mud volcano possesses a different geological setting than other mud volcanoes in Grobogan.

Based on this study, it has been revealed that Rare Earth Elements (REE), especially scandium (Sc), cerium (Ce), neodymium (Nd), and yttrium (Y), are enriched in mud volcano activities. The abundance of these elements in mud material can exceed 10 ppm. Scandium (Sc) is the highest among the REE. The findings of this study suggest that these elements can be extracted and utilized in the development of advanced green technologies.

Fig. 16: (a) Medang mud volcano, (b)Anak Kesongo mud volcano.

Scandium (Sc), in the development of green energy technology, plays a crucial role in advancing the lightweight components of electric vehicles and wind turbines. This usage improves the energy efficiency and component durability, supporting green transportation and more efficient wind turbine operations. Additionally, scandium is utilized in Solid Oxide Fuel Cells (SOFCs) to stabilize electrolytes made of yttrium (Y) and zircon, thereby reducing operational temperatures and improving fuel cell efficiency[37-39].

Cerium (Ce) is also crucial for several green technologies. In the automotive industry, cerium plays a key role in catalytic converters and serves as an additive in certain types of diesel fuels, enhancing combustion efficiency and reducing emissions (NOx). This application reduces harmful emissions and makes internal combustion engines more environment-friendly. Furthermore, cerium is being studied for its potential in energy storage, including rechargeable battery technology capable of providing stable and high-capacity energy storage. Cerium is utilized as a material in solar panels (cerium oxide) to improve the performance and durability of solar cells. Additionally, in water treatment, cerium compounds, particularly cerium oxide nanoparticles, are being investigated for their potential use in purifying water from contaminants and pollutants[40-43].

As the main component in neodymium-iron-boron (NdFeB) magnets, neodymium plays a crucial role in wind turbines by contributing to the efficient conversion of wind energy into electricity and enhancing the performance of electric motors in electric vehicles (EVs) and hybrid vehicles. Additionally, the presence of neodymium in energy-efficient lighting, such as compact fluorescent lamps (CFLs) and LEDs, improves efficiency and color reproduction. Ongoing research is aimed at exploring the potential of neodymium in enhancing the performance and density of rechargeable batteries[44-47].

Yttrium (Y), along with other rare earth elements, is used to produce phosphors for LEDs to improve the efficiency and lifespan of lighting technology. Moreover, in water treatment, yttrium oxide nanoparticles have been studied to remove pollutants from the water. In solid oxide fuel cell (SOFC) technology, yttrium is a crucial component of the yttria-stabilized zirconia (YSZ) electrolyte, offering a clean and efficient way to generate electricity. Yttrium also supports advancements in high-temperature superconductor technology and microwave applications such as yttrium barium copper oxide (YBCO) in various advanced technologies[48-51].

The Scandium (Sc) which is significantly present in Medang and Anak Kesongo mud volcanoes (243.9 ppm and 245.6 ppm respectively) can become new REE resources in Indonesia (Fig. 16). The abundance of Sc in Indonesian REE exploration target area is very minimum and almost neglected. Pegunungan Tiga Puluh in Sumatera dominantly has Ce in their host rock, this is including in Parmonangan area, Sikambu river and Isahan river[15]. Sibolga that has been a REE target area for a long time, contains Ce dominantly with almost neglected Sc[53]. Bangka-Belitung in Riau province also has Ce dominantly in their granitoid rock[54]. The tailing from the tin mining in Bangka Island shows the dominance of Dy, Nd, Tb, and Y, whereas Sc is very minor abundant in the tailing[55]. The abundance of Sc present in the lateritic Ni deposits in ultramafic rock, Soroako, Sulawesi[56]. Sc can occur up to 85 ppm, due to bedrock high pyroxene content (harzburgite). Sc also can potentially present in West Kalimantan (Tayan area) as a result of the altered granitoid rocks, namely bauxite[57]. The Sc content is up to 52.9 ppm from the diorite and granodiorite rock sample. It is still less than in Anak Kesongo and Medang mud volcanoes, which actually have the highest Sc content from the mud samples.

The Sc content in Nygan laterite deposits in New South Wales, Australia is around 409 ppm. Sc content found in red muds in Greece has content up to 100 ppm. Sc from carbonatites and alkaline rocks in Pakkanadu, India, has around 237 ppm. Meanwhile sample from Bayan Obo, China (the biggest REE mining field in the world) shows content around 111 ppm. Sc in Glenover pyroxenite-carbonatite complex in South Africa shows content around 300-500 ppm. The Sc content from carbonatite phoscorite deposit at Kovdor, Kola Peninsula, (Russia) is around 780 ppm (the highest Sc content in the world)[62]. Botelho Junior, et al. (2021) mentioned that REE deposits with scandium content greater than 20-50 ppm could be explored and mined by considering economic viability and aspects as summarized by Chen. (2011)[63,71]. This reference also concludes that all the Sc content from Grobogan mud volcanoes is economically viable to be mined and explored. In addition, in Botelho Junior, et al. (2021), the source of Sc in Mud volcanoes can be classified as an unconventional resource

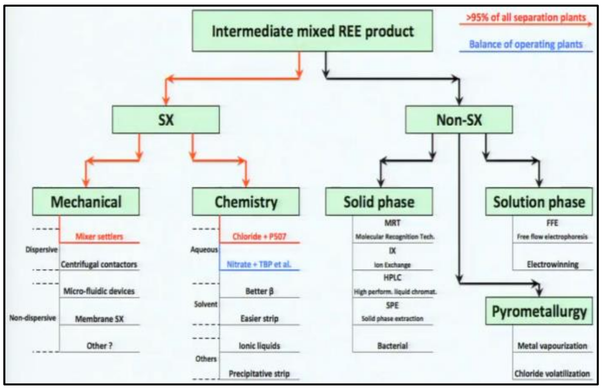


Fig. 17: REE separation options road map[59].

Another challenge in exploring the REE is the difficulties in separating the potential REE from the mud itself. Several extracting REE methods had been already used to separate the potential REE from the its other solid mixtures. Goode (2016) summarizes the mixture separation of REE into its component elements. The REE extraction-separation methods are divided into two major methods, they are solvent extraction (SX) and non-solvent extraction (Non-SX). The solvent extraction (SX) is the common industrial method currently used for REE separation, divided into two groups, mechanical and chemical (Fig. 17). SX method uses water immiscible organic solvents for extraction. On the other hand, non-solvent extraction or Non-SX method relies on solid ion exchanges, aqueous precipitation or electric fields for separation[59]. It is divided into 3 groups, they are solid phase, solution phase and pyrometallurgy (Fig. 17).

In chemical separation method, leaching and solvent extraction (SX) are the most mature method used in separating the REE (Fig. 18). Leaching is extraction metal into solution, using special reagents (acids, bases, or salts) followed by separation by filtration, precipitation through solvent extraction, and recovery by hydrometallurgy[58]. Meanwhile plasma separation is the mature technology in physical and thermal REE separation[58]. Plasma separation can be done by either heating a gas or applying electromagnetic field to ionize or to achieve a high energy state, regularly done by heating materials to very high temperatures to break bonds until atoms are ionized, leaving individual ions and electrons[58]. Nowadays, the use of liquid and gas chromatography and also sorbent and membrane separation methods are the growing methods in REE separation industries (Fig. 18)[58]. Other REE separation methods are emerging methods that will help to reduce the difficulties and high cost in REE separation industries.

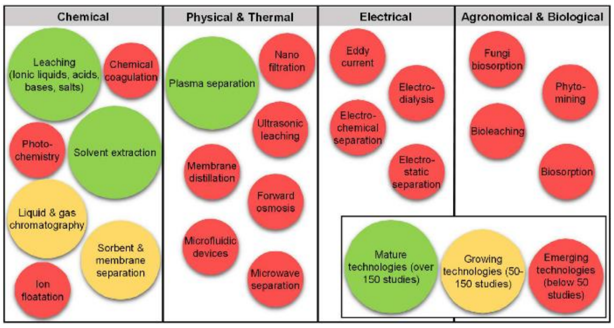


Fig. 18: Recent mature, growing, and emerging REE separation technologies (from January 2015 to January 2019)[58].

All the major 5 rare earth elements found in Grobogan mud volcano complex (Sc, Ce, La, Nd, and Y) can be extracted and separated using SX method. La, Ce and Y can be extracted and separated using SX method with naphthenic acid or any other alternative[59]. Sc can be extracted using the acid leaching with MgSO4 which is commonly used in extracting the Sc from the bauxite residue (known as red mud)[60]. Tri-n-Butyl Phosphate (TBP) is a well-known and widely used practical applications to separate light REE (LREE) from the middle and heavy REE (HREE). This method also can be used to separate the REE mixture into individual elements. Sc, La, Ce and Nd are included in light REE (LREE). The combination of Methyl Trioctylammonium Nitrate (TOMANO$_3$) and TBP organic mixtures are able to increase the extractability of the individual REE[61].

In general, there are at least three main categories of REE resources from various research sources, namely magmatic REE deposits, sedimentary REE deposits and extraterrestrial REE resources[4-11,70,71]. Mud volcanoes are a very unique geological phenomenon that occur and are distributed globally in different geological settings such as active margins (magmatic arcs and ridges) and passive margins, subduction and accretionary complexes, thrust and overthrust belts (collisions), deltas (sedimentary settings), shallow marine or hydrocarbon-bearing basins (clay bearing sedimentary environments)[72,73]. Mud volcanoes are also associated with a combination of geological processes, including overpressure in sedimentary basins (due to rapid sedimentation which increases the overpressure in the sediments), tectonic activity and the presence of gas and fluids at depth.

Mud volcanoes are present from both onshore and offshore, some of which are still in the process of understanding their formation and origin. It is also really strongly related to the shale or clay lithology in subsurface as the source of the mud. For this reason, we place mud volcanoes in a separate category from the previous group and refer to them as unconventional REE resources (see Fig. 19).

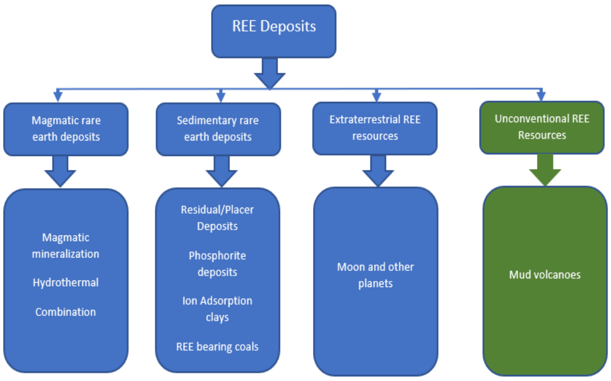


Fig. 19: Summary of the types of REE deposits from different sources[4-11,70,71]. The green box is the new category introduced in this paper, relating to the REE potential of mud volcanoes.

Balaram (2022) divided REE resources into three categories based on the current REE exploitation and future potential resources[61] (see Fig. 20). We include the mud volcano in the Alternate resources category as not many studies discussing the potential REE in mud volcano despite of the thousands of mud volcano manifestation in onshore and offshore.

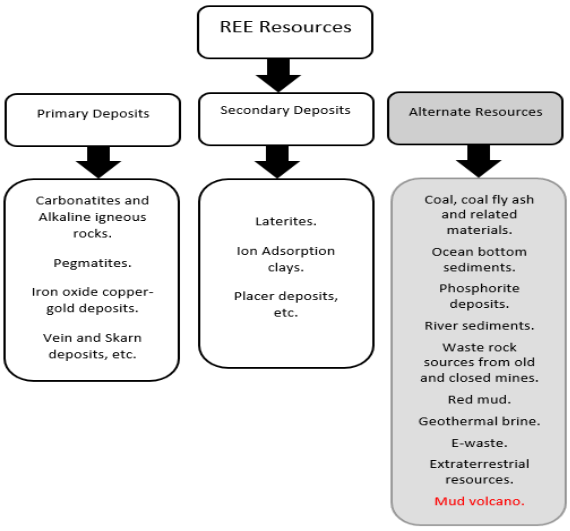


Fig. 20: Modified illustrative view of different types of REE resources based on Balaram, 2022[9]. We include the mud volcano in the Alternate resources category as its potential in the future.

4. Conclusions

This research concluded that the Grobogan mud volcanoes produced at least 5 dominant REE, which are Sc, Ce, La, Nd, and Y. Due to the challenging of extraction and separation of REE from the mud volcano deposits, the potential of REE in mud volcanoes is still neglected and still does not have significant economic impact nowadays. Although in the future, when the technology develops rapidly, this REE potential can have a significant economic value. This REE regression evaluation indicates that the origin of the mud from Grobogan mud volcanoes are not the same and exhibits different geological settings. Medan mud volcano is suspected to have different geological setting due to origin of its mud source, compared to other mud volcanoes. Similarities also are found among other mud volcanoes in Grobogan mud volcano complex (Kesongo and Anak Kesongo or Bledug Kuwu with other rest mud volcanoes). Mud volcanoes are not just bringing disaster, but also bringing important minerals that can be used for green technologies and high-tech applications in the future. Sc become the highest potential REE to be mined in mud volcano deposits, as result shown by Anak Kesongo (245.6 ppm) and Medang mud volcanoes (243.9 ppm) mud samples. This content indicates that the Sc is economically viable to be mined based on Botelho Junior, et al. (2021) classification[63]. The Sc content is one of the highest in the world, for comparison the Sc content from carbonatites and alkaline rocks in Pakkanadu, India, has around 237 ppm and from Bayan Obo, China shows content around 111 ppm, and Sc in Glenover pyroxenite-carbonatite complex in South Africa shows content around 300-500 ppm. Mud volcanoes in Grobogan can be an alternative exploration target area for REE, especially Sc, in the future. Methods that can be used to extract Sc include traditional ion exchange techniques and the use of ionic liquid[69].

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