

PETROGEOCHEMISTRY OF RARE EARTH ELEMENTS (REE) FROM HULU LANGAT AND BALING, MAIN RANGE GRANITE PROVINCE, MALAYSIA

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Abstract. The research focused on the petrogeochemistry of potential weathered granitoids containing rare earth elements (REEs) in Peninsular Malaysia's Main Range Granite, specifically in the Hulu Langat and Baling region. Through mineralogical and geochemical analyses using methods like petrographic examination, XRF, XRD, and ICP-MS. Both regions are in the Western Belt Main Range S-type granitoids, Peninsular Malaysia. However, the mineralogy and geochemistry characteristics of the rock will be different. Thin sections were done to study the rock petrology which indicates, samples are granite rocks. There are minerals like quartz, biotite, and mica in rock samples, indicating limited weathering. There were six samples from Hulu Langat which is 1A, 2A, 2B, 2C, 3B and 4A while seven samples from Baling which is 1A, 2A, 3A, 4B, 6C, 8E and 9E. Selected samples from Baling were carried out several analyses. XRD analyses from Hulu Langat shown that presents of clay minerals like kaolinite, nacrite, quartz, microcline, muscovite while Baling samples shown that present of kaolinite which was formed from the weathering process. XRF analysis shown that both samples consist of major oxide compounds such as Al_2O_3 and SiO_2 in the high concentration. ICP-MS results indicates that the TREE concentration of 8.583 ppm in sample 1A from Hulu Langat while 6.863 ppm in sample 1A from Baling. The lowest concentration 0.227 ppm in sample 3B.

Keywords: REE, petrogeochemistry, main range, Peninsular Malaysia

Article Info

Received 4th October 2023

Accepted 13th December 2023

Published 20th December 2023

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ISSN: 1823-7010, Eise: 2600-7444

Introduction

Rare earth elements (REE) are generally associated with the hi-tech industry due to their extensive uses in high-strength permanent magnets, lasers, automobile catalytic converters, fibre optics/superconductors, and electronic devices [1-2]. There is a growing need for REE on the international markets because of the ongoing development of cutting-edge technology, with an emphasis on identifying new sources to ensure an adequate supply for both the present and the future [3]. It has been demonstrated that rare earth elements accumulated either in the lower mantle during magmatic differentiation or in the REE-bearing minerals of igneous rocks. Some examples of these minerals include apatite, allanite, monazite, titanite, and xenotime [4-5].

In other words, monazite makes up a portion of these heavy minerals. In addition, the sands of beaches in Brazil, India, Malaysia, Thailand, and Vietnam have been mined for monazite. There have been further significant mineral discoveries, including xenotime and zircon [6-7]. Indeed, the three types of REE deposits, namely alkali feldspathoids, alkali pyroxenes, and alkali amphiboles, are classified based on their distinct characteristics, mineralogical composition, and geological origin [8]. These classifications are important in understanding the formation and distribution of rare earth elements, which can further aid in their exploration and extraction [9-10]. According to prior research that investigated the absorption of rare earth elements (REEs) in weathered granites, the most likely place for REEs to become absorbed is on the surface of clays like kaolinite [11].

According to [12], further explored the distribution of REEs in weathered granitic profiles in the Western Peninsular Malaysia, finding a significant increase in REY content in the lower portions of the profiles due to the high adsorption capacity of clay minerals. These studies collectively highlight the potential for REE exploration and extraction in the Main Range Granite province. In the past, Malaysia used to get rare earth elements from waste materials, like the minerals found in monazite and xenotime [13]. However, nowadays, Malaysia is more focused on mining rare earth elements (REE). Hulu Langat, Selangor and Baling, Kedah situated in the Main Range Granite province of Peninsular Malaysia, is thought to have potential rare earth resources. Unfortunately, there hasn't been much research in this area, especially in exploring REE. To better grasp the possible rare earth resources and deposits in this region, more research is needed in areas like sample mineralogy and geochemistry studies. This research focuses on petrogeochemistry of REE specifically on the major range granite regions of Hulu Langat (Selangor) and Baling (Kedah), which may have potential for REE deposits in Peninsular Malaysia.

Materials and Methods

Field research and on-site geological sampling methods were used to study Rare Earth Elements (REEs) in weathered granite. The investigation took place in Hulu Langat, Selangor and Baling, Kedah as both locations is located within the Western Belt Main Range S-type granitoids, Peninsular Malaysia. (Figure 1). The coordinates for the Hulu Langat according to the WSG 84 system, are 30° 4' 22.09" and 1010° 49' 49.36", and for Baling is 5° 38' 37.59" and 100° 50' 26.77". The study covers resource characterization, mineralogy, and geochemistry. Six samples were collected in Hulu Langat and seven samples were collected in Baling, Kedah. Mineralogy characteristics were analyzed by study petrography by thin section and X-ray diffraction (XRD) analysis. The thin sections were analyzed by using polarizing

microscope XOPTRON X80 POL. Loose samples were analyzed geochemistry analyses by X-ray fluorescence (XRF), and inductively coupled plasma mass spectrometry (ICP-MS). Prior to XRF, XRD and ICP-MS, the samples were dried, pulverized by agate mortar, and sieved through 75 microns mesh.

Location of Study

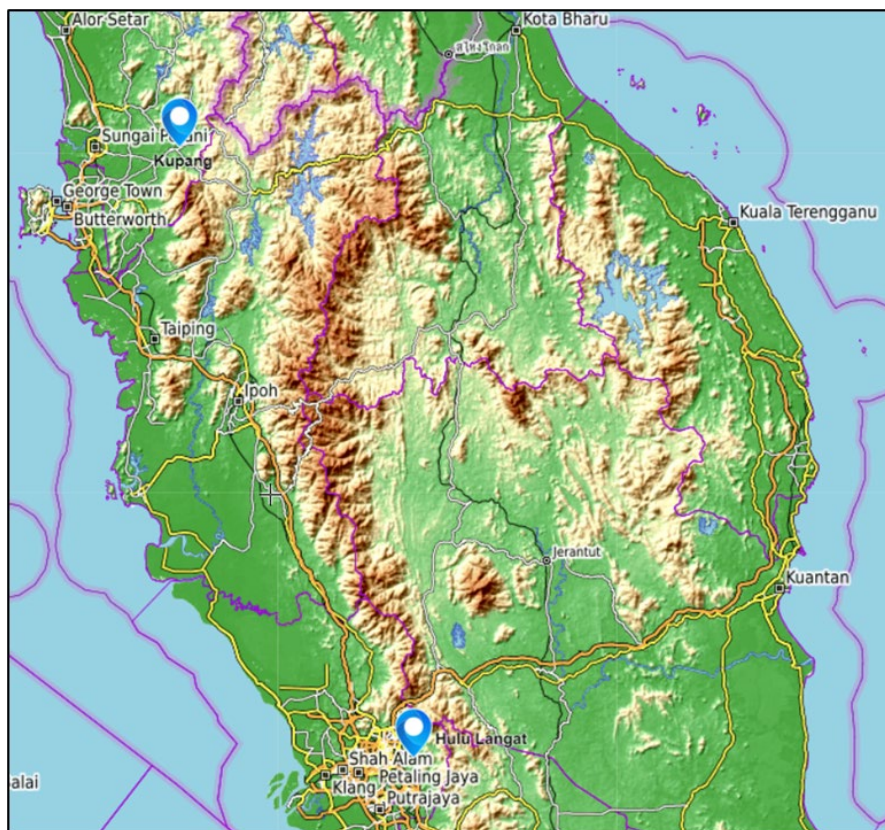


Figure 1: Location of study area (Markers shows the study area of Baling, Kedah and Hulu Langat, Selangor)

Results and Discussion

Petrology and Mineralogical Study

The microscopic view from Figure 2 illustrates the samples from Hulu Langat, Selangor and Figure 3 illustrates samples from Baling, Kedah. The presence of mineral quartz, biotite, and potassium feldspar in the granite rocks of Hulu Langat and Baling, Kedah indicates their classification as granite [14]. The major minerals in Hulu Langat are quartz and biotite, while in Baling, Kedah, they are biotite and K-feldspar, with the latter having a larger grain size. The color of quartz varies with the region due to the mineral composition [14]. These findings are consistent with the identification and characterization of geo-heritage resources in Hulu Langat, which highlight the presence of igneous and metamorphic rocks, including granite [15]. The relationship between mineralogical characteristics and mechanical properties of granitic

rock from Hulu Langat has also been studied, with minerals such as quartz, feldspar, mica, and clay-rich minerals being abundant [16].

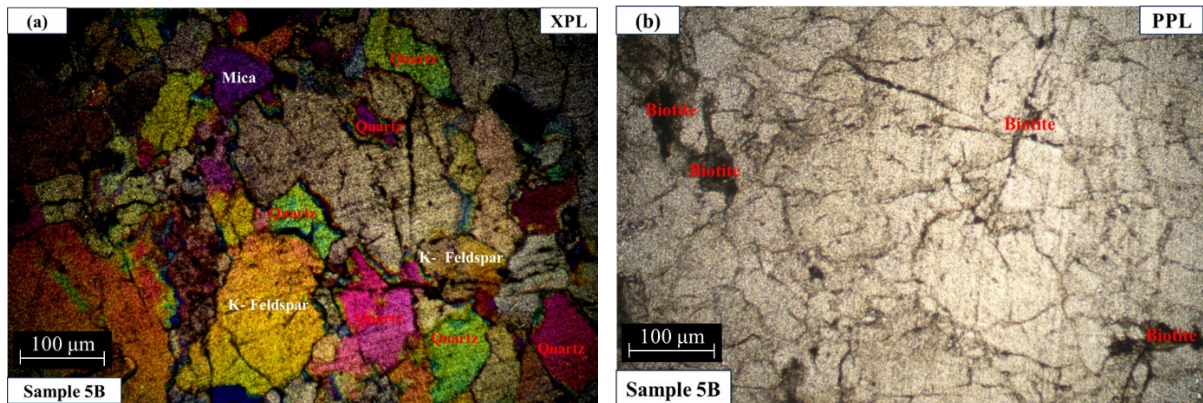


Figure 2: Microscopic view of sample 5B from Hulu Langat, Selangor (XPL: Cross Polarized Light, PPL: Plane Polarized Light)

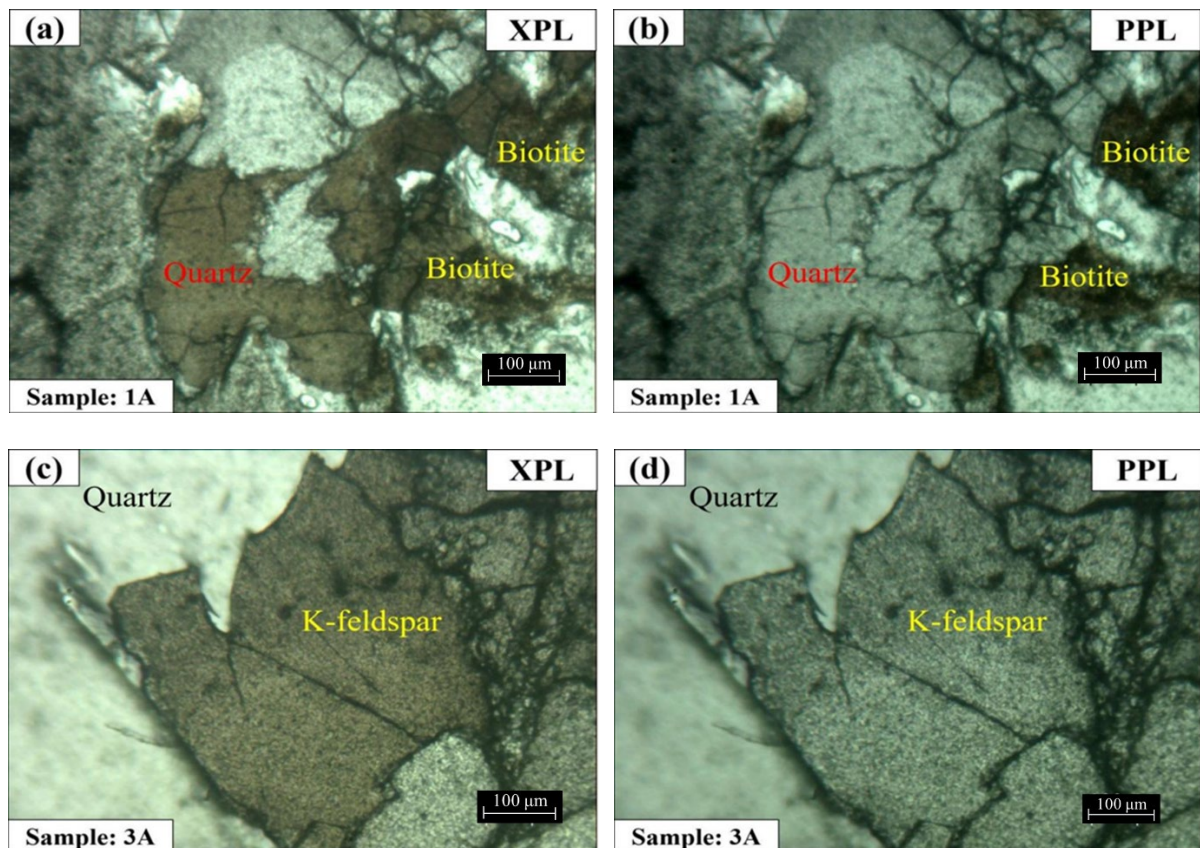


Figure 3: Microscopic view of sample 1A and 3A from Baling, Baling, Kedah (XPL: Cross Polarized Light, PPL: Plane Polarized Light)

Phase Analysis using X-Ray Diffraction (XRD)

X-ray diffraction analysis has been performed on the weathered crust of granites and their parent rocks at the sites. The X-ray diffractogram of Sample 1A, which consists of clay and quartz, is depicted in Figure 4. The nacrite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) mineral is the sort of clay that was discovered. The nacrite peak is the highest one for sample 1A. Quartz is composed of SiO_2 for the most part. The majority of Sample 2A consists of clay and quartz as well. Quartz, on the other hand, has the largest peak in sample 2A. The quartz present in this sample is secondary quartz which have undergone weathering. The X-ray diffractogram of Sample 2B is depicted here in Figure 4, kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and quartz comprise most of the constituents. Kaolinite can be found at the summit with the highest elevation. Clay minerals are of the type known as kaolinite. The X-ray diffractogram of Sample 2C is depicted here in Figure 4, kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and microcline (KAlSi_3O_8) are the two varieties of clay that can be found in this sample. The microcline peak is the highest one for the sample 2C.

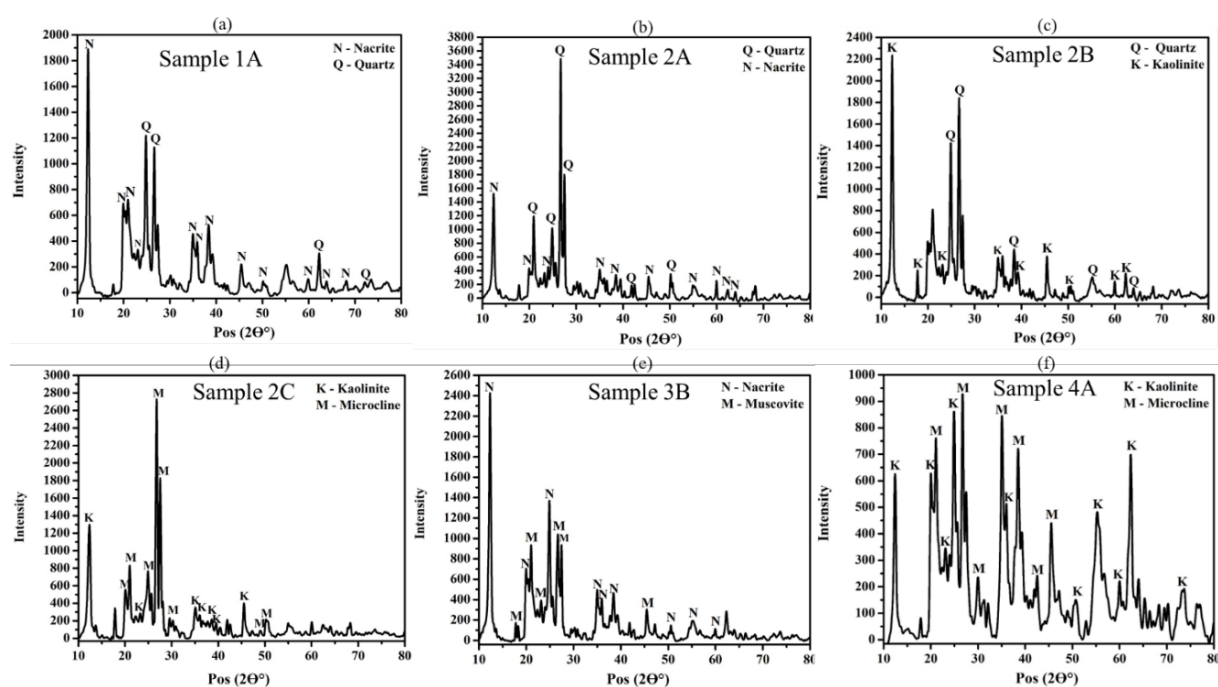


Figure 4: X-ray diffractogram of samples from Hulu Langat

The X-ray diffractogram of Sample 3B is displayed in Figure 4, both nacrite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and muscovite $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$, can be found in this sample. The concentration of nacrite in sample 3B reaches its greatest point. The mica group contains muscovite as one of its elements. This component is frequently discovered in rocks of igneous genesis. The X-ray diffractogram of Sample 4A is depicted in Figure 4, clay minerals may be found in Sample 4A. These clay minerals are kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and microcline (KAlSi_3O_8). The microcline peak is the highest one for the sample 4A.

Meanwhile, XRD results show that weathered granite consists of various type minerals. (Figure 5). Sample 1A characterised the peak of mineral feldspar, orthoclase, kaolinite, and zeolite. In sample 2A, it demonstrated that mineral orthoclase, xenotime (Tb), magnetite and quartz are existed.

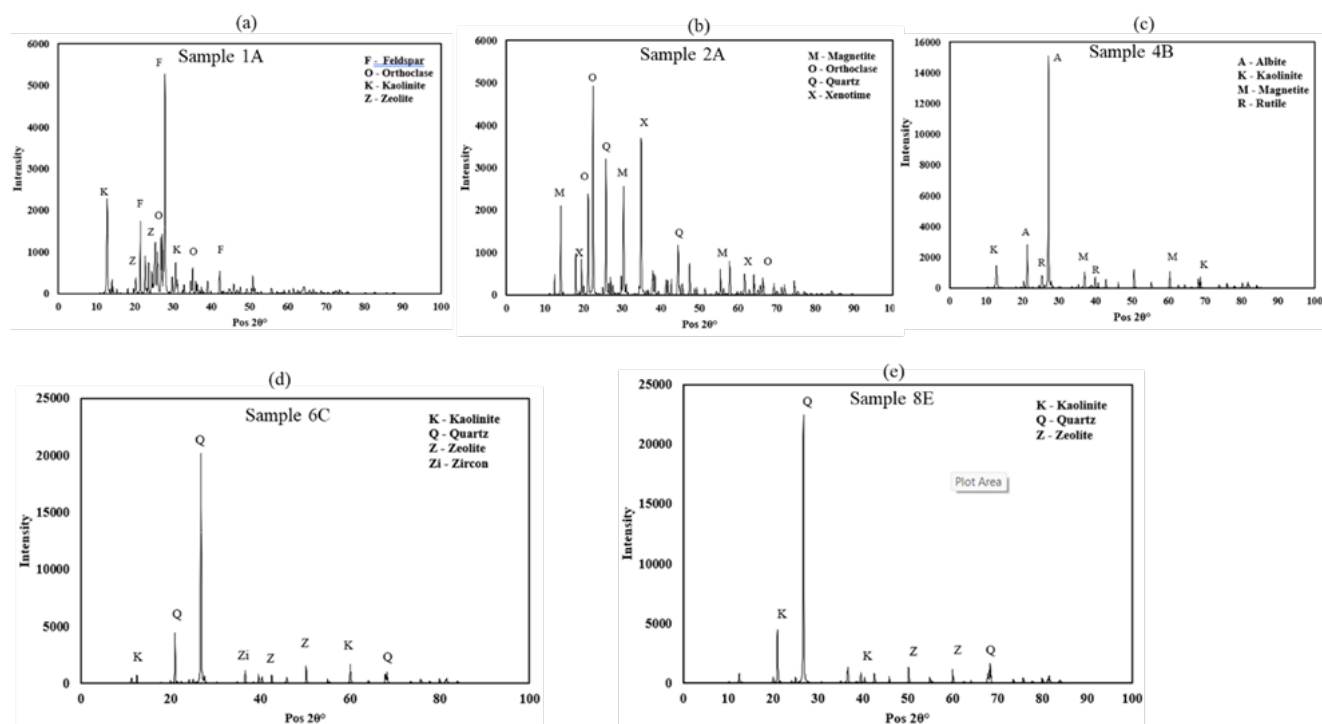


Figure 5: X-ray diffractogram of samples from Baling, Kedah

Sample 4B comprises albite, kaolinite, magnetite, and rutile. Meanwhile, sample 6C consists of kaolinite, quartz, zeolite, and zircon. Lastly, kaolinite, quartz and zeolite exist in Sample 8E. Formation of clay minerals by weathering process of granite minerals. Both samples from Hulu Langat, Selangor and Baling, Kedah consist of clay minerals which was formed from the weathering of feldspar minerals. Weathering can be occurred naturally by physical and chemical [16]. According to Ritonga et al. [17], chemical weathering alters the geochemical properties of the minerals.

X-Ray Fluorescence Study

The concentration of major oxide compounds and trace elements in two studied profiles, Hulu Langat, and Baling, show significant differences in table 1.. In the Hulu Langat samples, the concentration of Al_2O_3 increases, while it decreases in the Baling samples. Both samples exhibit a high concentration of SiO_2 , with other oxide elements present as trace elements due to chemical weathering. The presence of substantial quantities of elements like Aluminum (Al), Silicon (Si), Titanium (Ti), Potassium (K), and Calcium (Ca) may indicate a process of disintegration. Their frequent occurrence in the sampled region suggests that weathering has taken place in that specific location [18]. The geochemical characteristics of the samples indicate a range of weathering intensity, with the Hulu Langat samples showing a medium weathering intensity and the Baling samples showing a low weathering intensity. The differences in the concentration of Al_2O_3 and the weathering intensities between the two profiles may be attributed to variations in climate and material sources [19].

Table 1: Major oxide content in sample (Hulu Langat & Baling)

Sample No	1A	2A	2B	2C	3B	4A	1A	2A	3A	4B	6C	8E	9E
Region	Hulu Langat, Selangor						Baling, Kedah						
Rock Type	Weathered Granite/ Clay												
Na ₂ O (%)	54	55	0	0	0	0	1.68	9.64	2.91	2.97	5.71	3.35	2.52
MgO (%)	1	1.3	3.4	0.8	1	0.6	0.02	0.13	0.02	0	0	0.01	0.01
Al ₂ O ₃ (%)	20.3	16	32.9	31.4	35.1	36.8	39.5	43.2	22.4	32.8	28	30.6	27.7
SiO ₂ (%)	22.1	24.4	50.3	54.5	50.6	53.3	52.2	41.9	70.7	61.9	63.2	62.9	68.6
P ₂ O ₅ (%)	0.25	0.24	0.80	0.10	0.97	0.85	0.03	0.02	0.03	0.04	0.01	0.02	0.03
K ₂ O (%)	1.277	2.168	4.33	7.322	5.73	6.482	5.37	2.1	2.83	1.34	0.7	0.41	0.46
CaO (%)	0.083	0.0679	0.216	0.314	0.258	0.272	0	0	0	0	0	0	0
TiO ₂ (%)	0.0689	0.0536	0.261	0.203	0.219	0.184	0.39	1.62	0.23	0.56	0.16	0.36	0.36

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Table 2 tabulates the concentration of REE in both regions. The concentration of cerium (Ce) is high for both regions. The concentration of Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y and Yb of REE is relatively less than 1 ppm.

Table 2: REE content in samples (ppm) (Hulu Langat & Baling)

Samples									
Regions	Hulu Langat						Baling		
Elements	01A	02A	02B	02C	03B	04A	01A	02A	04B
Ce	2.48501	0.38774	0.3192	0.27849	0.0362	0.0372	3.101	0.435	0.74
Dy	0.32304	0.26614	0.2527	0.24686	0.0032	0.0094	0.135	0.094	0.143
Er	0.33046	0.30145	0.29609	0.29341	0.0017	0.0051	0.05	0.056	0.083
Eu	0.2665	0.26099	0.25999	0.25992	0	0.0002	0.035	0.011	0.023
Gd	0.3433	0.26464	0.24589	0.23576	0.017	0.0322	0.193	0.081	0.147
Ho	0.29427	0.28476	0.28153	0.28114	0.0001	0.0006	0.02	0.017	0.027
La	0.98235	0.45557	0.36541	0.27883	0.0227	0.0366	1.232	0.128	0.27
Lu	0.21156	0.20574	0.20494	0.20491	0.0058	0.0094	0.007	0.01	0.014
Nd	0.84633	0.38223	0.31765	0.23439	0.0008	0.0003	1.317	0.202	0.495
Pr	0.44757	0.29453	0.27084	0.25036	0.0048	0.0088	0.387	0.047	0.113
Sc	0.38806	0.37368	0.50583	0.55693	0.0004	0.0014	0	0	0
Sm	0.41571	0.3052	0.28741	0.27814	0.0172	0.0608	0.295	0.079	0.152
Tb	0.24407	0.23329	0.23114	0.2298	0.0019	0.005	0.027	0.014	0.023
Tm	0.18549	0.18066	0.17988	0.17974	0.0001	0.0009	0.007	0.009	0.014
Y	0.52759	0.3981	0.35086	0.31492	0	0.0003	0	0	0
Yb	0.29126	0.2552	0.24834	0.24843	0.1146	0.215	0.057	0.074	0.102
TREE	8.583	4.850	4.618	4.372	0.227	0.423	6.863	1.257	2.346

Meanwhile, the concentration La and Nd for sample 1A from Baling, Kedah has concentration is higher than 1 ppm. Total REE concentration in sample 2A and 4B from Baling, Kedah has 2.351 ppm and 4.420 ppm. Meanwhile the samples from Hulu Langat have REE concentration of 4.84992 ppm for sample 2A, 4.61771 ppm for sample 2B and 4.37202 ppm for sample 2C. Lastly, 2 samples have the lowest REE concentration which is 0.2265 ppm for sample 3B and 0.4232 for sample 4A. Figure 6 shows the REE pattern in granite samples in both regions. The peak of Ce, La and Nd is the highest. Lu and Tm has the lowest peak. Other REE elements are present in the trace amounts.

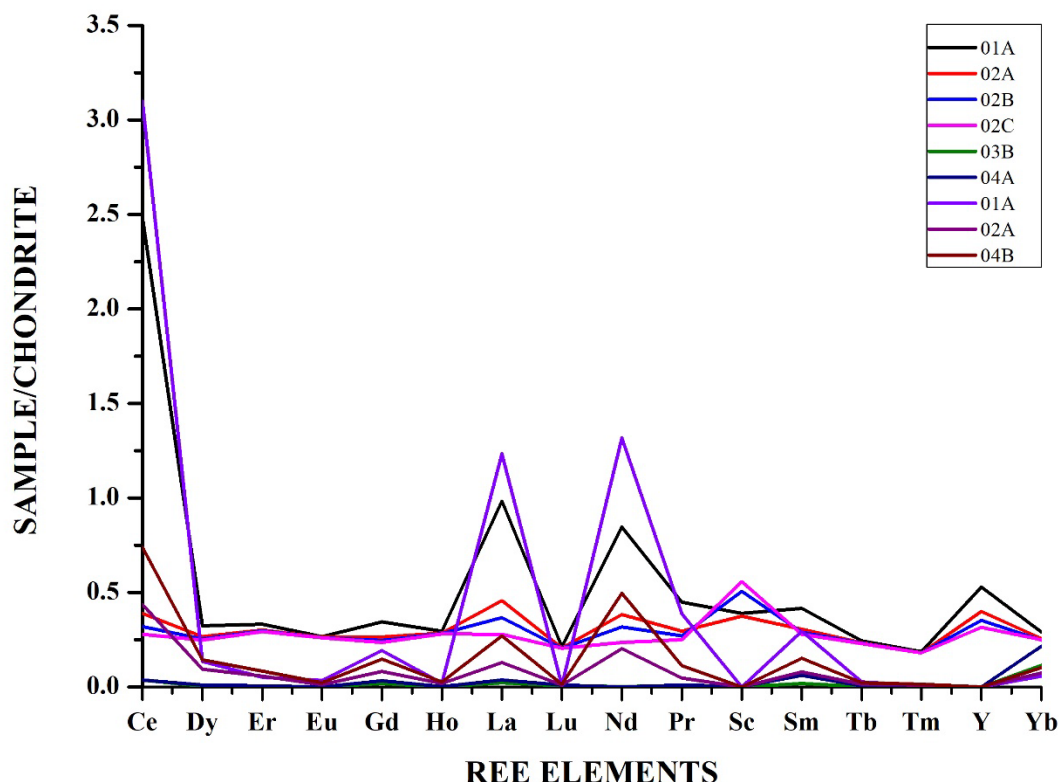


Figure 6: REE Pattern in Granite in Samples
(First 01-04A: Hulu Langat and Second 01A, 02A & 04B Baling)

Conclusions

This paper presented the petrogeochemistry of REE from different regions in Hulu Langat and Baling. As a conclusion, Hulu Langat and Baling study area locates in S-type Main Range Granite. The rock has different chemical composition due to weathering. Thin section images show minerals like quartz, biotite, and mica in rock samples, indicating limited weathering. Chemical analysis reveals the presence of major oxides such as Al_2O_3 , SiO_2 , Na_2O , MgO , K_2O , and others, with SiO_2 indicating clay mineral presence due to weathering. X-ray diffraction phase analysis is utilized to identify minerals such as nacrite, kaolinite, microcline, and muscovite in diverse samples, revealing distinct stages of weathering. These weathering stages have naturally transpired through the influences of wind and water. Hydrolysis, the process of mineral breakdown facilitated by water molecules, plays a significant role in this context. The modification zones exhibit alterations in mineral composition attributed to

fluctuations in both temperature and pH levels within the fluid. Some samples contain rare earth elements (REEs), with sample 1A from Hulu Langat having the highest concentration of TREE which is 8.583 ppm, followed by sample 1A from Baling has concentration of 6.863 ppm. Sample 3B contains the lowest concentration of REE. The results of the petrogeochemistry indicates that Malaysia have the potential to produce REE by mining. More samples need to be collected and further research needs to be conducted in these regions to prove that REE is mineable in Malaysia.

Acknowledgements

Authors are in debt to the team of the project ‘Petrogeochemistry of Rare Earth Elements (REE) From Main Range Granite Province, Malaysia’ for the logistic and research support. We gratefully acknowledge the School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia for providing the required research facilities and data for this work.

Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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