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Mineralogy and Geochemistry of Clay in Sokor and Jeli, Kelantan.

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Abstract. Clay is considered as fine-grained, natural and earthy argillaceous material which are widely distributed in sediments as the products of sedimentation and diagenesis. The sample of rocks and clay soil from Sokor and several areas in Jeli, Kelantan have been analysed for geochemical and mineralogical properties. For geochemical analysis, the concentration of major elements was analysed using X-Ray Diffraction Fluorescene (XRF) and X-Ray Diffraction (XRD) Spectroscopy in order to validate the clay mineral existence. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) also was used for trace element determination while the Scanning Electron Microscopy (SEM) were used to study the mineralogy of clay as well as petrography. From mineralogy and petrography studies using optical microscope and Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) analysis show that the mineral distribution in the sample from both Sokor and Jeli area dominantly by quartz, biotite and K-feldspar mineral. It is supported by XRD analysis which showing the prominent peaks of quartz on 27Å and kaolinite on 12Å from the graph is easily identified. Chondrite normalise pattern is generated from ICP-MS result to constrain rare earth element (REE) behaviour and geochemical information. The normalised fractionation trends recorded below than usual REE deposition. This is because there is no mineral association of REE such as apatite and titanite found from the sample.

1. Introduction

Clay is an abundant raw material available in the earth crust and a common component in thesedimentary rocks especially in shale and silts. Clay has a wide range of uses and properties that are determined by the mineral structure and composition. It plays as the most important industrial mineral [1]. Because of its properties, clay have been used widely in agriculture, ceramics industrial, paper cosmetics and many more.

Depositional of clay minerals can be either primary and secondary deposition. These minerals can be synthesizing by products of weathering, erosion and diagenesis. Illite and chlorite are example of clay minerals that deposited from weathering product of igneous and metamorphic rocks and kaolinite is the product from chemical weathering of feldspar in tropical area [2]. In terms of geochemistry, clay minerals are divided into few groups such as kaolinite group, pyrophyllite group and chlorite group. Each group of the mineral have different structure of minerals. Clay characteristic also knownas a material that have a great affinity to water that led them to have an electrically forces is bonded to the surface of clay particle that resulted from the thin film of water around the surface of the particle [3]. The electricity forces from the surface allows the clay minerals to have ability in ion exchange

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capacity. Clay minerals have the ability to absorb or desorb ion [4]. The total capacity of a soil to hold exchangeable cations is known as cation exchange capacity (CEC) where the soil's ability to hold positively charged ions is measured. Clay fraction of soils, crystallinity and rheology of clay mineral affected CEC values [5].

This research provides knowledge on the characteristics of clay minerals in Jeli and Sokor. Morphology and structure of clay minerals were analysed under Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) analysis. SEM-EDS analysis along with petrography analysis shows the presence of clay mineral which is quartz, K-feldspar, biotite and albite mineral. Result from X-Ray Diffraction (XRD) is validate the existence of clay mineral in the sample. Geochemical study also provides information for the trace element deposition in clay. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to determine the REE concentration in the samples.

2. Location and geological setting

The geological setting of Kelantan is located in three major belts which are Western Belt (Main Range), Central Belt (between Main Range and Lebir Fault) and Eastern Belt (east of Lebir Fault).The age of granites is varied from Cretaceous (Noring, Kenerong) to Late Triassic (Kemahang, Berangkat, Senting, Main Range, Boundary Range) which mainly consists of acidic intrusive igneous rock [6].

Figure 1: Location of research area

Jeli and Sokor, Tanah Merah is located in western part of Kelantan and at the foot of Main Range which is the backbone of Peninsular Malaysia. This main range consist of granitic rocks, sedimentary and metasedimentary rocks. These three types of rocks originated from different formation which are Gunong Rabong Formation which consist of shale, siltstone, sandstone, and limestone. Then, Gua Musang Formation consists of phyllite, slate, sandstone and limestone and also granitic rocks that consist of acid intrusive rocks [7].

Sokor, Tanah Merah is quite well known for the gold deposition and this area is dominantly of Taku Schist Formation and Kemahang Granite [6,8]. Taku Schist is recognized as a product of hydrothermal or regional metamorphism due to its extensive body of predominantly pelitic schist. According to [8], the lithology of Taku Schist Formation is predominantly by metamorphic rocks. The main composition of Taku Schist Formation is mica schist which comprised of quartz-mica schist, mica-garnet schist and quartz-mica-garnet schist. Other rocks that can be found in this formation are amphibolite schist, quartz schist, and carbonate schist. The location of the study area is marked on map in Figure 1.

3. Methodology

3.1. Mapping and Sampling
Mapping and sampling were conducted around selected area in Jeli and Sokor, Kelantan. Target sampling is based on the preliminary study on the literature review and geological study of the study area. The target sampling point are marked by GPS reading for the positioning and mapping purposes. Sample of clay (approximately 500-1000 g of soil) is collected by using hand auger. Rock specimen are also collected for further analysis. Ten samples have been used for geochemical analysis which 5 from Sokor (SK1, SK2, SK3, SK4 and SK5) 1 from Batu Melintang, Jeli (BT5) and 4 from Sg. Pergau, Jeli (BT1, BT2, BT3 and BT4).

3.2. Sample characterization and Petrographic analysis
Rock samples were sent to the laboratory in Universiti Sains Malaysia (USM) for the preparation of thin section samples for further mineralogical and petrographic studies. It is important to correlate mineral structure with the results of chemical analyses. The Scanning Electron Microscope (SEM) (Jeol JSM-IT100 SEM) and optical microscopy are used for investigating the mineral morphology and grain size evaluation of the samples. SEM imaging is used to characterize mineral association and significant textures for mineralogical relationships. Aside from identifying main mineral associationsin the sample, the petrographic studies are also significant in characterizing clay mineral types such as kaolinite, halloysite and etc. As the particle size of clay is small, thus the application of SEM is preferred for clay samples, in addition to measure the element composition using EDS.

3.3. X-Ray Diffraction (XRD) and X-Ray Diffraction Fluorescene (XRF) analysis
Mineral identification was analysed using X-Ray Diffraction (XRD), Bruker Benchtop XDR D2 Phaser and major elements have been identified by X-Ray Diffraction Fluoresence (XRF) analysis. Itis important to see the variation in element composition for each sample especially for mineral identification and geology correlation. The soil samples are dried, grind and pulverized into powder before pressed in the pellet. The raw data from XRD analysis was synthesized using Microsoft DIFFRAC.EVA Software.

3.4. Inductively Coupled Plasma Micro Spectrometry (ICP-MS) analysis
Inductively Coupled Plasma Microspectrometry (ICP-MS) were used to measure the trace element or Rare Earth Element (REE) in the sample. The advance of electron beam analysis techniques has made the accurate determination of trace elements in minerals with sub-ppb (part per billion) minimum detection limits. ICP-MS is an analytical technique that allows more sensitive detection in determining a wide range of extremely low detection limits of atomic element as low as 1ppq (part per quadrillion).

Soil sample was sieved into 60 µm size and sent to Universiti Sains Malaysia (USM) laboratory for analyses. Before analyzed by iCAP-TQ, Thermo Scientific ICP-MS, the sample underwent a digestion process using UltraWAVE, Milestone digestion machine.

4. Result and Discussion

4.1. Petrographic analysis

Hornblende, quartz, feldspar and olivine are common rock forming mineral that found in granite from Jeli. This granite originated from Stong Complex granite and some of the unit undergoes metamorphism. Anhedral hornblende have been identified scattered on the sample in Figure 2(a) with pleochroism from dark green to pale yellow colour together with K-feldspar in Figure 2(b). K-feldspar mineral with twining from white to gray colour was identified on the granite sample. Hornblende is common amphibolites mineral deposited from crystallization of magmatic rocks while K-feldspar which is a tectosilicates mineral that made up over 50% of the earth crust that easily found in anyrocks type. Some of the granite unit have undergone metamorphism as shown in Figure 2(c) where the arrangement of muscovite, biotite and quartz show the flowy-like arrangement to foliated arrangement. Mica group is a phyllosilicate mineral that found in the resulted crystallization and metamorphism process.

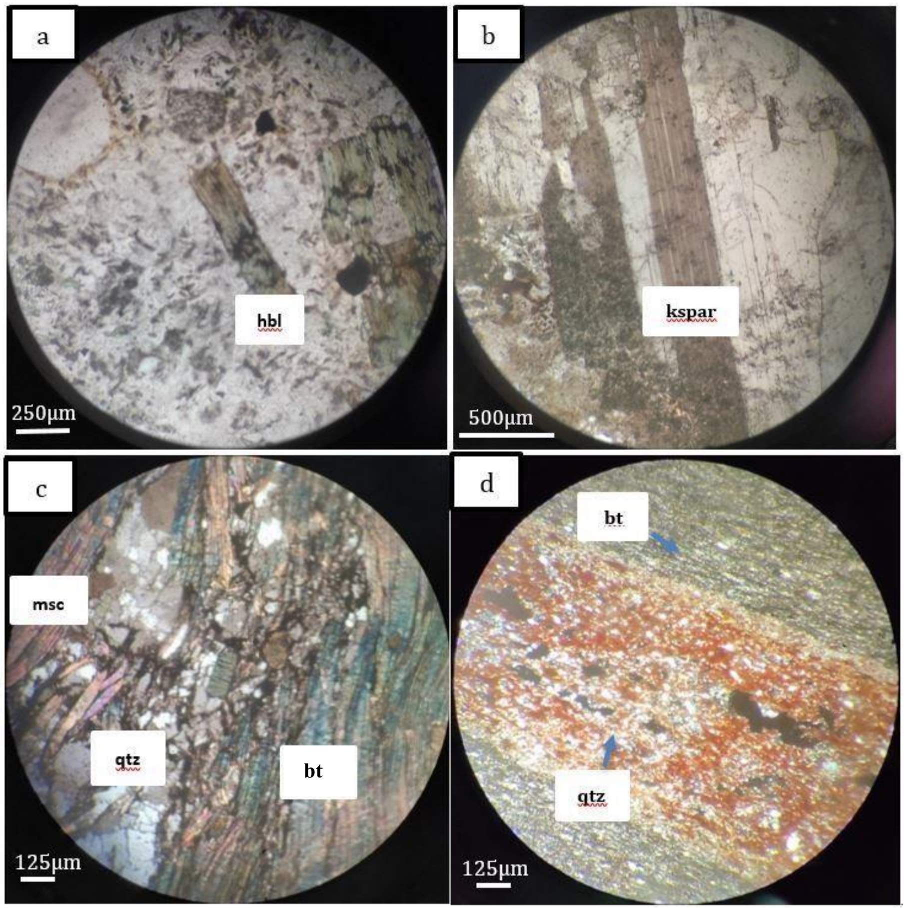


Figure 2: Microscopic analysis (a) hornblende mineral in granite (b) K-feldspar mineral (c)mica,hornblende contact with quartz (d)banded ion sample from Sokor area. [*hbl:hornblende, kspar:K-feldspar, msc:muscovite, qtz:quartz, bt:biotite*]

Reported by [9], part of the Taku Schist is associated with the metamorphism of argillaceous rocks close to the granite margin in Sokor area. Figure 2(d) shows the sample of banded iron from Sokor that is composed of feldspar and iron oxide. Biotite presence in needle-like elongated shape with brown colour. This banded iron reportedly to contain high concentrations of hematite and iron oxide.

4.2. X-Ray Diffraction (XRD) analysis

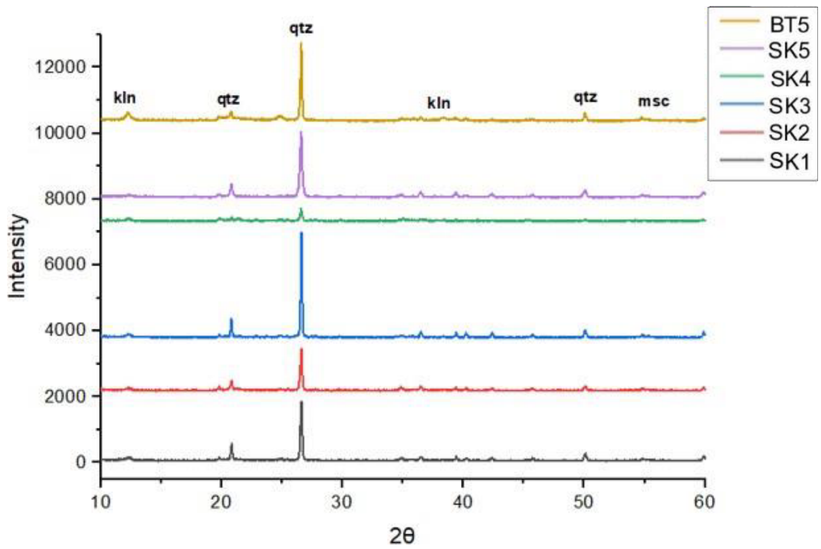
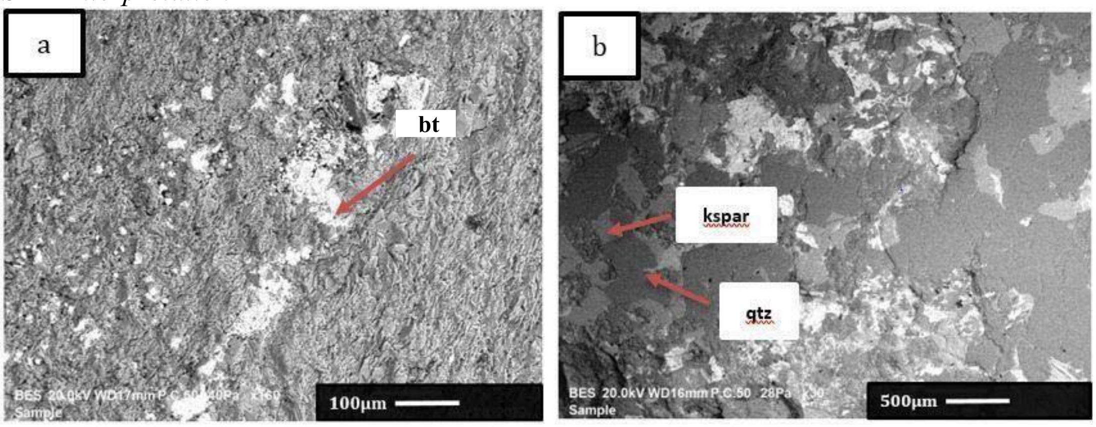


Figure 3: X-Ray Diffraction (XRD) analysis of soil samples from Jeli and Sokor area [*qtz:quartz,kln:kaolinite, msc:muscovite*; *Please note that the intensity scale is just comparison only because the XRD results are combined together*]

From XRD analysis the results show soil sample mineralogy from both Sokor and Jeli mainly dominated by quartz (qtz) and kaolinite (kln). Combination of powder X-Ray Diffraction (XRD) patterns of the samples are shown in Figure 3 as for comparison (by ignoring the intensity). The peaks shown here are from quartz and kaolinite. This is also supported by SEM-EDS analysis which show that the samples mainly contain higher SiO_2 and feldspar group mineral. Muscovite mineral was foundin the sample SK2 that originated from Sokor area and it was supported by [9]. The lithology is composed of chloride biotite muscovite schist that consisted more than 40% muscovite mineral, followed by biotite (20–30%), quartz (10–20%), chlorite (10%), plagioclase (>10%), and K-feldspar (>10%). Prominent peaks for quartz were easily identified at peaks of 27Å while kaolinite at 12Å. According to [10], quartz, K-feldspar and kaolinite are reported as major minerals in clay.

4.3. SEM Interpretation



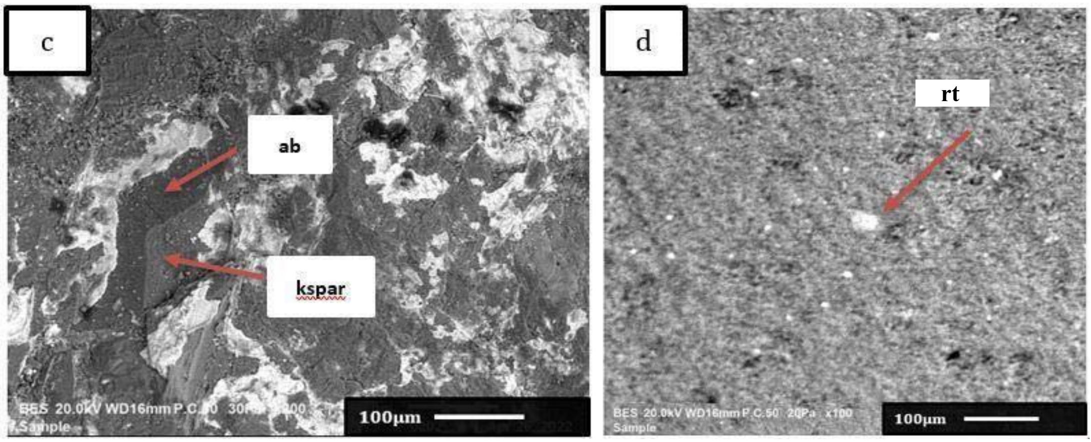


Figure 4: SEM petrography (a) biotite in feldspar domain (b) quartz and K-feldspar on granite from Jeli area (c) albite in detrital K-feldspar surface (d) Particle of rutile (TiO2) mineral in feldspar from sample SK5 (Rutile was confirmed by the spectra from SEM-EDS analysis). [*bt: biotite, qtz:quartz, kspar: K-feldspar, ab: albite, rt: rutile*]

20 kV SEM-EDS analysis along with petrography analysis shows the presence of clay mineral which is quartz, K-feldspar, biotite and albite mineral. Potassium feldspar ($KAlSi_3O_8$) is the major clay species that can be found in Jeli and Sokor area. K-feldspar exists in the microcline, tabular and plate- like crystal grains are in a compact arrangement. The grain size is around 10μm. From EDS analysis it shows that the element that presence are silicon (Si), aluminium (Al), potassium (K) and oxygen (O). In EDS graph, Si and Al element shows the highest peak. K-feldspar mineral found in granite which shown in Figure 4(b) which K-feldspar is in intercalation with quartz (SiO_2) mineral. SEM image of albite showing overgrowths as tiny rhombic crystals partially covering a detrital K-feldspar surface in Figure 4(c). The detrital and authigenic minerals are identified by EDS analysis, which yields the mainelements Si, Al, Na and O. Overgrowths of authigenic K-feldspar on a detrital K-feldspar grain [11]. Laminae of biotite in Figure 4(a) is analysed on banded iron formation sample. Through chemical weathering proses, biotite can be decomposed completely into kaolinite.

Rutile (TiO_2) mineral has been identified in sample SK5 as shown in Figure 4(d). This sample represent Sokor area that have lithology of banded iron formation. Based on SEM-EDS analysis this mineral has 60% of titanium (Ti) element. Rutile is an accessory mineral that come from detrital of ilmenite. This mineral has reddish brown colour, hard, metallic and often surrounded by other minerals and common to be found in detrital deposits.

4.4. Major element analysis
Table 1 shows the concentration of major element on the bulk soil sample of Jeli and Sokor. The concentration of silicon (Si), potassium (K) and aluminium (Al) are reported high while iron (Fe), calcium (Ca) and titanium (Ti) are low. This is harmonious with the mineralogy analysis that showed the presence of quartz, K-feldspar, albite, biotite and kaolinite. These samples composed of SiO_2 in the range of 50 to 60 wt%, followed by Al_2O_3 (averagely around 10 wt.%), Fe_2O and K_2O. High concentration of potassium (K) in Jeli area than Sokor is supported by the findings of granite in Jeli area that composed dominantly by feldspar minerals.

Table 1: Major element composition (wt.%) of soil sample from Batu Melintang and Sokor

Area	Sample	Element composition(wt.%) in oxide					
		SiO_2	Al_2O_3	K_2O	Fe_2O_3	TiO_2	CaO
BATU MELINTANG	BT1	56.30	11.40	18.00	9.15	1.12	1.20
	BT2	57.20	11.90	20.00	7.50	1.14	0.55
	BT3	63.30	6.95	24.30	1.79	0.352	1.61
	BT4	53.90	16.20	14.60	BDL	1.30	1.33
	BT5	57.30	6.91	2.36	30.37	0.73	0.53
SOKOR	SK1	61.29	9.54	3.44	18.36	5.00	0.85
	SK2	54.04	2.82	0.86	3.31	0.25	0.22
	SK3	51.37	18.81	6.41	21.55	0.61	0.92
	SK4	37.99	21.20	3.40	15.02	0.10	0.21
	SK5	52.35	9.64	3.66	3.22	0.21	0.50

4.5. Trace element and REE analysis

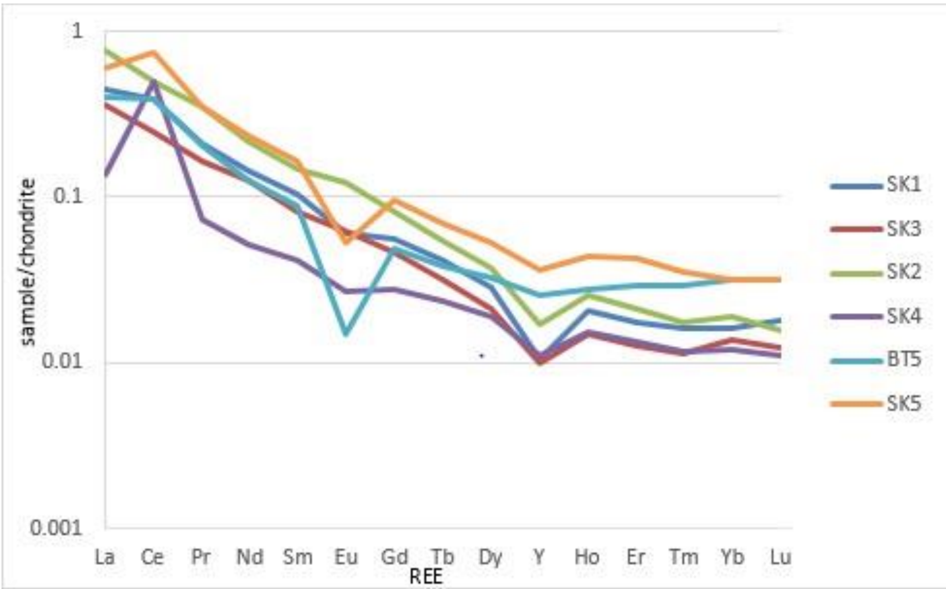


Figure 5: Chondrite Normalized pattern of selected samples from Sokor and Jeli, Kelantan.

All six samples of soil were selected for ICP-MS analysis to measure the concentration of rare earth element (REE) and the data is presented in Figure 5. The normalisation factor follows McDonough and Sun [12]. The pattern shows negative Ce anomaly for all sample where (Ce/Ce*≤1). Similar chondrite pattern was observed from the samples except for the sample from SK4 and SK5 which shows slightly high in Ce concentration. Both SK4 and SK5 are samples from Sokor, Kelantan. The fractionation trend of the sample is below 1 which is lower than usual deposit. This is because the sample is randomly picked and there is no existence of common accessory minerals that can carryREE together with them such as titanite and apatite. However, the existence of a tiny particle of rutile mineral (TiO_2) mineral in sample SK5 does not contribute to the total REE concentration. Structure of rutile mineral can carry rare earth elements as doping in their elemental structure [13].

5. Conclusion

Petrographic analysis shows that the lithology dominated in Jeli and Sokor are composed of granite and metasedimentary rocks. Mineral distribution mainly composed of quartz, K-feldspar, hornblende and mica. It was supported by XRD analysis with the existence of clay and others minerals peaksbased on the results. Albite, K-feldspar and biotite have been analyzed under SEM-EDS analysis. The analysis shows the majority element that exist in the sample are biotite and K-feldspar. However, the composition of majority REE in the soil/clay samples are very low and less than 50ppb except for lanthanum (La), cerium (Ce) and thorium (Th) which could reach hundred ppb based on the results of ICP-MS analysis. In addition, the chondrite normalised REE trends also found distributed below than common deposits.

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