PHYSICAL AND CHEMICAL CHARACTERIZATION OF CLAY DEPOSITS FOR REE UTILIZATION

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BY

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Physical and Chemical Characterization of Clay Deposits for REE Utilization”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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ABSTRAK

Elemen Nadir Bumi (REE) adalah sumber yang berpotensi untuk memenuhi teknologi termaju pada masa ini kerana penggunaannya telah ditemui pada tahun 1955 sebagai sebahagian daripada komponen penting dalam pembuatan televisyen. Memandangkan China telah mengurangkan had eksport REE disebabkan oleh langkah perlindungan alam sekitar, sumber REE alternatif dimulakan secara meluas. Kajian ini mencirikan mendapan tanah liat penjerapan ion (IAC) dari Kenering, Perak secara fizikal dan kimia melalui analisis saiz zarah, petrologi, pengenalpastian fasa mineral, dan kajian geokimia. Berdasarkan pencirian fizikal, sampel di bahagian atas kebanyakan tanah gelap hingga coklat kemerahan menunjukkan tekstur lembap pada rupa fizikalnya. Wajaran saiz zarah purata adalah banyak dalam saiz yang lebih kasar (> 100 μm) secara relatif. Ia mengandungi kandungan Feldspar K dan mineral kuarza yang tinggi serta mineral aksesorinya mengandungi mineral biotit dan garnet. Apabila diplot pada Klasifikasi IUGS, sampel boleh dikategorikan sebagai syenite (terluluhawa). Pengecaman fasa mineral menunjukkan sampel dikawal oleh kuarza, kaolinit, mikroklilin, dan mineral tanah liat seperti *dickite*. Unsur SiO_2 adalah kepekatan tertinggi diikuti oleh Al_2O_3 berdasarkan analisis X-ray Fluorescence (XRF). Berdasarkan rajah TAS, kebanyakan sampel bertaburan dalam kumpulan syenit dan diorit. Sampel diperkaya dengan unsur LREE sebagaimana La yang mendominasi graf ternormal kondrit. Kepekatan LREE dan HREE menunjukkan perbezaan yang ketara iaitu 23.19 ppm dan 4.74 ppm masing-masing. Secara amnya, kajian ini mendedahkan bahawa sampel adalah batu igneus plutonik (terluluhawa) dan mempunyai nilai yang signifikan terhadap unsur-unsur REE yang diminta. Oleh itu, ia adalah prospektif untuk dilombong pada masa hadapan.

ABSTRACT

Rare Earth Elements (REE) are potential resources to meet the advanced technologies currently as its usage have been discovered in 1955 as part of the significant component in television manufacture. Since China has reduced REE export limitations due to environmental protection measures, alternative REE resources are initiated widely. This study characterized ion adsorption clay (IAC) deposit from Kenering, Perak physically and chemically through particle size analysis, petrological, mineral phase identification, and geochemistry study. Based on physical characterization, the samples on the top are mainly dark- to reddish-brown soil indicates moist texture on its physical appearance. The weightage of the average particle size is abundance in coarser size (> 100 μm) relatively. It comprises high content of K Feldspar and quartz mineral and its accessory minerals contain of biotite and garnet minerals. When plotted on IUGS Classification, the sample can be categorized as syenite (weathered). The mineral phase identification indicates the sample is governed by quartz, kaolinite, microcline, and clay minerals such dickite. SiO_2 element was the highest concentration followed by Al_2O_3 based on X-ray Fluorescence (XRF) analysis. Based on TAS diagram, most of the sample were scattered in syenite and diorite group. The sample enriched with LREE as La element dominating the chondrite normalized graph. The LREE and HREE concentration shows significant different which 23.19 ppm and 4.74 ppm respectively. In general, the study reveals that the sample is plutonic igneous rock (weathered) and have a significant value on demanded elements of REE. Hence, it is prospective to be mined in future.

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LIST OF SYMBOLS

μm	Micrometer
mm	millimeter
Ψ	Width span

LIST OF ABBREVIATIONS

ppm	Part per million
ppb	Part per billion
REE	Rare Earth Element
LREE	Light Rare Earth Element
HREE	Heavy Rare Earth Element
CIA	Chemical Index Alteration
IAC	Ion Adsorption Clay
IUGS	International Union Geological Sciences
TAS	Total Alkali Silica

CHAPTER 1
INTRODUCTION

1.1 Background Project

In order to regulate the production and export of Rare Earths, China has recently lowered REE export limitations. Its increasing environmental protection measures and supply for its expanding domestic market contributed to a dynamic pricing development in 2011. China's export quotas have led to a market price explosion as a result. Regarding supply security, this led to significant uncertainty in the high-tech sector globally, which culminated in political conflicts.

Identifying and utilizing REE resources and deposits outside of China is necessary to end this reliance on Chinese supply. However, the downside of the historically used and mined conventional resources (mostly monazite and bastnäsite) is that they contain relatively little of the more desirable HREE and have larger concentrations of radioactive components. The investigation of the clay samples provides the basis for the development of an ion adsorption clay exploration model with the aim to identify potential occurrences and deposits in Malaysia.

After 19th century with the introduction of red phosphors using Eu and in television cathode ray tubes, the need for REE surged significantly. In around 1900, an alloy of Sm and Co with the formula $SmCo_5$ about 34% Sm by mass, was created. NdFeB magnets were then created in 1982. They have between 2% and 9% Dy and Tb as well as roughly 30% Nd. Pure Nd can be replaced by a combination of Pr and Nd, which is less expensive because the challenging Pr-Nd separation is eliminated. The primary application for REEs is still NdFeB magnets, which also mainly regulate REE output and demand today.

Historically, the Asian Rare Earth Sdn Bhd (ARE) is incorporated to extract yttrium from monazite Bukit Merah, Perak. Asia Rare Earth Sdn Bhd ceased its operation following increasing pressure locally and internationally with its factory being closed in 1994Till now, Asia Rare Earth Sdn Bhd ceased its operation following increasing pressure locally and internationally with its factory being closed in 1994. The outcome of the pollution case took several years to complete with no acknowledgement of responsibilities from companies involved despite the closure of factory in 1994 that become the source of pollution.

1.2 Importance of Project

This project is focusing on physically and chemically characterize the clay deposit from Perak. The laterites sample may consist of abundance of REE ores as it shows similar geological occurrence as Bukit Merah, Perak. Recently, industries have demanding lanthanides elements as it is beneficial to current technology. Monazite is one of the phosphate minerals that contained rare earth elements such as cerium, lanthanum and neodymium with chemical formula $Ce,La,Nd,Th(PO_4)$. Therefore, the information from this research can be utilized for exploiting valuable minerals in the deposits.

1.3 Problem Statement

Characterization of clay deposits is challenging as it can deform it physical when react with other substance. To support the findings of the mineral presence, an evaluation of the elemental composition and mineral identification should be carried out. To accomplish the goals, a competent technique is needed for the physical characterization of the sample's size range and mineral liberation.

1.4 Objectives

The objectives of the research are as follows:

1. Physically characterize the sample to assist the further extraction process.
2. Chemically characterize the sample to acquire the chemical composition.
3. Determine the concentration of rare earth elements in sample based on LREE and HREE.

1.5 Scope of Research

The physical and chemical characterization of involving several assessments such as moisture content, particle size distribution, elemental composition, identification of mineral phases, and mineral identification.

Chapter 2 will be discussing on the geology of Perak where the sample was located. This section will demonstrate the previous studies regarding characterization of clay deposit for REE utilization. Most of the research works have discussed characterization studies on ion adsorption clay also known as weathered elution deposit.

Chapter 3 explains in detail the procedure of the analysis conducted in the characterization of ion adsorption clay deposit. One third of the samples that have undergone physical characterization is further analysed for petrology study and geochemistry study. Whereas another part of the samples will be used for particle size analysis and mineral identification.

The results from overall assessment will be discussed in Chapter 4 significantly. The data obtained from petrology were further confirmed with scientific prove of geochemistry and XRD analysis. Chapter 5 are the list of conclusions and future recommendations of this research study.

1.6 Location of Research

Sample of the research was located at Kenering, Perak where it is within the western tin belt of Peninsula Malaysia. The sampling from Universiti Sains Malaysia Engineering Campus, Nibong Tebal, Penang tooks 1 hour and 52 minutes to reach at the site by car.

Figure 1.1 Map of Perak, Malaysia.

1.7 Research Limitation

The sample given were limited to small analyses as the average weight of each sample was less than 200g. A proper study and workflow should be implemented to avoid excess damage sample. Due to this, the analyses were conducted in small scale for every sample.

Lack of knowledge relating to REE in clay deposit type and characterization of soils. The study of the sample is challenging since it is among new study of REE deposit from ion adsorption clay in Malaysia. Few published papers in English are insufficient as the method proposed were different. Moreover, some of the research are not available in English version resulting less knowledge on the topic.

The clay sample is plastic as it deforms when react with water. In order to characterize the sample in petrological study, the specimen was carried away by water when trimming the thin section. Furthermore, most of the research paper does not provide the preparation for thin section make it difficult to obtain the accurate procedure.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

Rare earth elements (REE) a group of seventeen chemical elements found in the periodic table, including the fifteen lanthanides, as well as scandium and yttrium as defined by International Union of Pure and Applied Chemistry (IUPAC) (Tohar and Yunus,2020; Young, 2019). Nevertheless, there are sixteen elements with the exception of Promethium (Pm) that commonly characterize in REE mining (Young, 2019). These group are classified into three class which are Light Rare Earth Element (LREE), Middle Rare Earth Element (MREE), and Heavy Rare Earth Element (HREE).

Large specific surface areas and a powerful ability to adsorb REE ions are characteristics of clay minerals that host ion-adsorbed REE ores. Kaolinite, illite, chlorite, and vermiculite were the most common clay minerals. REEs adsorbed on the clay minerals by ion-exchangeable phases comprise more than 80% of the overall REE content in weathering crust elution-deposited REE ores (Chi and Tian, 2003; Chen et al., 2020).

The recovery of REE ore is depending on the characteristics of the REE ore, the type and concentration of the leaching reagent, and the leaching process' hydrodynamics, kinetics, and mass transfer all play a role in controlling leaching. In strongly leached soil layers, kaolinite and kaolinite interlayer minerals dominated, whereas illite and montmorillonite suggest a cool, humid climate with poor chemical weathering. Clay minerals of different crystal characteristics differ in physical structure and properties (Chen et al., 2020).

Previously, in the granite weathering region of Longnan County study, the ratio of kaolinite to quartz and other rock-forming minerals was only weakly correlated. The average kaolinite content was low, and the chemical weathering index (CIA) was in the range of 61% to 65%. In contrast, the amount of kaolinite was significantly connected with quartz in the metamorphic terrain of Anyuan County, and the CIA ranged from 68% to 75%. This shows that feldspar weathering and conversion to clay minerals in metamorphic bedrock occurs to a greater extent (Chen et al., 2020).

In the adsorption of REEs, halloysite outperforms kaolinite. Previous research discovered that the clay minerals' characteristics, as opposed to the electrolyte solution or the amount of dissolved carbon dioxide, regulate the adsorption of REE. It is commonly accepted that the horizon enriched in REE typically contains substantial amounts of halloysite and kaolinite (Estrade et al., 2019; Tohar and Yunus,2020), and that soil particle size and particular leaching conditions influence clay mineral migration (Chen et al., 2020).

Previous research has demonstrated that illite is produced by the alteration of potassium feldspar in two distinct microsystems: the first occurs along crystal joints of orthoclase with muscovite or biotite early in the weathering process, and the second occurs in the final stages of weathering when the parent rock's original structure is destroyed. Illite develops alongside other clay minerals like smectite in the early weathering stage and kaolinite in the late weathering stage in both situations (Chen et al., 2020).

Vermiculite is formed in two stages. In the first stage, mica dissolution is more advanced and corroded zones of polyphase assemblage of dioctahedral hydroxy-vermiculite appear within mica crystals. The common weathering products of mica are dioctahedral vermiculites, whose layer charge is lower than that of the parent mica (Chen et al., 2020).

Compared to their parent rocks, the weathered profiles had a higher concentration of total REE (Maulana et al. 2016). REE minerals commonly occur mainly with kaolinite and small amount of halloysite (Tohar and Yunus,2020). Chi et al. explained that montmorillonite has the highest cation adsorption capacity relative to kaolinite and halloysite whereas kaolinite has the lowest cation adsorption capacity among the three common clay minerals. Hence, varied source rock lithologies result in different weathering crust structures and clay mineral compositions (Chen et al., 2020).

2.1.1 Properties and usage of REE

Figure 2.1 and Figure 2.2 show the distribution of REE consumption worldwide in 2016 and 2020

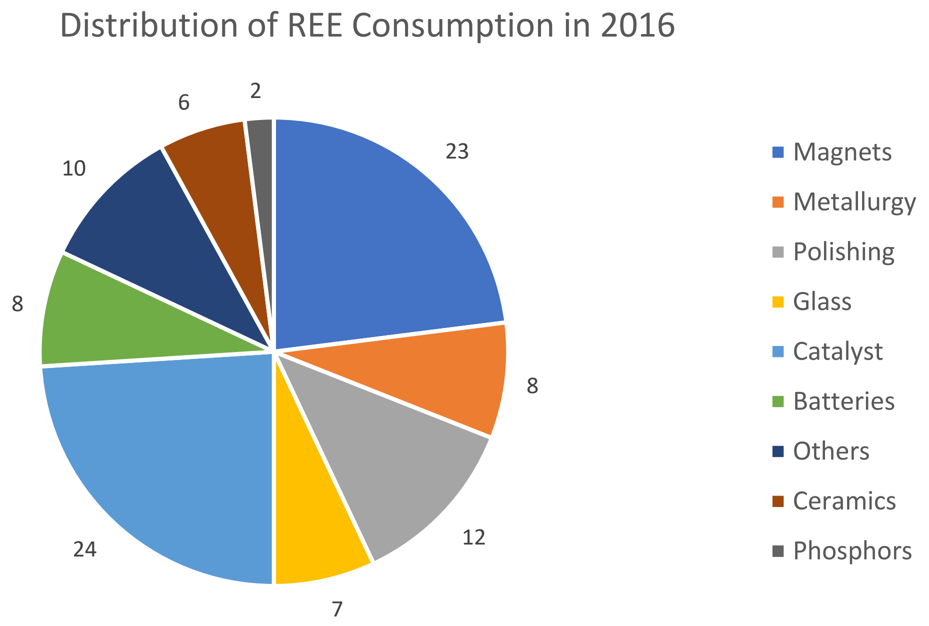


Figure 2.1 Distribution of REE Consumption in 2016 (after Young, 2019)

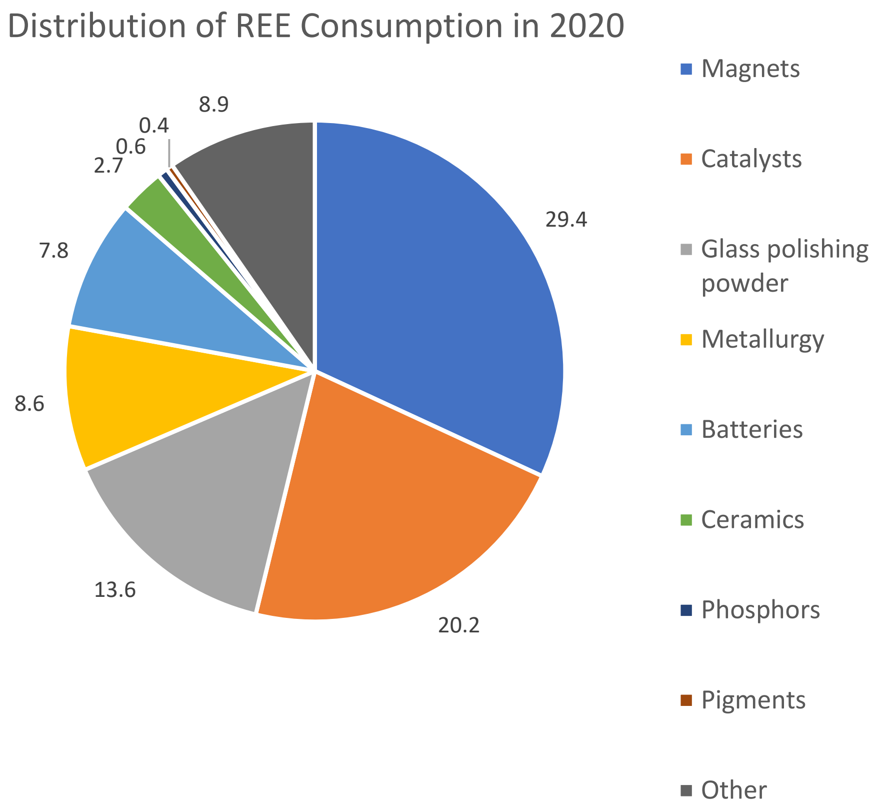


Figure 2.2 Distribution of REE Consumption in 2020 (retrieved from www.statista.com)

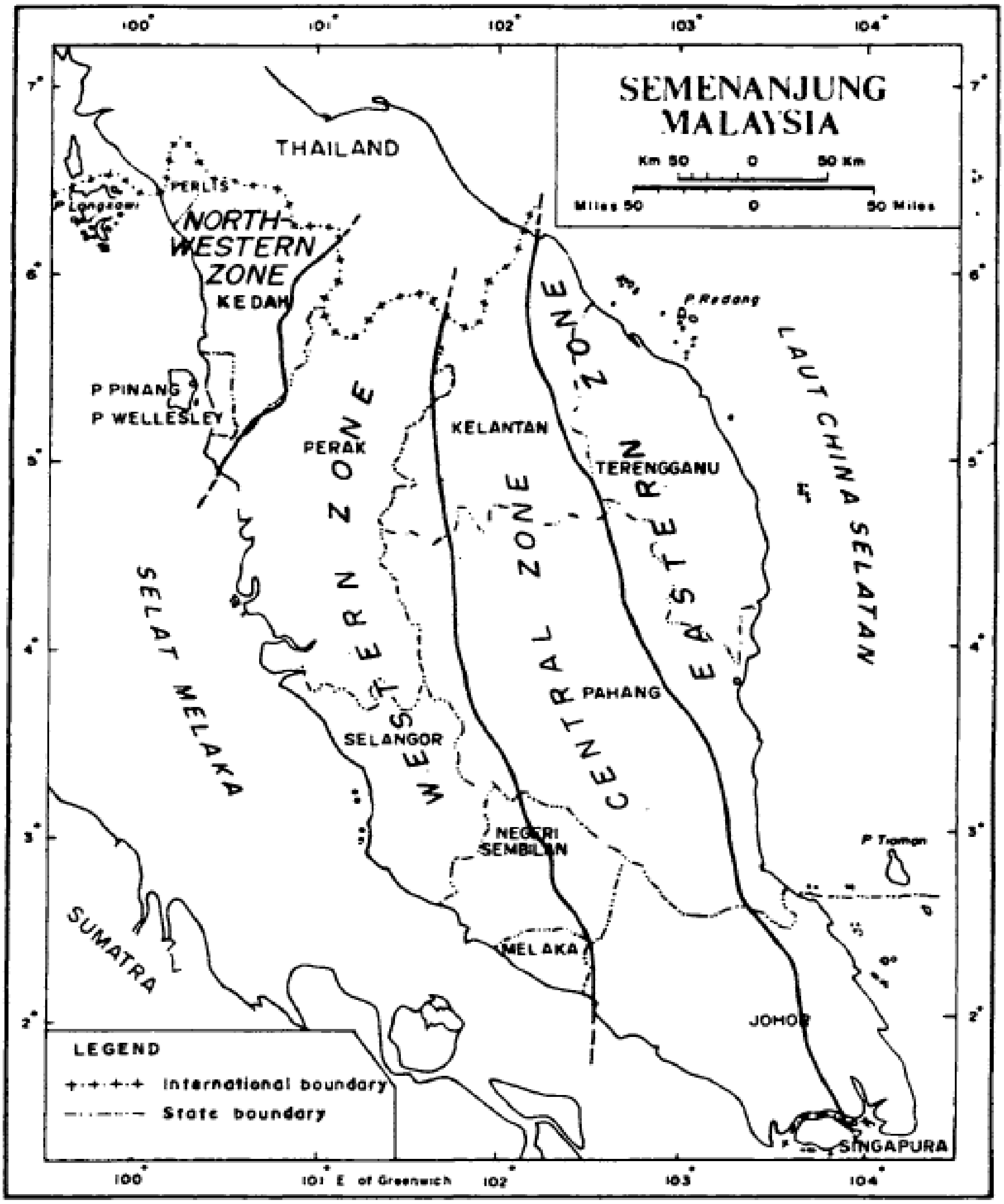
In four years, the demand for RE element are rise to 6.4% and 1.6% for the use of magnets and glass polishing respectively. This indicates that REE are the elements that meets the necessities of current living. The percentage recovery of each REE is typically similar, and REE deposits contain each REE in specific amounts. As a result, a given mine will unintentionally generate a specific amount of the other REE in the deposit in order to produce a given mass of a particular REE. This has some deviations depending on the precise mineralogy and processing techniques. It is often true, nevertheless, that some REE with great demand are somewhat valuable, whereas others with low demand or low pricing tend to be unmarketable. As new applications are created and outdated technology are abandoned, the history of REE demand has altered.

2.2 Geology of Perak

In Southeast Asia, granites are distributed into four provinces which Northern provinces in Thailand, Western provinces covers the southwest Thailand to the east Myanmar, Eastern provinces in east Malaysia, and Main Range provinces covers the south Thailand to the west of Peninsular Malaysia (Hutchison, 1986; Cobbing et al., 1992). The Eastern and Main Range provinces are also known as Eastern and Western Belt granites respectively (Tohar and Yunus,2020). The granites of the Western Province show higher REE contents (up to 670 ppm) compared with the other granites in Thailand (Wu and Ishihara, 1994; Sanematsu et al, 2013).

In general, Peninsular Malaysia is divided into four stratigraphic zones, eastern zone, central zone, north-western zone, and western zone. Figure 2.3 shows the division of each zone cited from Yee, 1983. The eastern and central zone was discovered to be in Eastern belt granites whilst north-western and western zone in Western belt granites. Western zone is represented by the Baling group, Bentong group, Kinta limestone, Kuala Lumpur limestone, Kati formation, Kenny Hill formation, Hawthornden schist, and Dinding schist.

Two main stratigraphic groups of the western zone are the Baling group in north Perak and the Lower Palaeozoic Bentong group (Yee, 1983). Western zone is significant in this project as it represents the geology of the sample. The Baling group is in the age of Ordovician to early Devonian comprises phyllite, schist, and slate. Moreover, it comprises with minor limestone interbedded with volcanic and sandstone.



KBM(Rm), D-36-83

Figure 2.3 Stratigraphic zone of Malaysia (Yee, 1983)

Climatic and environmental change is one of the causes of compositional differentiation in clay minerals. As the tropical climate in Southeast Asia promotes weathering of granites in a similar way as in southern China, the ion-adsorption type prospects in Southeast Asia have been identified recently in Thailand, northern Vietnam, Laos and southern Myanmar (Sanematsu and Watanabe, 2016; Tohar and Yunus,2020; Sanematsu et al. 2013).

Physical and chemical weathering processes cause clay minerals to change into kaolinite minerals during the weathering process. The chlorite and mica debris concentration, and the subsequent transformation of chlorite and mica into montmorillonite and vermiculite, closely govern the composition of clay minerals in the soil surface, which then follows the acidic soil formation process (Uzarowicz et al. 2011; Chen et al., 2020).

2.3 Basic Concept of Rare Earth Element

The U.S. Geological Survey (USGS) divides REE deposits into nine types: peralkaline igneous rocks, carbonatites, iron oxide copper–gold, pegmatites, porphyry molybdenum, metamorphic, stratiform phosphate residual, paleoplacer, and placer. The concentration and distribution of REE minerals are influenced by rock-forming and hydrothermal processes, as well as by solution of minerals and subsequent redistribution and concentration by sedimentary processes and weathering.

The British Geological Survey (2017) classifies REE deposits into four primary deposit types which are the carbonatite associated, associated with alkaline igneous rocks, iron–REE deposits, and hydrothermal deposits. Marine placers, alluvial placers, paleoplacers, lateritic deposits, and ionic clays are the five different forms of secondary deposits (Young, 2019). Relatively, REE deposits were divided into primary and secondary deposits (Kanazawa and Kamitani, 2006; Walters, et al. 2011). Alkaline complexes, hydrothermal deposits, and carbonatite complexes are the main types of deposits while ion-adsorption clays and other deposits created by lateritic weathering, such as various type of placer deposits, are examples of secondary deposits.

Table 2.1 Major REE deposits type (Walters, et al. 2011)

Deposit Type	**Description**	**Mine Example**
Primary Deposits		
Carbonatite associated	Deposits associated with carbonate-rich igneous rock associated with alkaline igneous provinces and zone of major faulting	Mountain Pass, USA; Bayan Obo, China; Amba Dongar, India; Iron Hill, USA.
Associated with alkaline igneous rocks	Deposits associated with igneous rock characterized by abundant alkali mineral and enrichment of HFSE	Khibhina and Lovozero, Russsia; Weishan, China; Brockman, Australia; Pajarito Mountain, USA
Iron Oxide-(Cu-U-Au-REE) deposits	Copper-gold deposits rich in iron oxide and diverse in character and form.	Olympic Dam, Australia; Pea Ridge, USA
Hydrothermal deposits (unrelated to alkaline igneous rocks)	Typically quartz, fluorite, polymetallic veins and pegmatites of diverse origin	Karonge, Burundi; Naboomspruit and Steenkampskrall, South Africa; Lemhi Pass and Snowbird and Bear Lodge, USA

Table 2.1 Major REE deposits type (Walters, et al. 2011) cont.

Secondary Deposits		
Marine placers	Accumulation of resistant, heavy minerals, concentrated by coastal processes and found along or close to existing coastlines	Eneabba, Jangardup, Capel WIM 150, Australia; Green Cove Springs, USA; Richards Bay, South Africa; Chavara, India
Alluvial placers	Concentration of resistant, heavy minerals in river channels	Perak, Malaysia; Chavara, India; Carolina monazite belt and Horse Creek, USA; Guandong, China
Paleoplacers	Ancient placer deposits typically forming consolidated, cemented rocks	Elliot Lake, Canada; Bald Mountain, USA
Lateritic deposits	Residual surface deposits formed from intense chemical weathering of REE-enrinched igneous rocks	Mount Weld, Australia; Araxa, Brazil; Kangankunde, Malawi
Ion-adsorption clays	Residual clay deposits formed from the weathering of REE-enriched granites	Longnan and Xunwu, China

According to deposit type and within deposit type, the elemental distribution of the REE varies greatly inside each deposit. Carbonatites and weathered carbonatites often contain very little HREE since the minerals in carbonatite deposits are frequently bastnaesite, monazite, and other REE-bearing minerals. Additionally, HREE deposits of placer and paleoplacer tend to be low concentration. In contrast, intrusive peralkaline deposits typically have HREE concentrations that are rather high. Because of how the weathering and ion exchange processes lead the Ce to be oxidised and precipitate as cerianite, Ce(Th)O2, a refractory mineral, as opposed to being sorbed on the clay, the products from the ionic clay deposits also tend to be rich in HEE.

2.3.1 Carbonatite Complex

More than 50% of the minerals in carbonatites, including calcite, dolomite, siderite, and ankerite, are carbonate-containing and have an igneous origin. They frequently occur near alkaline complexes and in stable cratonic regions with rift structures (Walters, et al. 2011). Along with carbon dioxide, uranium, and thorium, carbonatites contain a variety of other abundant elements. Majority of all the rare earth elements found in minerals including bastnasite, allanite, apatite, and monazite are found in REE-carbonatite (Gupta and Krishnamurthy, 2005). Another significant carbonatite-bound REE deposit is the Mountain Pass mine in California. For many years, this mine was in charge of the vast bulk of the world's output. However, due to environmental issues and a lack of economic viability, it was temporarily shuttered beginning in 2002 (Walters, et al. 2011).

2.3.2 Alkaline Igneous Complex

Sodium and potassium minerals are found in abundance in alkaline rocks, which are produced from magmas with high alkali-metal concentrations (Walters, et al. 2011). REE deposits in alkaline complexes are distinguished by higher HREE-values and consequently lower LREE / HREE ratios (Castor and Hendrick, 2006). If alkaline rock has a higher molecular fraction of combined sodium and potassium than aluminium, it can be further categorised as peralkaline. Extreme enrichment of alkaline metals with high field strengths, such as zirconium, titanium, yttrium, and REE, is a typical characteristic that distinguishes peralkaline rocks from other types. When an igneous rock crystallises, high field strength elements are those that are not easily absorbed into the structures of typical rock-forming silicate minerals (Walters, et al. 2011).

2.3.3 Hydrothermal Deposit

Hydrothermal processes separate REE, and this can result in accumulations of an economically significant size (Maruejol et al., 1989). Alluvial and marine processes cause heavy weather-resistant minerals to accumulate with sand and gravel in placer deposits, where they are concentrated and gathered (Walters, et al. 2011). The minerals may come from several original sources and frequently contain significant levels of the minerals Ti, Zr, and REE. Low REE values of 0.5 to 0.1 percent are typical for the deposits. Monazite is the placer deposit's most prevalent REE-leading mineral (Walters, et al. 2011).

2.3.4 Placer Deposit

REE are primarily discovered in pegmatites, vein tracts, and deposits connected to magmatic intrusions. Additionally, there are accumulations of placer deposits and secondary deposits in beach, dunes, and alluvial sand areas (Walters, et al. 2011; Castor and Hendrick, 2006). Tertiary or Quaternary age placer deposits are the most significant ones that include considerable amounts of REE materials. Paloeplacer, however, refers to deposits that date back to the Precambrian. In placer deposits, monazite is the mineral that contains the most REEs, with only small concentrations of xenotime, fergusonite, euxenite, allanite, and pyrochlore (Walters, et al. 2011).

The most significant placer deposits were created at or close to the present shorelines and are of marine origin. Wave action, tides, and currents concentrate the mineral in these deposits. Monazite and xenotime are present in substantial quantities in Malaysia's alluvial tin deposits, and this nation has historically dominated yttrium production from xenotime.

2.3.5 Ion Adsorption Clay

Most of the world's supply of REE, particularly in HREE, comes from weathered crust elution-deposited, also known as ion adsorption deposits as it geochemically bonds with Yttrium and produced from the same deposits (Yaraghi et al., 2020; Tohar and Yunus, 2020; Sanematsu et al., 2013). Ion adsorption deposits also referred to as ion adsorption clays are inferred to be weakly adsorbed onto clay minerals such kaolinite and halloysite (Borst et al., 2020). The term ion adsorption deposit is broadly used in the literature to describe easily leachable REE deposits associated with lateritic weathering (Borst et al., 2020).

The ion-adsorption type deposits are composed of a reddish soil-like weathering crust that forms on parent granite. Even though the grades of REE are dependent on the parent granite (Bao and Zhao, 2008), it significantly resulted a lower REE content on the upper part (89–398 ppm) than the middle to lower parts (201–1131 ppm). In situ lateritic weathering of REE-rich felsic rocks mostly granites resulted in the production of weathered profiles containing residual REE-clays, which led to the formation of these deposits (Ishihara et al., 2008; Tohar and Yunus,2020).

Previously, according to a regional clay mineral study, ion-absorbed REE ores produced on various bedrock lithologies have similar clay mineral compositions. Granite undergoes highly weathering process mostly produces ion-absorbed REE ore. It is a loose, earthy material composed mostly quartz, feldspar, and clay minerals. Clay minerals have a controlling effect on REE ore migration and release. From the weathering crust surface to the lower layer, where clay minerals are changed from hydromica and montmorillonite to halloysite, kaolinite, and gibbsite, the clay mineral composition decreases significantly (Bao and Zhao, 2008; Chen et al., 2020).

As China are dominantly supplied 87% of LREE and approximately 99% of HREE mostly in southern region of China, the REE have been widely classified as the critical metals in the United States and also Europe (Sanematsu and Watanabe, 2016). Besides, the per cent has reduced to roughly 80% of global supplies (Borst et al., 2020) as the utilization of REE have been increased currently and hence it expands the urgency to identify alternative REE resources (Sanematsu and Watanabe, 2016; Tohar and Yunus, 2020).

2.4 Characterization of Ion Adsorption Clay Deposit

In 2016, Sanematsu and Watanabe described the main bearing minerals of the ion-adsorption deposit differ from those of other common REE deposits. Ion-adsorption deposits are mostly driven by bearing minerals like clay minerals and bastnaesite (Sanematsu et. al., 2013), whereas conventional REE deposits are primarily driven by monazite-(Ce) and xenotime-(Y) minerals (Bao and Zhao, 2008; Tohar and Yunus,2020).

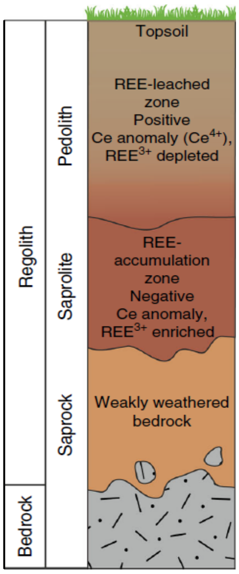


Figure 2.4 Schematic regolith profile indicating leaching in the top of the weathering profile (pedolith) and accumulation of rare earth elements (REEs) in the saprolite, in which REEs are inferred to be adsorbed to clay minerals (after Tohar and Yunus,2020).

The surface to the bottom is divided into layers of soil, saprolite, weathered rock (saprock), and parent granite (Figure 2.4). It has small amounts of rock-forming minerals and is richer in organic materials, clay minerals, and quartz (Tohar and Yunus, 2020). Moreover, it is evidently shows that the surface comprise of dark brown soil is enriched in organic matters, clay minerals, and quartz, containing small amounts of rock-forming minerals while saprolite is enriched with reddish- and yellowish-brown clay and low organic content (Sanematsu et al., 2013).

Kaolinite and halloysite are abundant clay minerals in these strata where the saprock gradually change into the saprolite. The major element of clay minerals is kaolinite, with low content of halloysite, illite, and a mineral assemblage similar to the saprolite layer (Tohar and Yunus,2020). Previously, Sanematsu et al., shows that on this weathering profile, the clay minerals are mainly comprised of kaolinite and halloysite-7Å with small amounts of illite, smectite, and vermiculite. Two samples that have been observed from this profile are white in colour and seem to have experienced hydrothermal alteration.

The adsorptive substance was not certainly understood since it was challenging to analyse minimum amounts of REE dispersed on the surface of fine-grained weathering products and amorphous materials. Therefore, various adsorptive components, such as clays, affect REE adsorption in weathered granite. Few research papers were listed in Table 2.2.

Table 2.2 Research studies about Ion Adsorption Clay

No.	**Author (Year)**	**Title**	**Analysis Proposed**
1.	Tohar, S. Z., & Yunus, M. M. (2020)	Mineralogy and BCR sequential leaching of ion-adsorption type REE: A novelty study at Johor, Malaysia.	XRD,XRF, ICP-MS, SEM/EDX.
2.	Sanematsu, K., Kon, Y., Imai, A., Watanabe, K., & Watanabe, Y. (2013)	Geochemical and mineralogical characteristics of ion-adsorption type REE mineralization in Phuket, Thailand.	XRD, XRF, ICP-MS, SEM/EDX
3.	Chen, L., Jin, X., Chen, H., He, Z., Qiu, L., & Duan, H. (2020).	Grain size distribution and clay mineral distinction of rare earth ore through different methods.	Malvern Mastersizer, XRD, XRF, Simulated leaching.
4.	Maulana, A., Sanematsu, K., & Sakakibara, M. (2016)	An overview on the possibility of scandium and REE occurrence in Sulawesi, Indonesia	XRF, ICP-MS

2.4.1 Particle Size Analysis

One of the fundamental physical characteristics of weathered granite is particle size distribution, which has a significant impact on the permeability, water-rock interaction, physical and mechanical properties of the ore, and consequently affects the mining of ionic rare earth ore bodies. As a result, the size of the mineral grain strongly correlates with the loose soil mantle created by surface weathering. The cumulative curves of regional particle size distribution are S-shaped (Figure 2.5).

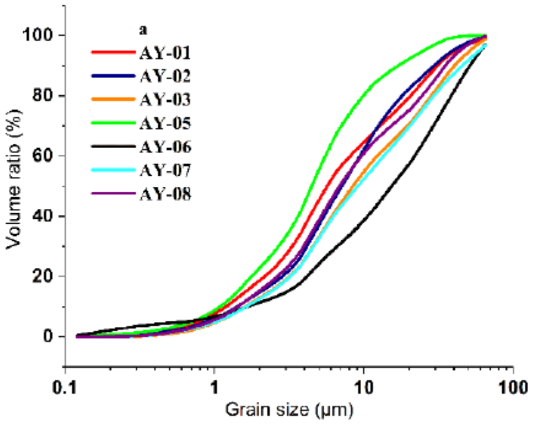


Figure 2.5 Cumulative particle size distribution curves from ion-absorbed RE representing eight samples (Chen et al., 2020).

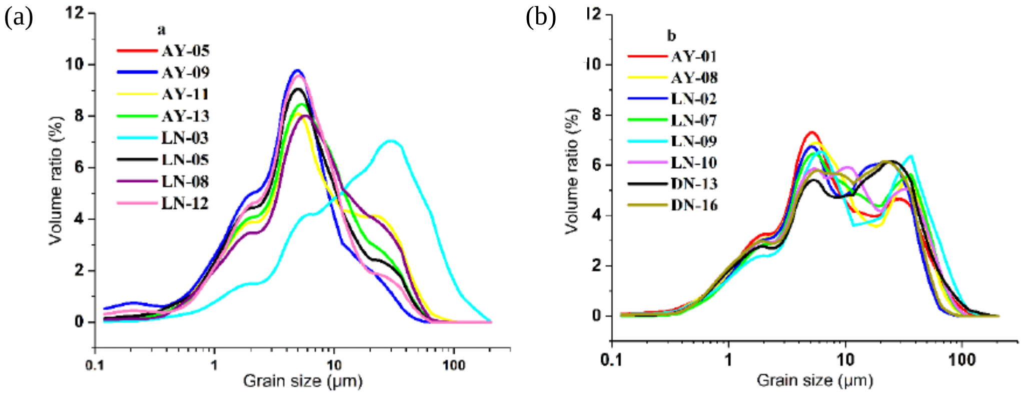


Figure 2.6 Grain size distribution of 27 regional samples: (a) shows unimodal patterns; and (b) shows bimodal patterns (Chen et al., 2020).

Particle size distribution in the REE mine does not appear to follow a single normal distribution pattern, according to the particle volume distribution curves, reflecting significant variations in soil particle size gradation. Previous research on the Dabu rare earth ore has shown a bimodal distribution pattern, with a high content of fine gravel-coarse sand and powder-clay and a low content of intermediate components. Yan et al. (2018) used a wet sieving method to classify REE ores into eight types of particle size distribution. As compared to Chen et al. (2020), both wet sieving and laser diffraction were used to analyse the REE ores.

The cumulative particle size distribution curve hits 90% of the volume at a particle size known as D90. The maximum, lowest, and standard deviation values for the average particle size, Dav, and volumetric average particle size, D [4,3], are equivalent. The median particle diameter standard deviation, D50 is the particle size at which the cumulative particle size distribution curve reaches 50% of the volume, while D [3,2] are the average particle sizes for the surface area. The correlation between average particle size (Dav) and potassium feldspar, quartz, and kaolinite indicates that the mineral particle size had a negligible impact on the mineral content of clay (Chen et al., 2020).

Malvern Mastersizer E, a laser diffraction tool, was used in Suhaina et al. studies to analyse the particle size distribution of ground ore samples. In a recirculating cell, the entire sample is exposed to the laser beam, allowing for the collection of diffraction data from each particle. Volume moment diameter (VMD) was determined by Malvern Mastersizer's software, and the d90, d50, and d10 values stand for the 10th, 50th, and 90th percentiles of cumulative passing (v2.15). For a sample distribution, the span value (Ψ) is defined by equation (1).

$$\Psi = \frac{D_{90} - D_{10}}{2D_{50}} \qquad (1)$$

Where,

D_{90} is 90th percentile

D_{50} is 50th percentile

D_{10} is 10th percentile

2.4.2 Elemental Composition using X-ray Fluorescence

X-ray fluorescence was used to analyse the major oxide elements of the powdered samples while inductively coupled plasma mass spectrometry was used to analyse the trace elements (Tohar and Yunus,2020). Approximately 1.5g of -75 mm sample, was flattened with a glass slide before being mounted inside a sample holder. XRF analysis was done using the PANalytical MiniPal4 XRF instrument. Similar preparation was done for XRD using Bruker D2 PHASER X-ray diffractometer.

XRF has the benefit of being a brief analytical instrument for elemental composition, which makes it superior to other techniques. XRF may be used on solids, liquids, and powders to measure concentrations in the range of ppm to 100%. Additionally, the approach offers a high degree of precision and can be non-destructive to the sample (Young, 2019).

2.4.3 Phase Identification using X-ray Diffraction

The REEs are mainly found in accessory phases such micas and amphibole, as well as zircon, monazite, titanite, rutile, ilmenite, and fluorapatite. X-ray diffraction was used to identify the main rock-forming minerals and alteration minerals (Borst et al., 2020; Tohar and Yunus, 2020; Sanematsu et al, 2013). The sample was analysed by Borst et al. from 5° to 70° 2° at a scanning rate of 0.01°/min, whereas the scan range was from 3° to 60° with a scan step of 0.02° and scan speed of 2°/min was used by Tohar and Mohd Yunus and Sanematsu et al.

The kaolinite diffraction peak is the same as that of halloysite because the chemical composition of kaolinite and halloysite are identical, with the exception of weakly bonded interlayer water. The characteristic diffraction peaks of halloysite and kaolinite were 7.30-7.45, 4.5-4.6, 3.58-3.60, and 3.32-3.37 based on research of the clay minerals in six REE mining locations in southern Jiangxi Province (Tohar and Yunus, 2020).

2.4.4 Mineral Identification using Microscope

Monazite (Ce), allanite (Ce), apatite, and zircon represent a majority of the REE-bearing minerals found in the parent granite from three islands in Johor, Malaysia. Monazite-(Ce) occurs as colourless, anhedral to subhedral grains that are frequently found with zircon, biotite, and other minerals. In weathered granite profiles (saprock and saprolite), some monazite-(Ce) appears to have been unstable as it has ragged outlines or looks disaggregated due to hydrothermal alteration (Hoshino et al., 2016). It is pale yellow, has high birefringence, and high relief. A subhedral tabular biotite mineral with apatite inclusions is shown in the Figure 2.7. Apatite single crystals and aggregates were frequently discovered with zircon and monazite in the same granite samples (Ce) (Tohar and Yunus, 2020).

According to SEM analyses, Fe-Mn-rich areas are locally connected with kaolinite, Kfeldspar, Fe and Mn oxyhydroxides with supplementary zircon and traces of cerianite (Ce). When distinct bright REE-rich phases cannot be distinguished in backscatter or by SEM-based energy-dispersive X-ray (EDX) investigations, hotspots of Y associated with clay minerals appear. These hotspots could be nanoscopic REE phases or Y that heterogeneously adsorbed (Borst et al., 2020).