

**CHARACTERIZATION STUDY OF
MALAYSIAN ION-ADSORPTION CLAY NR-
REE (NON-RADIOACTIVE RARE EARTH
ELEMENT)**

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CHARACTERIZATION STUDY OF MALAYSIAN ION-ADSORPTION CLAY
NR-REE (NON-RADIOACTIVE RARE EARTH ELEMENT)

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled ‘Characterization Study of Malaysian Ion-Adsorption Clay NR-REE (Non-Radioactive Rare Earth Element)’. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

y	Mass of crucible and sample
z	Mass of crucible and sample after heating
x	Mass of crucible

LIST OF ABBREVIATIONS

REE	Rare earth elements
NR-REE	Non-radioactive rare earth element
HREE	Heavy rare earth element
LREE	Light rare earth element
GPS	Global positioning system
KDO	Kedah overburden samples
KDT	Kedah tailing samples
ODS	Oxide dispersion strengthen
OLP	Organolanthanide phosphor
XRF	X-ray fluorescence
XRD	X-ray diffraction
LOI	Loss of ignition
SEM	Scanning electron microscope
FESEM	Fourier emission scanning electron microscope
ICP-MS	Inductively coupled plasma mass spectrometry

PSA	Particle size analysis
SERC	Science and Engineering Research Centre
PPKBSM	Pusat Pengajian Kejuruteraan Bahan dan Sumber Mineral
USM	Universiti Sains Malaysia

ABSTRAK

Industri sumber nadir bumi pada masa ini mendapat banyak perhatian terhadap tanah liat penjerapan ion (IAC), kerana banyak sumber REE yang mungkin bernilai untuk dikaji adalah yang berkaitan dengan tanah liat penjerapan ion ini. Kajian ini memberi dari Kedah, dan penyelidikan berkenaan kriteria mineral tanah liat penjerapan ion tersebut. Setelah pengasingan tanah liat daripada sampel untuk memperoleh sample orientasi, lebih sample yang lain digunakan pula untuk melakukan penyelidikan berkenaan ciri-ciri sumber nadi bumi menggunakan analisis-analisis seperti XRF, XRD, SEM, FTIR, dan PSA. Mineral tanah liat seperti halosite, kaolinite, dan quartz adalah antara tanah liat yang dijumpai di kawasan tersebut. Bagi menyelidik mekanisma sumber nadir bumi yang terdapat di dalam sampel, analisa menggunakan ICP-MS dijalankan untuk mengetahui kandungan sumber nadir bumi tersebut. Ianya dijalankan selepas kedua-dua sample dicerna untuk menukar bentuk pepejal kepada cecair, bagi membolehkan sampel tersebut dikesan oleh ICP-MS. Dua sampel yang akan dianalisa adalah daripada kawasan *tailing* dan *overburden*. Sampel-sampel ini diberi nama KDO (Kedah *Overburden*) dan KDT (Kedah *Tailing*). Selepas sampel-sampel tanah liat ini diasingkan dari sampel asli, sampel-sampel ini akan dijadikan sampel orientasi untuk dianalisa menggunakan *X-Ray Fluorescence (XRF)*, *X-Ray Diffraction (XRD)*, *Scanning Electron Microscope (SEM)*, *Particle Size Analysis (Malvern)* and *Fourier Transform Infrared Spectroscopy (FTIR)*. Halosite, kaolinite, dan quartz are clay adalah antara tanah liat mineral yang dapat dikesan di dalam kedua-dua sampel ini. Untuk analisis XRF, elemen-elemen terbanyak adalah Silikon (Si), Kalium (K), Aluminium (Al) dan Ferum (Fe). Kedua-dua sampel mengandungi kandungan quartz yang banyak, merujuk analisis XRD. Analisis *Loss of Ignition* dibuat sebelum XRF dibuat, dan memberi nilai 9% kepada KDT dan 5.8% kepada KDO. Ini menandakan KDT mempunyai bahan-bahan organic lebih banyak dari KDO. Yang terakhir,

untuk analisis menggunakan ICP-MS, terdapat 17 elemen REE yang terdapat di dalam kedua-dua sample ini. Manakala untuk kandungan yang terdapat antara sumber nadir bumi ringan (LREE) dan Sumber Nadi Bumi Berat (HREE) bagi sampel KDO adalah lebih tinggi dari sampel KDT. Pada masa yang sama, nisbah LREE kepada HREE untuk KDO adalah 1.17, lebih kurang berbanding sampel KDT dengan 4.41.

ABSTRACT

The REE industry has recently paid a lot of attention to ion-adsorption clays (IAC), as many possible sources of REEs that are worth researching are those connected to ion adsorption clays. This study focuses on the characterization method of ion-adsorption clay from Kedah, Malaysia, comprises of two samples, one from overburden area, and another one from tailing area. The samples from overburden area were assigned as KDO (Kedah Overburden), meanwhile, samples from tailing area were assigned as KDT (Kedah Tailing Area). After separating the clay minerals from the samples to create oriented clay samples, the remaining clay minerals are examined using X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Particle Size Analysis (Malvern) and Fourier Transform Infrared Spectroscopy (FTIR). Halloysite, kaolinite, and quartz are clay minerals found in the area. For XRF Analysis, the major traced elements that were found in both of the samples are Silicon (Si), Potassium (K), Aluminium (Al) and Iron (Fe). Both samples have an abundance of quartz in both samples. Loss of Ignition is done prior to XRF analysis, and the results showed that KDT has LOI of 9%, while KDO with 5.8%. This shows that KDT has higher organic substances than KDO. For ICP-MS, the results indicate that all 17 elements of REEs are present in both samples, For Light Rare Earth Elements (LREE) and Heavy Rare Earth Element (HREE) content for KDO is higher than KDT, meanwhile the ratio for LREE to HREE for KDO is 1.17, lower than KDT with 4.41 ratio.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Malaysia has many potential mineral resources that can be classified as light rare earth (LREE) and heavy rare earth (HREE). The occurrence of these elements are always in the association with other ores such as the ones containing phosphates and oxides of Cerium (Ce), Lanthanum (La), Neodymium (Nd) and Thorium (Th) (Sanjith et al, 2018). The group of rare earth elements (REE), called also lanthanides, is composed of 17 chemical elements (fifteen lanthanides, La to Lu, as well as Y and Sc). These REE are found in different geological settings such as igneous, sedimentary and metamorphic environment and are associated with several mineral phases such as apatite (Calas, 2012). The lanthanides exhibit similar chemical and physical properties but have different number of electrons in the 4f shell (Lipin and Mackay, 1989). In addition, the difference in the size of REE ions increases cationic exchange with other elements in different minerals (i.e. calcite and apatite) (Jia, 1991; Lipin and Mackay, 1989). In this study, Non-radioactive REE are the on will be focusing throughout the experiments.

Rare earth elements (REE) are a group of 17 chemical elements, all metals, that tend to be found together in geologic deposits. Rare earth metals and the alloys that contain them are used in a variety of high-tech applications, such as wind turbines, electric vehicles, rechargeable batteries, radar systems, and laser crystals. For this reason, they are called "vitamins of modern industry." The importance of these elements for key i3+-1industries and the dominance of China in their global supply puts REEs at the center of power struggle. The group of REEs includes the lanthanides, from lanthanum to lutetium, plus

yttrium and scandium. The major minerals containing REEs are bastnaesite, monazite, and xenotime, which contain 60% to 75% rare earth oxide (REO) equivalent by weight. The REEs are relatively abundant in the earth's crust. For example, cerium, one of the light rare earth elements, is more abundant than copper (Helmenstine et al., 2020).

Rare earth elements play an essential role in our national defense. The military uses night-vision goggles, precision-guided weapons, communications equipment, GPS equipment, batteries, and other defense electronics. These give the United States military an enormous advantage. Rare earth metals are key ingredients for making the very hard alloys used in armored vehicles and projectiles that shatter upon impact. Substitutes can be used for rare earth elements in some defense applications; however, those substitutes are usually not as effective and that diminishes military superiority (Gao et al., 2019).

Many researchers have been carried out experiment to determine the best leaching methods of various sources of clay-hosted REE in Malaysian weathered granitic crust. It is foreseen that the western Malaysian weathered granitic crust hosts a considerable amount of REE-bearing minerals. Many researches had been carried out to determine the leachability of various sources of clay-hosted REE in Malaysian weathered granitic crust. However, the fractionation of REE cannot be explained fully from whole-rock geochemical data because (1) it is controlled by the occurrence of REE-bearing minerals and (2) their varying resistance to alteration (weathering) (Yusoff et al., 2013). As the results, method that will be used to extract REE are different in ever region or location in order to achieve high recovery of REE. Hopefully, by the end of this work, the methods that are being used to characterize the REE could be beneficial for REE industry and its development in the future.

1.2 Problem statement

The problem that are arising in REE industry in Malaysia is quite significant due to the fact that the industry is very new and still undergoing a lot of planning and research. Various experiments still not yet conducted and SOPs are still not yet finalized and implemented. The standard operating procedures (SOP) for non-radioactive rare earth elements (NR-REE) to ensure sustainable mining activities is expected to be completed either at the end of the month or early next month.

The mining of REE minerals is different than regular ores such as gold or other industrial minerals. This is because, REE minerals aren't abundantly deposited in an area, but they were scattered everywhere in a small amount. This is very hard if we want to use the same method of mining this REE because it will be impractical to implement, as well as costing too much money and also it be hard to preserve the area and closing the mine area after mining has been done. However, the fractionation of REE cannot be explained fully from whole-rock geochemical data because it is based on the occurrence of REE-bearing minerals, in which the REE are differently distributed, and their varying resistance to alteration (weathering).

To solve the problems regarding the REE-bearing minerals, several tests can be done to identify and characterized these REE minerals. Firstly, is the leaching of ion adsorption clay REE in laboratory sequential extraction procedure by using single-stage extraction (IS) determine the concentration of ion-exchangeable elements in the sample, and and 5-step extraction (5S) to determine the concentration of REE of different reacting materials

in the sample. Lixiviants are also added in this method as it is useful for assessment of the mobility and accessibility of ion exchangeable REEs.

Other techniques also are used for the characterization of REE minerals which are SEM-EDX to examine the polished section and clay minerals morphology, XRD analysis for the study of crystalline phases present in minerals thus reveal the chemical composition information. and total sample digestion followed by ICP-MS to determine the REE concentration. Other technologies such as LA-ICP-IMS is also use to provide more information regarding each of the NREE minerals.

1.3 Significance of study

This research will solely be focusing on various methods of characterization for the purpose of development of REE industry in Malaysia that is slowly arise in area of research, exploration, and extraction. The characterization methods are aimed to determine the REE elements present in the samples, as well as labelling and characterized them based on their properties, be it physical or chemical. Common characterization procedures are use thoroughly in this experiment, as they are the most effective methods available, at least in this particular moment. Another significant of this study is, the evaluation of Malaysian Ion-adsorption clay REE is inadequate, thus is should be in our best interest to continue the research of REE in Malaysia as it helps in bringing clarity and sufficient information for future use.

1.4 Objectives of research

The main objectives of this research are:

- 1) To characterize Malaysian's Ion adsorption Clay of Non-radioactive Rare Earth Element (NR-REE) including its physical and chemical properties.

1.5 To assess the concentration of REE for potential REE mining

1.6 Scope of research

In this research study, the raw ion-adsorption clay (IAC) samples will be prepared from two different locations, tailing and overburden. For the samples from tailing area, the samples has been assigned as KDT (Kedah Tailing) where else, the samples from overburden area is assigned as KDO (Kedah Overburden). Some of the samples are ground to 75 μm and some are used in its original size, in order to distinguish these two forms such as characterization of polished section by using Field Emission Scanning Electron Microscope that will determine the microstructure of the IAC samples. Other characterization method such as XRF, XRD, LOI, FTIR, Particle Size Analysis, are also carried out to evaluate the REE's physical and chemical properties. For XRD, clay portion of samples were made to be sent out for thorough XRD analysis to determine the crystallographic structure and mineralogical phases of the minerals.

For chemical characterization, raw samples were sent to the lab to be digested and then to carry out a crucial and most fundamental steps which is REE Analysis by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The sole purpose of

this analysis is to determine the REE elements present in the samples as well as the REE content.

1.7 Thesis outline

This thesis is presented in 5 chapters. Chapter 1 contains the background of the study, problem statement, objectives, and scope of research. In Chapter 2, it covers more depth upon REE's, the introduction of IAC of REE, the geological occurrence of REE, the Malaysian and Global REE, Classification of REE and the brief explanation on the mineral characterization that is done in every bits of this study, which are XRF, XRD, PSA, FTIR, SEM, LOI and ICP-MS. The third chapter consists of the detailed explanation of all the methods that has been used and executed in this research from the preparation of the samples until each of the respective characterization methods. Chapter 4 is focusing on the results of the experiment and discussions of the outcome. Lastly, the chapter ends with a conclusive summarization of the whole experiment, whether the objectives of the study is achieved or failed, and the outcome of the conducted research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to ion-adsorption clay NR-REE

Rare earth elements (REEs) consist of 17 elements, which include 15 lanthanides (La-Lu), yttrium (Y), and scandium (Sc) (Meija et al., 2016; Xiao et al., 2016). REEs are rich with REE-bearing minerals of igneous rocks, such as apatite, allanite, monazite, titanite, xenotime and etc. in the lower mantle during the process of differentiation of magma (Hedrick, 2006), except continental rifts, which contain carbonatite and kimberlites (Hoshino et al., 2016). The depositions of REE are generally divided according to their mineralogy and geneses: primary deposits associated with igneous and hydrothermal activities and secondary deposits assembled through sedimentary processes and weathering (Lusty and Walters, 2010). Two major types of secondary deposits are the placer and ion-adsorption clay deposits. The latter, which is called “regolith-hosted REEs,” came from weathering process of plutonic or volcanic rocks that contain high REE; this process resulting in an accumulation of REEs in igneous weathering profiles (Hoshino et al., 2016). Meanwhile IAC deposits are the host of larger than 80% of middle and heavy REEs (Hu et al., 2017).

There were numerous studies of NR-REE from different places all around the world. The mineralogy and leachability of the rare earth elements (REE) from the Kipawa deposit, a Heavy REE (HREE) mine project of Matamec Resources (Quebec, Canada), was investigated to predict geochemical behavior and as well as assessing the components of controlling the REE mobility in ambient conditions. Every parts of the lithology deposit

has been given their own definitions including waste rocks and ores that were also sampled and characterized using multiple mineralogical techniques such as SEM-EDS, EPMA-WDS, XRD. The results were then sent to the lab for kinetic testing using weathering cells to determine their REE release potential. The results of the mineral characterization shows that REE bearing minerals are mainly represented by mosandrite, fluorbritholite, apatite, monazite and Zr silicates (i.e., aqualite, reidite) (Edahbi et al., 2018). In this study, characterization for REE elements were quite similar to most of the studies that has been done before due to the efficient of the methods to characterized these complex elements.

2.1.1 Global REE

According to the US Geological Service (USGS) Mineral Commodity Summaries 2016, the total REE reserve are estimated to be around 130 million tons. The largest shares of REE reserves are Brazil and China, with corresponding figures of 16.9% and 42.3%, followed by Australia, India, and the United States with corresponding shares of 2.5%, 2.4%, and 1.4%. The US and world REE resources, typically of LREE, are majorly consist in bastnäsite, a REE-carbonate-fluorine mineral, and monazite, a REE-thorium-phosphate mineral (Fernandez, 2016).

China has led the total world mine production and reserved in 2012 which stands at 97%, India at 2%, and Brazil at 1% (USGS, 2010). When it comes to total global mining reserves in REEs, China represents almost half of total at 48%; the Commonwealth of Independent States at 17%, the US 12%; India 3%; Australia 1%; and others at 19%. The domination of the west give the US and EU the confidence to voice out upon highlighting the defense and strategic elements of the debate, given that many military components are relying on China source of REE (USGAO, 2010).

Figure 2.1 (a) below shows the global Rare Earth Reserves by countries. It is defined by USGS (2010) as the “*the part of the reserve base which could be economically extracted or produced at the time of determination*”. While, Figure 2.1 (b) shows the Top countries in Rare Earth mine production worldwide 2010-2013 (USGS, 2014).

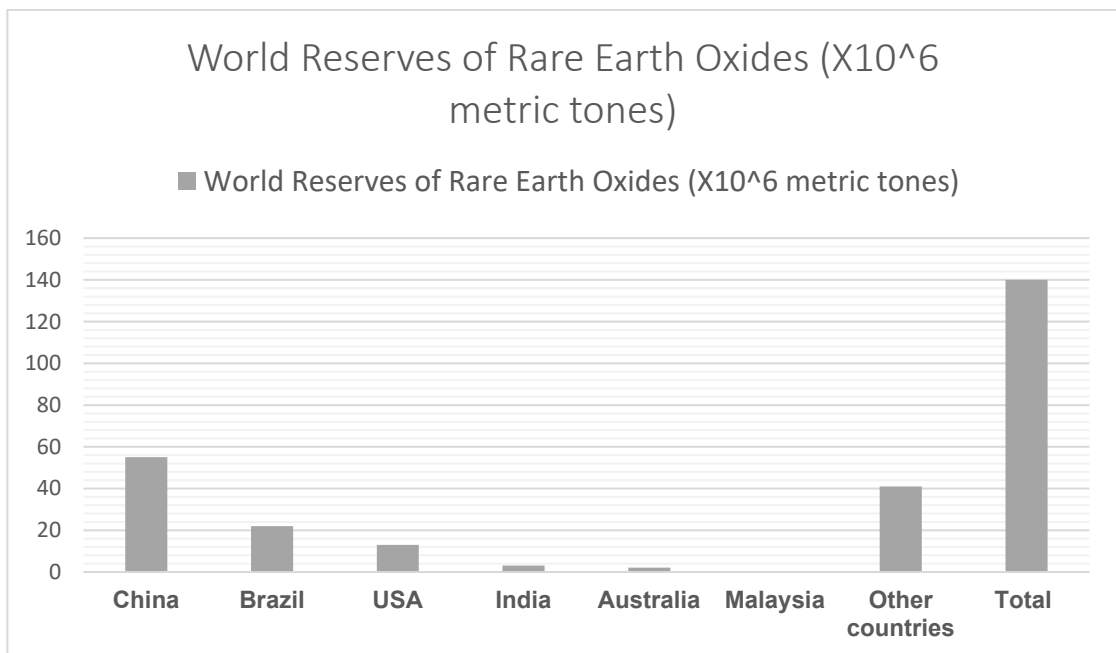


Figure 2.1 (a): World Reserves Ores of Rare Earth Element

Figure 2.1 (a) shows that China has abundance or rare earth oxides compared to other countries, followed by Brazil and United States of America. China has been conquering the market for REE industries for so long, it is hard to beat their reputation on REE (USGS, 2014).

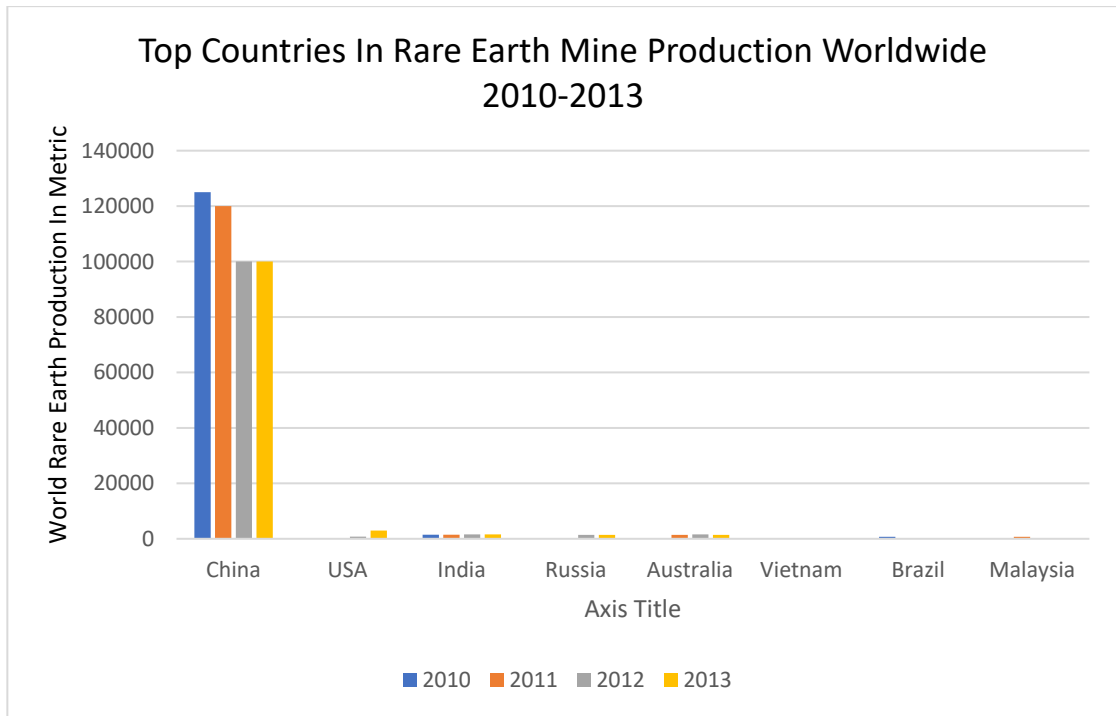


Figure 2.1 (b): Top Countries In Rare Earth Mine Production Worldwide 2010-2013

Figure 2.1 (b) shows that the REE production in Vietnam, Brazil and Malaysia is not negligible, instead, the amount are very low compared to the other countries like China or USA, thus, the production values aren't visible in the graph above.

China's monopoly on REE production has been solely motivated by profit maximizing factors. China also controls nearly all the world's processing facilities, with some REE were taken underground in other countries and being sent there for refining because China owns the technology and have much better facilities than other countries (Dreyer, 2020).

2.1.2 Malaysian REE

Even in global REE, Malaysia has been known for its involvement in the extraction of REEs for economic purposes. This is due to the fact that Malaysia has abundance of REE-bearing deposits that are scattered all over the states. Perak, Kelantan, and Kedah is known for their richness REE content due to its geographical formation.

A recent study conducted by Ali Yaraghi (2020), on representative samples from two different locations, which are Lumut and Teluk Murok, located within Malaysian Western granite belt. In both profiles, the parent rocks are documented as medium-grained mica (phlogopite)-rich, S-type, peraluminous, ilmenite-series granite with metamict texture. (A. Yaraghi et.al., 2020).

Figure 2.1 (c) shows the schematic map of the southeast Asian tin belt that indicates the distribution of granitic rocks. The big three granitic were found in the area called “Eastern belt” with a high percentage of I-type granites, “Central belt” with a high portion of S-type granites, and “Western belt” with a mixture of I-and S- type granites.

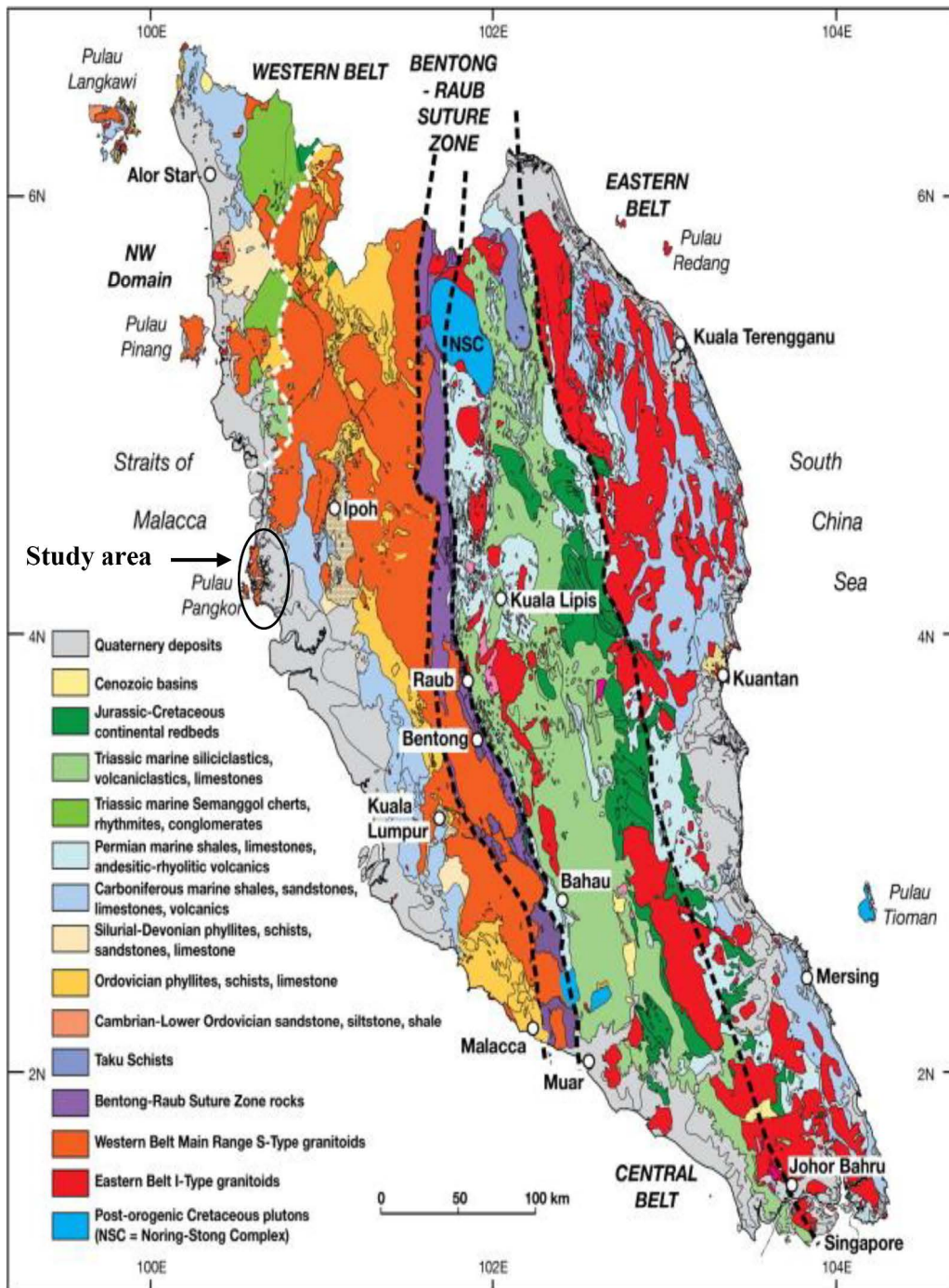


Figure 2.1 (c): Simplified geological map of Peninsular Malaysia showing study area; modified after (Hutchison and Tan, 2009)

Malaysia has been producing REE minerals from alluvial tin mining by-products in Kinta Valley (5% of the world production in 1993) for a few decades, and has a long experience

in upstream REE industry. Malaysian xenotime also used to be the main source of yttrium before 1988 (Academy of Science of Malaysia and National Professors' Council, 2011)

2.2 REE crustal abundance

The main economic sources of rare earths are minerals such as monazite, loparite, monazite, and lateritic ion-adsorption clays. Rare earths are relatively abundant group of 17 elements that consists of scandium, yttrium and lanthanides. The elements range in crustal abundance from cerium, which is the 25th most abundant element out of 78 elements in the Earth's crust at 60 parts per million, to thulium and lutetium, which are the least abundant rare earth elements. The elemental form of rare earths are iron grey to silvery lustrous metals that are commonly soft, malleable, and ductile are usually are reactive, especially when having an increase in temperature or when divided in a fine manner (National Minerals Information Centre, 2020).

According to the EPA, United States Environmental Protection Agency 2012, the abundance of REE in the earth's crust shows that lanthanides that have lower atomic numbers are more abundant than the elements with bigger atomic numbers as presented in Table 2.2 (a) (Kumari et al., 2013).

Table 2.2 (a): Crustal abundance of REE elements in the Earth's crust

Element	Atomic number	Abundance (ppm)
Lanthanum	57	30
Cerium	58	60
Praseodymium	59	6.7
Neodymium	60	27
Promethium	61	10 ⁻¹⁸
Samarium	62	5.3
Europium	63	1.3
Gadolinium	64	4.0
Terbium	65	0.7
Dysprosium	66	3.8
Holmium	67	0.8
Erbium	68	2.1
Thulium	69	0.3
Ytterbium	70	2.0
Lutetium	71	0.4

Table 2.2 (b) shows the approximate percentage of REE oxide content from some of the REE minerals (Hedrick, 2004; Kumari et al., 2013). Among 250 recognized REE minerals, there are only three that considered to be the vital ore that is most viable for extraction: bastnasite, monazite, and xenotime. Nonetheless, weathered crust elusion-

deposited rare earth ores usually known as ion-adsorbed rare earth ore is also practicable for recovery.

Table 2.2 (b): The Approximate Percentage of REE Oxide Content from some REE Minerals (Hedrick, 2004; Kumari et al., 2013).

Carbonate	Mineral	Baestnaesite (Ce, La)(CO ₃)F	Parisite Ca (Ce, La) ₂ (CO ₃) ₃ F ₂	Synchisite Ca(Ce, La)(CO ₃) ₂ F	Cebaite Ba ₃ Ce ₂ (CO ₃) ₅ F ₂
	REO (%)	75	61	51	32
Phosphate	Mineral	Apatite Ca ₅ (PO ₄) ₃ (F, CL, OH)	Monazite (Ce, La, Nd, Th)PO ₄	Xenotime YPO ₄	Florencite CeAl ₃ (PO ₄) ₂ (OH) ₆
	(REO %)	19	65	61	32
Silicate	Mineral	Gadolinite (Ce, La, Nd, Y) ₂ Fe ²⁺ Be ₂ S i ₂ O ₁₀	Allanite (Ce, Ca, Y) ₂ (Al, Fe ³⁺) ₃ (SiO ₄) ₃ O H	Kainosite Ca ₂ (Y, Ce) ₂ Si ₄ O ₁₂ C O ₃ .H ₂ O	Britholite (Ce, Ca) ₅ (SiO ₄ ,PO 4) ₃ (OH, F)
	(REO %)	60	38	38	32

Oxide	Mineral	Fergusonite (Ce,La,Nd) ₃ bO ₄	Loparite (Ce, La, Na, Ca, Sr)(Ti,Nb)O ₃	Euxenite (Y, Ca, Ce, U, Th)(Nb, Ta, Ti) ₂ O ₆	Brannerite (U, Ca, Y, Ce)(Ti, Fe) ₂ O ₆
	(REO %)	53	30	24	9

2.3 Classification of REE

Every REE has its own unique characteristics and importance, with lanthanide elements that are divided based on electron shell configuration into the light REE (LREE; La to Gd) and heavy REE (HREE; La to Lu). Nevertheless, global mining industry has their own way to classify these iridescent minerals, where HREE includes Pm, Sm, Eu, and Gd. Though Y has a relatively low molecular weight, it is typically classified as a HREE, while Sc is not formally classified as either LREE or HREE but in most time it is considered together with the REE as a whole (Weng et al., 2013).

In Table 2.3 (a), it can be clearly shown that typical REE abundances in Earth's crust vary significantly, with Ce having an average crustal concentration (63 ppm) that is higher than the average concentrations of Cu (47 ppm) and Pb (17 ppm) within the Earth's crust (Rudnick and Gao, 2003). In comparison, the average crustal concentration of Tm is 0.3 ppm, meanwhile for Lu, it is 0.31 ppm, which is much lower than most of economically important metals, but still higher than Au, Ag and platinum group elements (Rudnick and Gao, 2003).

Table 2.3 (a) Summary of the chemistry and average crustal abundances of the REE;
 adapted from Jowitt et al. (2013)

Element	Atomic Number	Element Name	Classification		Average Crust/ppm	Uses
			IUPAC	Mining		
La	57	Lanthanum	Light	Light	31	Optics, batteries, catalysis
Ce	58	Cerium	Light	Light	63	Chemical applications, colouring, catalyst
Pr	59	Praseodymium	Light	Light	7.1	Magnets, lighting, optics
Nd	60	Neodymium	Light	Light	27	Magnets, Lighting, Lasers, Optics
Pm	61	Promethium	Light	Heavy	N/A	Limited use to due radioactivity, used in paint and atomic batteries; very rare in nature
Sm	62	Samarium	Light	Heavy	4.7	Magnets, lasers, masers

Eu	63	Europium	Light	Heavy	1	Lasers, lighting, medical applications
Gd	64	Gadolinium	Light	Heavy	4	Magnets, glassware, lasers, X-ray generation, computer applications
Tb	65	Terbium	Heavy	Heavy	0.7	Lasers, lighting
Dy	66	Dysprosium	Heavy	Heavy	3.9	Magnets, Lasers
Ho	67	Holmium	Heavy	Heavy	0.83	Lasers
Er	68	Erbium	Heavy	Heavy	2.3	Lasers, steelmaking
Tm	69	Thulium	Heavy	Heavy	0.3	X-ray generation
Yb	70	Ytterbium	Heavy	Heavy	2	Lasers, chemical industry applications
Lu	71	Lutetium	Heavy	Heavy	0.31	Medical Applications, chemical industry applications
Sc	21	Scandium	N/A	N/A	14	Alloys in aerospace

						engineering, lighting
Y	39	Yttrium	Heavy	Heavy	21	Lasers, superconductors, microwave filters, lighting

*Notes: We have provided that the International Union of Applied and Pure Chemistry (IUPAC) definition of REE based on electron configuration of the elements as the definition of REE differs from the common definition used in mining industry (shown as ‘mining’). The comparison is made to allow easy comparison for the reader to understand.

2.3.1 Deposits type

Table 2.3 (b) shows the deposits type and the elements that are formed prior to the depositions.

Table 2.3 (b): REE deposits Classification (Dill H. G., 2010)

Type of deposits	Elements of deposits
Magmatic rare earth deposits	REE-P-Nb-Ta-Y-F-(Be-Zr-Th) deposits related to carbonites
	REE-P-Ti deposits related to alkaline igneous complexes
	REE-U-Nb-bearing hydrothermal iron deposits (in places transitional into intragranitic deposits with Mo-W-U-Be
	REE-Nb-P-F-bearing hydrothermal deposits
	Be- and Y- bearing alkaline intrusive rocks (nepheline syenite)
Structure-related rare earth deposits	REE-F-Ba-Th-bearing vein-type deposits
Sedimentary rare earth deposits	REE-(Ti-P-Nb) residual deposits / placers on alkaline igneous and carbonatites complexes
	REE in bauxite
	REE-bearing phosphorites
	Ion adsorption clays
	REE-bearing coals

There are more recent work focusing on classification of REE deposits that was proposed by Weng et al. (2013) shown in Table 2.3 (c). These classifications that they proposed are highlighting the geological processes that concentrate and form REE minerals and initiate the formation of REE minerals deposits using key examples rather than focusing on mineralogy and host rocks.

Table 2.3.(c): REE deposit type classification scheme proposed by Weng et al. (2013) adapted to include the new consolidated sediment(*) class.

Process	Mineral Deposits Type		Key example
Igneous	Silica undersaturated	Carbonatite	Bayan Obo China, Araxa, Brazil; Karonge, Burundi; Mountain Pass, USA; Nolans Bore, Australia; Steenkampskraal, South Africa
		Alkaline complexes and alkaline pegmatites	Khibina and Lovozero, Russia; Nora Karr, Sweden; Bokan, USA; Thor Lake, Canada; Kipawa Lake; Canada; Kola Peninsula, Russia
	Silica saturated to oversaturated	Rhyolites	Round Top USA; Foxtrot, Canada
		Granites and granitic pegmatites	Khibina Massif, Russia; Motzfelfdt Greenland; Ytterby, Sweden
Hydrothermal	Iron oxide copper gold ore deposits (IOGC)		Olympic Dam, Australia; Milo, Australia
	Skarn	Granit-related	Mary Kathleen, Australia

		Carbonatite-related	Saima, China
Secondary Sedimentary /	Heavy mineral sands		WIM150, Australia
	Laterite		Tantalus, Madagascar
	Tailings		Steenkampskraal, South Africa; Port Pirie, Australia; Mary Kathleen, Australia
	Shale-hosted		Buckton, Canada
	Alluvial/Placer		Charley Creek, Australia; India; Sri Lanka; FL, USA
	Consolidated sediments (arsenite, quartzite, arkose)		Vale de Cavalos and Monfortinho Portugal; Beira Baixa Province, Portugal

As stated before, all classification schemes are invariably dependent on the amount of information that are provided. That's why it's very important to gather all the information that accessible to improve the classification of the REE deposits.

The occurrence in Portugal of less known types of REE deposits and their occurrences that weren't stated in the table below are noteworthy; example are of those occurring in the consolidated sediments that outcrop in the northern Ossa Morena Zone and in the northern Central Iberian Zone; named Vale de Cavalos (Portalegre) and Monfortino (C. Branco) (s.l), respectively, must be stated in the classification scheme in Table 5.

2.4 Applications of REE in the industry

REEs are not particularly 'rare' in terms of abundance, but they are usually separated from each other based on their chemical characteristics (Hurst, 2010). Although REEs are distributed in a wide range geographically, they are chiefly mined, concentrated, and separated in China.

The dominance of China in REE markets have made them powerful enough to restrict the supply REOs and consolidate its rare earth industry. Their rare earth production and export limits for 2013 are 93,800 tons and 31,000 tons respectively.

These REEs are used in mature markets such as catalysts, glassmaking, lighting and metallurgy, which takes up 59% of total world consumption of REEs, meanwhile in newer market such as battery alloys, ceramics, magnets, which take up 41% of the total worldwide consumption of rare earth elements. In mature market segment, lanthanum and cerium make up about 80% of rare elements used, and in new market segments, dysprosium, deodmium, and praseodymium take up 80% of rare earth use. Whatever

the end use are, rare earth elements aren't recycled abundantly, but only if recycling become mandated or rare earth elements have a feasible way to be recycled.

In 2008, 129,000 metric tons (t) of REOs was used worldwide (Cordier and Hedrick, 2010). Mature applications use about 60% of the total, the remaining 40% was used in development of high-growth technologies such as battery alloys, ceramics, magnets and other sectors that grow at 4 to 10% per year) (USGS, 2011).

The mature REE markets, consume majorly cerium (45%) for lanthanum (39%), yttrium (8.0%) oxides. Dysprosium, Gadolinium, neodymium and praseodymium oxides are other REEs that contribute the remaining 7.0% of total REE consumption in these respective sectors. The main industrial application are shown in Table 2.4 (a).

Catalysis: In 2008, 27,400 t of REEs were consumed as catalyst for fluid cracking (72%) and automobile catalytic converters (28%), lanthanum oxide used about 66%, cerium oxide 32%, neodymium oxide 0.8% and praseodymium 0.6%.

Glass: REE are used as an absorbent to absorb ultraviolet light, altering the refractive index, and coloring or decolorizing (USGS, 2011). Yttrium is used with garnet to form yttrium-aluminium-garnet (YAG) lasers. Neodymium and some other REEs are used as dopants to alter properties of the YAG lasers (Anscombe, 2002). Neodymium is used to produce YAG lasers.