CHARACTERIZATION OF POTENTIAL WEATHERED REE BEARING GRANITOID FROM HULU LANGAT, MAIN RANGE GRANITE, PENINSULAR MALAYSIA

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Abstract. Rare earth elements (REEs) have become essential minerals in contemporary society, akin to petroleum. Their demand is particularly pronounced in various sectors, notably in electronics and green technology. In Malaysia, the prevalence of granitoid and intrusive volcanic rocks presents an opportunity to fulfil the demand for REEs in industries and among the population. Previous studies suggest that Malaysia's S-type granite is notably enriched in yttrium. Consequently, this study aims to scrutinize the mineralogy of potential ion adsorption clay deposits based on their physical and chemical attributes. The research was conducted in Hulu Langat, Selangor. To accomplish this goal, a meticulously designed flowchart was implemented, delineated into three segments: physical characteristics, mineralogy characteristics, and geochemical characteristics. Various methodologies were applied, encompassing the use of a polarizing microscope, X-ray diffraction (XRD), X-ray fluorescence (XRF), and inductive coupled plasma mass spectrometer (ICP-MS). The coexistence of granite and ion adsorption clay, with the latter formed through the physical and chemical weathering of granite. Most samples exhibit coarse-grained, deformable clay, with notable exceptions like kaolinite and hard, orange-hued granite. Microscopic observations detail the presence of biotite, quartz, and chlorite, indicating oxidation processes in weathered granite. X-ray diffractogram results highlight the prevalence of quartz as a key mineral indicator. The major oxide content analysis reveals fluctuating concentrations, with SiO_2 being the highest at a range of 20.1% to 24.7%. Rare earth elements (REE) present diverse patterns: Scandium (Sc) ranges from 36.28 ppm to 52.383 ppm, Yttrium (Y) maintains a consistent range of 5.215 ppm to 6.007 ppm, while other elements exhibit varying concentrations.

Keywords: Rare earth elements (REEs), weathered granite, main-range granite

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1. INTRODUCTION

Rare earth elements (REEs), a group of metals with unique properties essential for modern technologies, are more common in nature than many nonferrous metals and are typically found in various compounds [1]. The global demand for REEs is on the rise, driven by the needs of various sectors, including emerging economies, green technology, and research & development initiatives [2]. According to [3], the most common REE mineral deposit types are carbonates, alkaline/peralkaline igneous rocks, placers, and ion adsorption clays, with froth flotation being the as separation technique. These elements can be incorporated into common minerals like hematite and magnetite, with REEs preferentially incorporated into the magnetite structure [4]. China's dominance in the REEs market has prompted a global exploration boom for alternative sources [5]. This is due to the strategic importance of REEs in advanced technology and the potential for supply disruptions [6]. However, the environmental and social impacts of REE mining must be addressed, and strategies for sustainable production and recycling are needed [7].

According to [8], both identified high potential for REEs in granitoid rocks in Gua Musang, Kelantan, with the latter also noting the presence of light and heavy REEs. Research on rare earth elements (REEs) in granite rocks in Peninsular Malaysia, including Hulu Langat, Selangor, has shown varying concentrations and distributions of these elements [9]. According to [10] further highlighted the high REE abundance in A-type Unggan Granite in West Sumatra, suggesting the potential for similar findings in Peninsular Malaysia. Collectively, these studies suggest that rare earth REEs are present in granite rocks in Hulu Langat, Selangor. Further investigation is necessary to ascertain the precise concentrations and distributions of these elements.

Hulu Langat, Selangor, falls within the Main Range Granite region, presenting a potential for REE deposits in Peninsular Malaysia. Regrettably, there has been a relatively limited amount of research conducted in this area, especially concerning REE exploration. This paper highlighted the mineralogy and geochemical characteristics of the Hulu Langat sample which possibly contains significant amounts of REE which considered to be exploited in future.

2. MATERIALS AND METHODS

Sampling was carried out in Hulu Langat, and 11 collected samples were labelled as HHL01A, HHL01B, HHL01C, HHL01D, HHL01E, HHL01F, HHL01G, HHL02A, HHL02B, HHL02C, and HHL02D. The samples were then pulverized to attain a size of less than 75 microns. To verify the appropriateness of the particle size for subsequent analysis, an ASTM sieve with a 75-micron size was employed. In the lab preparation, the samples were cut using a cutter blade machine and a trim machine to produce a smooth cut for polishing and thin-section preparation. The epoxy resin and hardener were mixed homogeneously and poured into a mounting mold containing a sample. Samples marked as 1A and 2A were impregnated for thin-section preparation to ensure they would not easily break. The rock section was stuck to a glass slide with a strong adhesive. The excess part of the section was cut off using a Petro Thin Machine. Finally, the sample was polished by hand with 600-grit silicon carbide powder abrasive paper. The thin-section samples were observed using a polarizing microscope XOPTRON X80 POL. ICP-MS is used for analysis of the elements.

2.1 Location of Study

Hulu Langat lies in Western Belt Main Range Granite, Peninsular Malaysia (Figure 1). The geological formation in this area is believed to have formed during the Late Triassic to Early Jurassic periods, making it several million years old. The exact processes that led to its formation involve the intrusion of molten magma into the Earth's crust, followed by cooling and solidification [11].

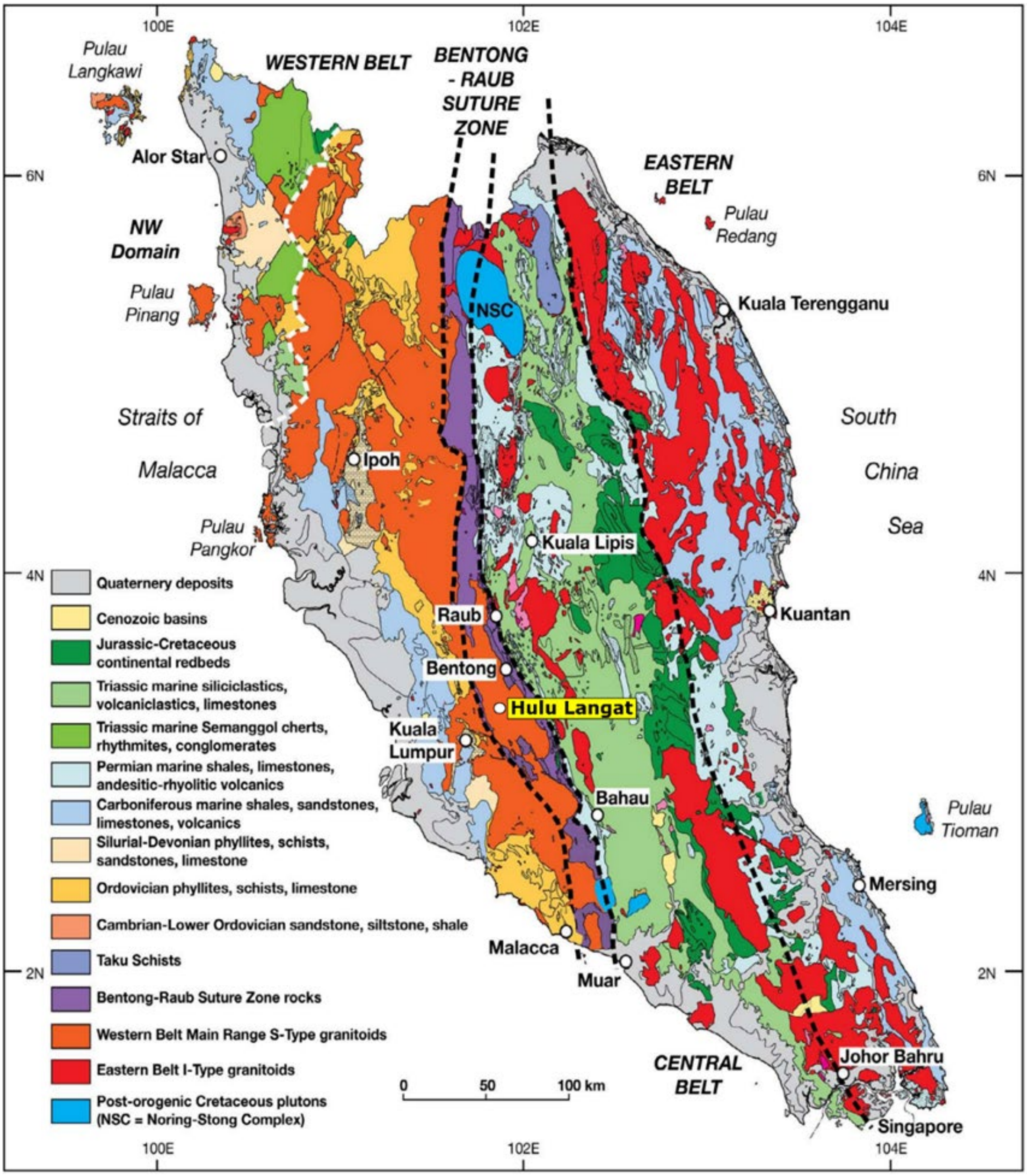

Figure 1: A simplified geological map of the Malaysian Peninsula, modified from Metcalfe (2000), indicates Hulu Langat as the research location with a yellow rectangular marker

3. RESULTS AND DISCUSSION

3.1 Physical Characteristics and Visual Assessment

The visual characteristics presented in Table 1 indicate that the sample comprises ion adsorption clay. These samples are affected by the combined presence of rare earth elements, clay, and humic acid in the weathering crust of granite. The transformation of granite into clay is also influenced by climatic and topographic factors, resulting in the sequential distribution of clays in conjunction with weathering products.

Most of the samples consist of coarse-grained weathered granite in various shades of brown and reddish-brown, all displaying deformability under strong hand pressure. Notably, one sample, HHL01D, is identified as kaolinite, characterized by plasticity and a pinkish to yellowish-gray color. Additionally, there is a granite sample (HHL02B) described as hard, grey to white-grey, with a slightly orange hue, and breakable by a hammer. These observations provide valuable insights into the diverse geological features present, encompassing different types of clay, a distinctive kaolinite specimen, and the presence of hard granite in the sampled areas.

Table 1: Collected studied sample from Hulu Langat, Selangor.

Sample Code	Description	Samples
HHL01A	Weathered coarse-grained, reddish brown, material can be deformed by strong hand pressure	
HHL01B	Coarse-grained, khaki to yellowish-brown, material can be deformed by strong hand pressure	
HHL01C	Coarse-grained, reddish brown, material can be deformed by strong hand pressure	
HHL01D	Kaolinite, plasticity, fine grained, pinkish to yellowish-gray, material can be deformed by strong hand pressure	

Sample Code	Description	Samples
HHL01E	Coarse-grained, reddish brown, material can be deformed by strong hand pressure	
HHL01F	Coarse-grained, strong reddish brown, material can be deformed by strong hand pressure	
HHL01G	Coarse-grained, brownish-gray, material can be deformed by strong hand pressure	
HHL02A	Coarse-grained, reddish brown, material can be deformed by strong hand pressure	
HHL02B	Granite is hard, ranging in color from grey to white grey with hints of orange, and can be broken by a hammer.	
HHL02C	Coarse-grained, reddish brown, material can be deformed by strong hand pressure	
HHL02D	Coarse-grained, reddish to yellowish-brown, can be deformed by strong hand pressure	

3.2 Petrology and Mineralogical Study

The thin section of the selected rocks was examined under a polarizing microscope, revealing plain polarized light (PPL) images and cross-polarized light (XPL) images. In Figures 2 and 3, only biotite and quartz are visible under PPL, while the presence of chlorite is evident under XPL. Chlorite, a green, iron-rich mineral, often forms during the weathering and oxidation of primary minerals in granite, such as biotite and amphibole. Weathering processes break down these primary minerals, releasing elements like iron and magnesium, which contribute to chlorite formation [12]. Typically, in weathered granite, chlorite may be present as a secondary mineral, often occurring as small flakes or aggregates. The presence of chlorite in weathered granite can indicate the oxidation processes that have occurred over time, transforming the original minerals in the granite into new mineral assemblages. This is significant because quartz typically occurs as large crystals in granite and contributes to the rock's overall appearance and durability. The mineralogy of weathered granite can vary depending on factors such as climate, local geology, and the specific minerals present in the original granite.

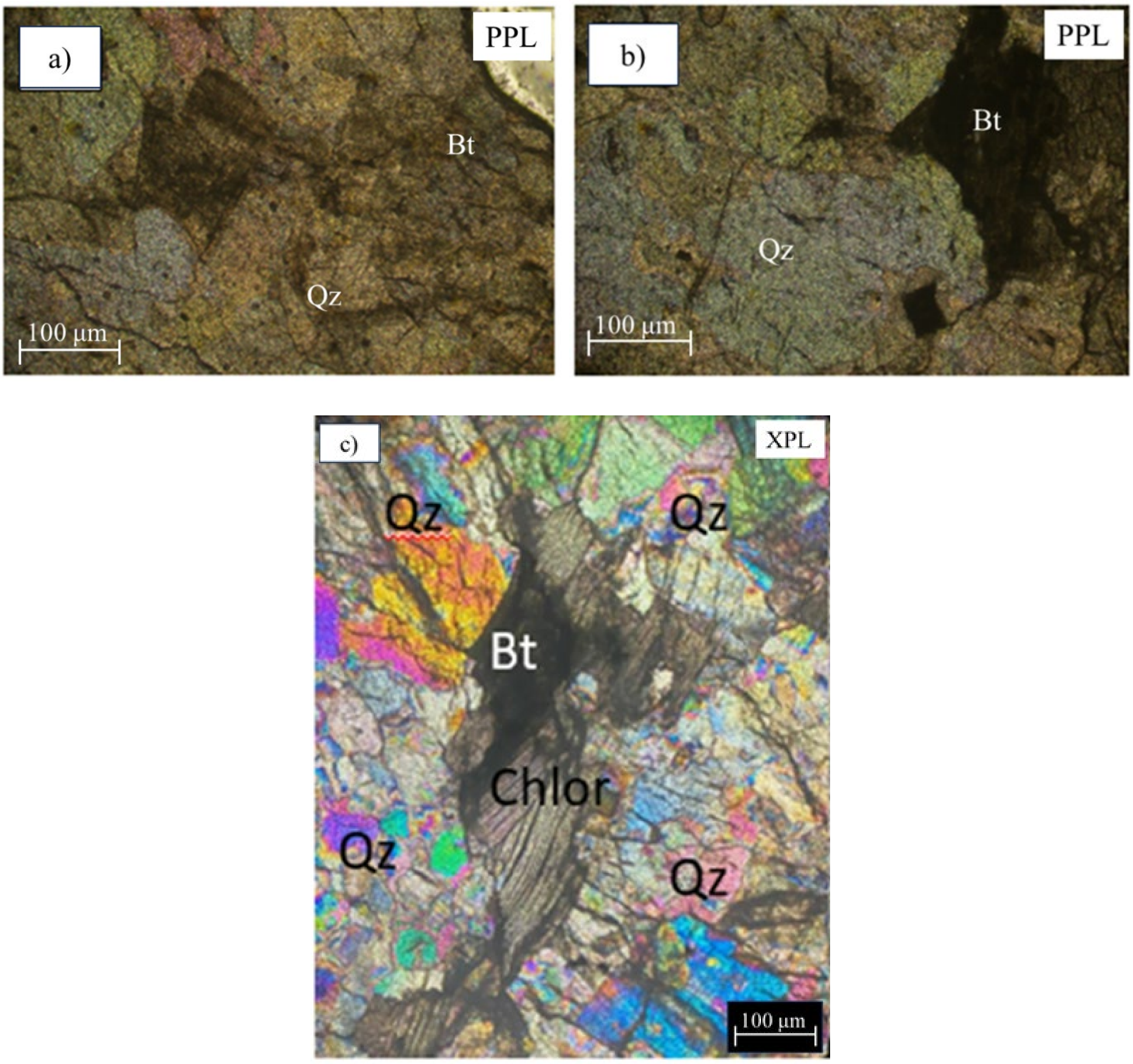

Figure 2: Microscopic view of sample 1A from Hulu Langat, Selangor.
Abbreviations: XPL = Cross Polarized Light, PPL = Plane Polarized Light, Qz = Quartz, Bt = Biotite and Chlor = Chlorite.

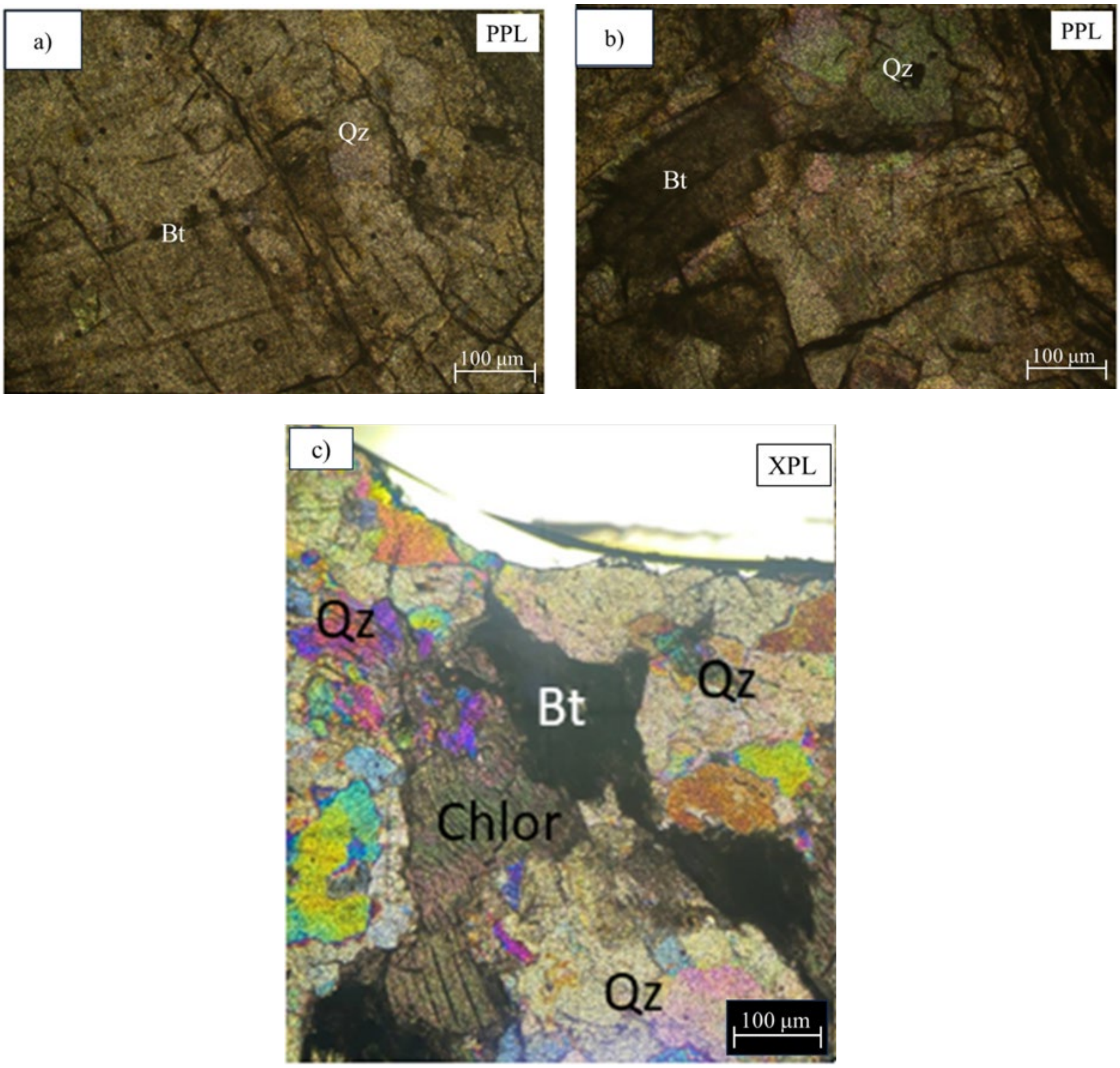

Figure 3: Microscopic view of sample 2A from Hulu Langat, Selangor.
Abbreviations: XPL = Cross Polarized Light, PPL = Plane Polarized Light, Qz = Quartz, Bt = Biotite, and Chlor = Chlorite.

3.3 Phase Analysis using X-Ray Diffraction (XRD)

The x-ray diffractogram in Figure 4 displays the results for the 11 analyzed samples. The peak corresponding to quartz is the most prominent across all samples. In XRD analysis, the quartz peak serves as a crucial indicator of the mineral composition in rocks, including weathered granite.

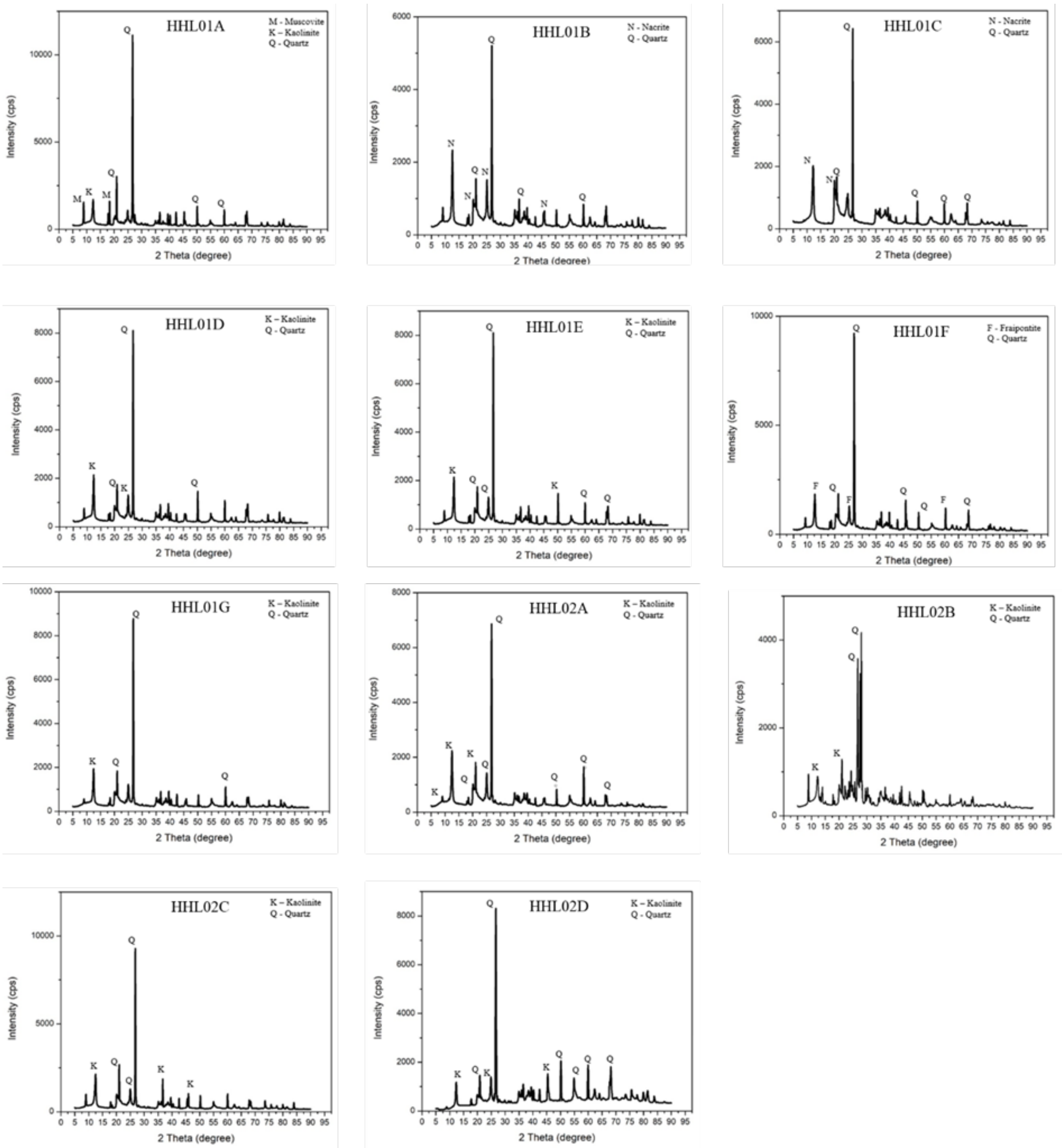

Figure 4: X-ray diffractogram of Samples from Hulu Langat

Quartz is a versatile mineral found in various geological settings, including both ion adsorption clay and weathered granite. Ion adsorption clays are often composed of a variety of minerals, and quartz is one of the common components [13]. In granite, quartz is a major constituent. Granite is a felsic igneous rock primarily composed of quartz, feldspar, and mica. Sample HHl01A is the only sample that contains muscovite. Muscovite is a mineral that belongs to the mica group of sheet silicates. It is a common rock-forming mineral found in felsic igneous rocks, pegmatites, and metamorphic rocks. In granite, muscovite often occurs in the form of large-sized crystals that have a pseudo-hexagonal structure.

Other samples have shown peaks in kaolinite and nacrite. Kaolinite and nacrite are minerals present in both clay and weathered granite. Kaolinite, a clay mineral, results from the weathering of aluminum-rich silicate minerals like feldspars, which is a primary mineral in granite. Nacrite, classified as a kaolinite polymorph, shares the same chemical composition as kaolinite but exhibits a distinct crystal structure [14]. In the weathering process of granite, feldspar breaks down into kaolinite through chemical and physical processes. Kaolinite is a clay mineral and is one of the primary components of kaolin clay. It tends to be white or light in colour.

Moreover, three peaks have shown fraipontite appeared in sample HHL01F. Fraipontite is not typically associated with weathered granite, but it can be found in clay-rich environments. Fraipontite is a member of the zeolite group and is often associated with hydrothermal oxidation in metamorphic rocks or as secondary minerals in sedimentary rocks. In the context of clay, fraipontite is not a widely recognized component. Clay minerals typically include groups like kaolinite, montmorillonite, and illite.

3.4 X-Ray Fluorescence Study

Table 2 shows the major oxide content in the eleven analysed samples.

Table 2: Major Oxide Content in sample

Sample	01A	01B	01C	01D	01E	01F	01G	02A	02B	02C	02D
Rock Type	Weathered Granite/ Ion Adpsorption Clay										
SiO_2 (%)	58.00	57.00	57.00	60.00	58.00	56.00	57.00	57.00	58.00	59.00	58.00
TiO_2(%)	0.07	0.06	0.06	0.03	0.05	0.06	0.07	0.06	0.05	0.04	0.04
Al_2O_3 (%)	24.30	20.10	22.30	20.40	21.40	22.30	20.70	20.70	24.70	22.90	23.90
Fe_2O_3 (%)	0.54	0.82	0.73	0.08	0.65	0.67	0.78	0.79	0.60	0.52	0.58
MgO (%)	1.40	1.60	1.30	1.30	1.70	1.60	1.50	1.60	1.50	1.50	1.30
MnO (%)	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.03	0.01	0.01
CaO (%)	0.06	0.06	0.06	0.05	0.06	0.06	0.06	0.55	0.10	0.05	0.05
Na_2O (%)	3.30	3.90	4.50	2.30	4.60	1.60	3.90	2.90	4.50	1.50	3.70
K_2O (%)	0.90	0.50	0.64	0.13	0.49	0.49	0.50	0.48	1.33	0.43	0.49
P_2O_5 (%)	0.23	0.24	0.24	0.23	0.24	0.24	0.24	0.24	0.24	0.23	0.23

The SiO_2 is the highest concentration in all the samples. Silicon dioxide (SiO_2) is a major component of quartz, which is commonly found in granitic rocks [15]. SiO_2 content ranges from approximately 57% to 60%. TiO_2 content ranges from approximately 0.03% to

0.07%. Al_2O_3 content ranges from approximately 20.10% to 24.70%. Fe_2O_3 content ranges from approximately 0.08% to 0.79%. Higher values of Fe_2O_3 might indicate increased weathering or oxidation processes, where iron-containing minerals in the original granite are breaking down. High iron content may contribute to a reddish or brownish color. The varying colors in the samples can provide visual clues about mineralogy and oxidation history. MgO content ranges from approximately 1.30% to 1.70%. Magnesium oxide and magnesium are commonly found in minerals such as olivine and certain micas. The variations in MgO content can provide insights into the mineralogy differences between samples. MnO content in the provided samples suggests that manganese is present as a minor component. MnO content in the provided samples suggests that manganese is present as a minor component. CaO content is generally low, ranging from 0.05% to 0.1%. Calcium may be associated with clay minerals or other secondary minerals. Na_2O content in samples ranging from 1.50% to 4.60%. It is commonly associated with minerals like feldspar, which is present in both granite and clay. K_2O content in samples ranging from 0.13% to 1.33%. Potassium is commonly associated with minerals like orthoclase feldspar and mica. Samples show consistent P_2O_5 content, ranging from 0.23% to 0.24%. Phosphorus is a minor component in many rocks and soils. Its retention may be influenced by the specific mineralogical changes occurring during weathering. Figure 5 illustrates the degree of chemical weathering experienced by the 11 samples collected in Hulu Langat.

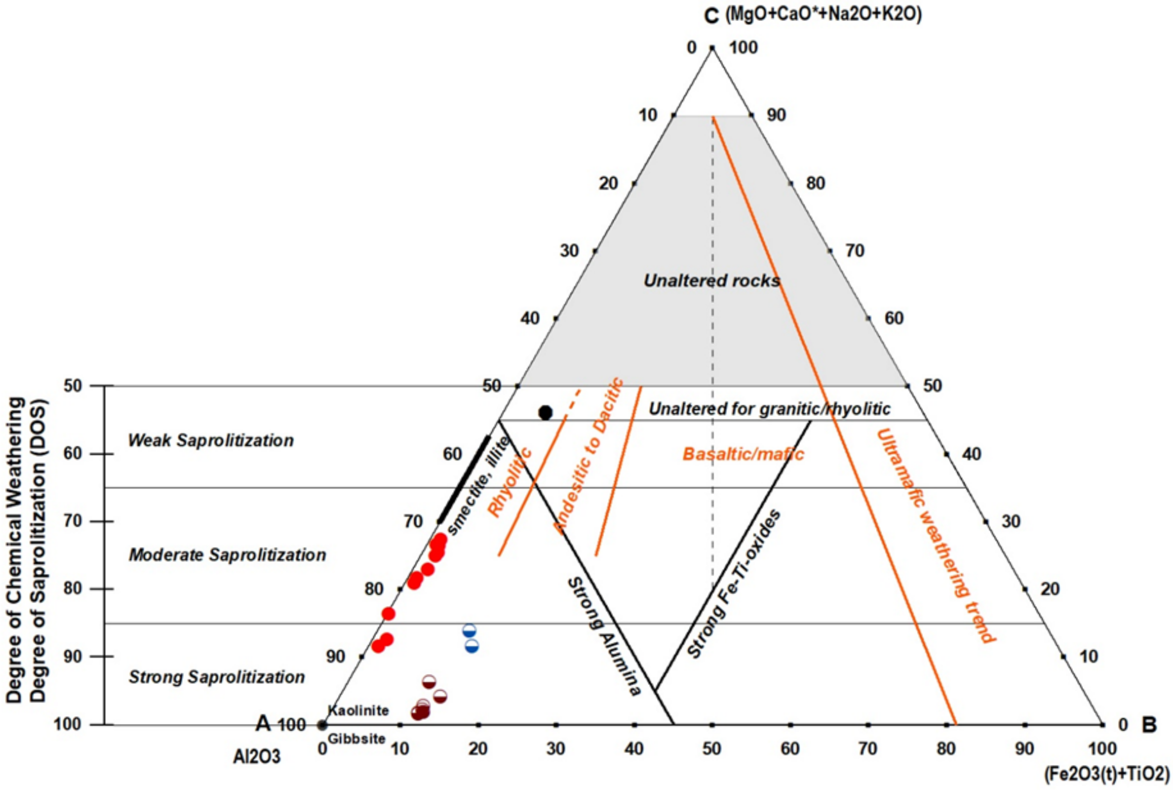

Figure 5: Ternary Degree of Saprolitization (DOS) diagram of studied sample from Hulu Langat, Selangor.

The red dots denote samples in Hulu Langat that have undergone chemical oxidation, as indicated by the XRF data. The soil in Hulu Langat has undergone moderate saprolitization, initially manifesting as ion adsorption clay [16]. XRD data confirms the presence of kaolinite in the samples.

3.5 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Table 3 shows the concentrations of REE resulted from ICP-MS analyses. The concentrations of rare earth elements (REE) across the samples exhibit diverse patterns and trends. Scandium (Sc) demonstrates a notable range from 36.28 ppm to 52.383 ppm, showcasing a peak at HHL01G. Yttrium (Y) maintains a relatively narrow range from 5.215 ppm to 6.007 ppm, indicating consistent concentrations. Lanthanum (La) concentrations vary from 3.552 ppm to 4.512 ppm, with a peak in HHL01G. Gadolinium (Gd) concentrations vary from 1.963 ppm to 2.576 ppm. Overall, the ranges in concentrations highlight the diverse geological influences and mineral compositions across the samples, offering valuable insights into the complex processes shaping these formations [17].

Table 3: REE content (ppm) in samples

No	Element		Samples				
	Analyte	Symbol	HHL01B	HHL01C	HHL01F	HHL01G	HHL02A
1	Scandium	Sc	39.353	41.618	46.971	52.383	36.282
2	Yttrium	Y	6.007	5.464	5.305	5.215	5.675
3	Lanthanum	La	4.512	4.011	3.654	3.552	3.944
4	Cerium	Ce	5.092	5.952	4.842	5.659	4.521
5	Praseodymium	Pr	4.020	3.494	3.371	3.235	3.658
6	Neodymium	Nd	3.420	3.051	2.815	2.762	3.029
7	Samarium	Sm	4.529	4.099	3.972	3.853	4.288
8	Europium	Eu	4.303	3.840	3.764	3.637	4.063
9	Gadolinium	Gd	2.576	2.115	2.042	1.963	2.228
10	Terbium	Tb	4.326	3.896	3.813	3.697	4.112
11	Dysprosium	Dy	4.337	3.961	3.864	3.764	4.155
12	Holmium	Ho	4.151	3.779	3.699	3.595	3.981
13	Erbium	Er	4.237	3.901	3.811	3.719	4.093
14	Thulium	Tm	3.940	3.629	3.549	3.459	3.817
15	Ytterbium	Yb	3.856	3.591	3.501	3.435	3.750
16	Lutetium	Lu	3.665	3.388	3.312	3.231	3.557
	ΣREE		102.320	99.790	102.290	107.160	95.150
	ΣLREE		73.810	73.640	76.740	82.260	67.690
	ΣHREE		28.510	26.150	25.550	24.900	27.470

The chondrite-normalized rare earth element (REE) patterns of the weathered crust and related syenogranite from Sc show enrichment, primarily in light rare earth elements (LREE), as depicted in Figure 6. The term Large Ion Lithophile Element (LILE) and High Field Strength Elements (HFSE) is used to determine type of REE. Normalized to chondrite, the REE patterns reveal that the parent granitic rock in the Hulu Langat site is more enriched in LREE than in heavy rare earth elements (HREE), exhibiting a pronounced negative Y anomaly. Additionally, there are negative anomalies observed in Nd, Ce, Gd, Dy, Er, and Yb.

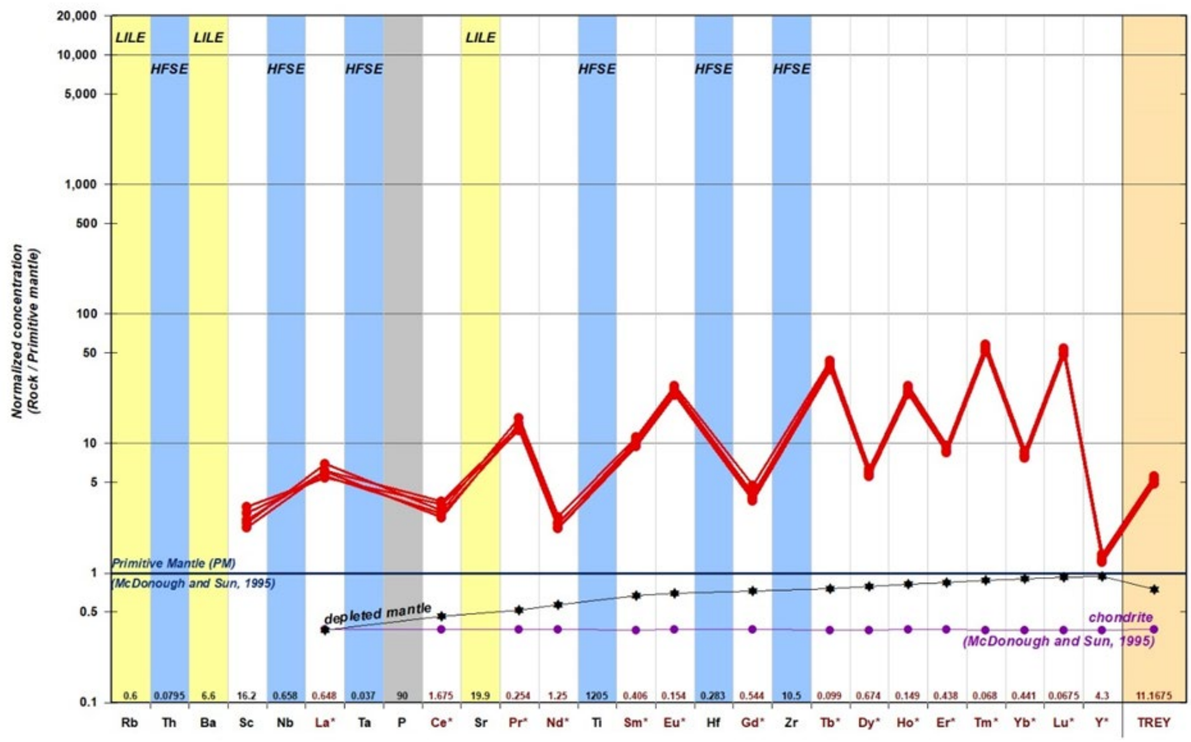

Figure 6: Chondrite-normalized REE diagram of weathered crust of granite and related parent rock from Hulu Langat (values of chondrite are from (Sun and McDonoughan, 1995))

4. CONCLUSIONS

In conclusion, the formation of ion adsorption clay results from both physical and chemical weathering processes acting upon the parent rock, which is granite. This weathering phenomenon is closely tied to the interplay of rare earth elements, clay, and humic acid within the weathering crust of granites. The distribution of ion adsorption clays in conjunction with weathering products is influenced by various climatic and topographic factors. Most of the samples exhibit coarse-grained in a range of shades, displaying deformability under strong hand pressure. Notably, sample HHL01D is identified as kaolinite, characterized by its brittleness and pinkish to yellowish-gray coloration. Furthermore, granite sample HHL02B is described as hard, with hues ranging from grey to white-grey, and breakable by a hammer. These observations offer valuable insights into the diverse geological features present, including different types of clay, a distinctive kaolinite specimen, and the presence of hard granite within the sampled areas. Thin section observations under a polarizing microscope reveal the presence of biotite, quartz, and chlorite in certain samples. Chlorite, being a green, iron-rich mineral, is discussed within the context of weathered granite, suggesting oxidation processes occurring over time. The x-ray diffractogram results for the 11 samples emphasize the quartz peak as a crucial indicator of mineral content in rocks such as granite and clay. Furthermore, the analysis of major oxide content highlights varying concentrations, with SiO_2 being the most abundant element (ranging from 20.1% to 24.7%). These variations in oxide contents provide insights into mineralogical differences, weathering processes, and potential associations with specific minerals. Rare earth elements (REE) exhibit diverse patterns; for instance, Scandium (Sc) ranges from 36.28 ppm to 52.383

ppm, while Yttrium (Y) maintains consistency between 5.215 ppm and 6.007 ppm. Other elements show fluctuating concentrations, contributing to the complexity of the geological system under study.

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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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