Distribution of light (LHREE) and heavy rare earth elements (HREE) in Kelantan granitoids rock

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Distribution of light (LHREE) and heavy rare earth elements (HREE) in Kelantan granitoids rock.

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Abstract: Peninsular Malaysia is being distributed into three parallel belts (Western, Central and Eastern). Kelantan is one of the states in Peninsular Malaysia and consider as a unique territory to have all three belts (Western, Central and Eastern). Each belts divided into several formations which are Western Belt (Main Range Granite), Central Belt (Jeli Granite, Kemahang Granite, Noring Granite, Kenerong Leucogranite, Berangkat Tonalite and Senting Granite) and Eastern Belt (Boundary Range Granite). Rare Earth Elements (REEs) are usually concentrated related to the alkaline – peralkaline, carbonalite igneous rocks, as well as sedimentary rocks. Granitoid and some intrusive volcanic rocks are widely exposed in Malaysia, as well as Kelantan state. REEs are relatively abundant in the Earth crust, however these elements are rarely concentrated in the mineable ore deposit. There are a lot of research about granitoids, but very limited studies about the distribution of the REE. The objective of this study is to investigate the distribution of REEs in different type of granitoid rocks in Kelantan. For this purpose, 15 samples were selected and analysed using Inductive Coupled Plasma Mass Spectrometry (ICP-MS). Result shows that, distribution of light REEs in all samples up to 78% and heavy REE up to 22% with total value 5350.69 ppm and 1491.27 ppm respectively. Surprisingly, Jeli Granite formation (LT15) is high potential of REE among the samples tested with total REE 3164.93 ppm and Kemahang Granite (JD18) is least potential with total REE 31.95 ppm. The granitoid distribution can be found widely in Kelantan with special characteristic and detailed study about mineral composition will help identifying the REE potential as well as generate more relatable study about genesis and nature of rocks in Malaysia.

1. Introduction

Demand for minerals is increasing nowadays as the global population growing, mineral used/application also increased to occupied population needs. Rare Earth Element (REE) is an important mineral today and highly demand today in varies field such as petroleum, electronic and green technology. Although, REEs are relatively abundant in the Earth crust, which are rarely concentrated in the mineable ore deposit. They are usually concentrated related to the alkaline – peralkaline, carbonalite igneous rocks, as well as sedimentary rocks [1]. Granitoid and some intrusive volcanic rocks are widely exposed in Malaysia, as well as Kelantan state [2] which is interesting for study and research especially their REE concentration.

The rare earth element (REE) or also called rare earth metal are set of seventeen metallic elements which the oxides classed as the rare earth and which include the elements of the lanthanide series and sometimes yttrium and scandium. Known as Lanthanum group or Light Rare Earth Element (REE) consist of La, Ce, Pr, Nd, Pm and Sm. Hence, Terbium group or Heavy Rare Earth Element (REE) consist of Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y and Sc. In the other hands, REE also known as rare earth oxide as they are economically sold as oxide compound [1].

On the previous research by Hassan [3] related tot REE pattern in some granitic rocks in Peninsular Malaysia found that total REE range from 85.00 ppm to 414.00 ppm. Respectively sample from Main Range Granite and Noring Granite show the result exceeding 200.00 ppm. Test has been conducted using Instrumental Neuron Activation Analysis (INAA). Factors that control the REE concentration are due to partial melting, fractional melting or consist of both partial and fractional melting. As we know, melting proceses involve related to the genesis of the rock such as peraluminous and metalumious of I-type and S-type granite.

Previously Wu et al. [4] conduct a study about the Rare Earth Element (REE) from stream sediment sampling along Kelantan River and Pahang River, highlight that REE composition differs in different grain size and mineral composition. Clay minerals cause high REE content in clay component and the dilution effect of the quartz and feldspar lead to low REE content in medium fine silt component. Furthermore, heavy minerals especially zircon play important roles to REE content in coarse silt components as the grain size increase will contribute to enrichment of HREE. Geologically, all the factors lead to enrichment of REE content either mineral content or grain size will related to the rock genesis.

Study using ICP-MS to the granitoid sample has been done before with focussing on the Gua Musang area. The abundance of light REE compared to Total REE in the majority of samples from granite at Gua Musang area is up to 90% with the highest concentration is 574.39 ppm and the lowest is 79.79 ppm [5]. This finding also relate the enrichment of REE based on their genesis and mineral compostion as the main factors.

Thus, this paper will discuss the potential of REEs in Kelantan's granitoid based on their zone covering from western belt, eastern belt to central belt. Besides that, as shown in the Figure 1, rock formation also one of main factor contributes to the genesis and minerals content for each sample collected.

2. General Geology

The regional geology of Kelantan has been addressed in several small-scale investigations to be consisting of a central zone of sedimentary and metasedimentary rocks bordered with Main Range granite in the west and Boundary Range granite in the east and this study has been done extensively by [6]. Further study said that within the central zone, there are windows that allow the intrusion of the pluton which are Ulu lalat (Senting) granite, Stong Igneous Complex and Kemahang Granite. These granites belt and country rock trend toward north-south and resulted the northen continuation towards Pahang, northward into south Thailand for west and central Kelantan.

The oldest rocks at northerly-trending belt bordering foothill of Main Range and extending eastward to Sungai Neggiri become the evidence for Lower Paleozoic age. They are mainly metapelites with lesser volcanic fragments and minor arenaceous and calcerous intercalation. Besides that, occurrence of amphibolite and serpentinite also rare [7].

The youngest rocks are continental rocks that overlie the Boundary Range granite age from Jurassic-Cretaceous, Gunung Gagau sediments located between Kelantan, Terengganu and Pahang and also to the west Gunung Perlis and Gunung Penumpu from Triassic age. Conversely, Rishworth [8] mention that sequence of those rocks consist of conglomerate overlain by sandstone with sporadic volcanic intercalation.

3. Methods

3.1 Sampling

The sampling method used is stratified sampling method which is granite distributions in Kelantan divided into several types based on their occurrence and genesis. As shown in the Figure 1 and Table 1, 15 sampling points were selected to represent each granites distribution in Kelantan. Those samples are collected from western belt, eastern belt and central belt detailed with rock formation from Main

Range Granite, Jeli Granite, Noring Granite, Berangkat Tonalite, Kemahang Granite, Senting Granite, Kenerong Leucogranite and Boundary Range Granite. As shown in Figure 2 and Table 1, sample has been labelled as LG21, SS30, MR9, LC5, LT15, JD18, AR33, BM20, LK23, LB22, JL26, TE11, LJ1, BG27 and GS2.

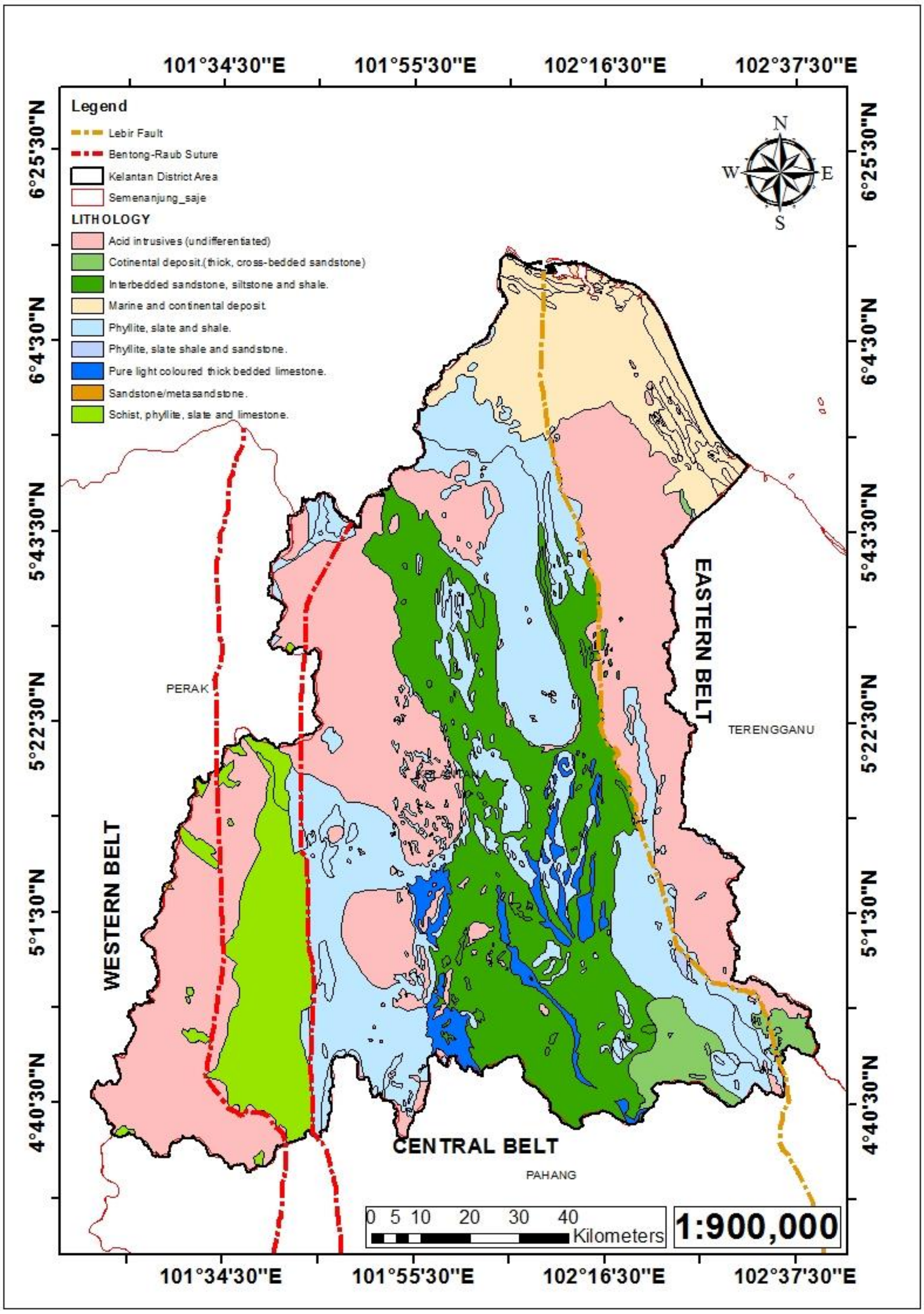

Figure 1. Regional Geology Map of Kelantan showing different formation of granite

Table 1. List of 15 granites samples information's together with macroscopic characteristics

Sample ID	Zone	Formation
LG21	West Belt	Main Range
SS30	Central Belt	Serting Granite
MR9	Central Belt	Berangkat Tonalite
LC5	Central Belt	Noring Granite
LT15	Central Belt	Jeli Granite
JD18	Central Belt	Kemahang Granite
AR33	East Belt	Boundary Range
BM20	East Belt	Boundary Range
LK23	East Belt	Boundary Range
LB22	East Belt	Boundary Range
JL26	East Belt	Boundary Range
TE11	East Belt	Boundary Range
LJ1	Central Belt	Noring Granite
BG27	Central Belt	Noring Granite
GS2	Central Belt	Kenerong Leucogranite

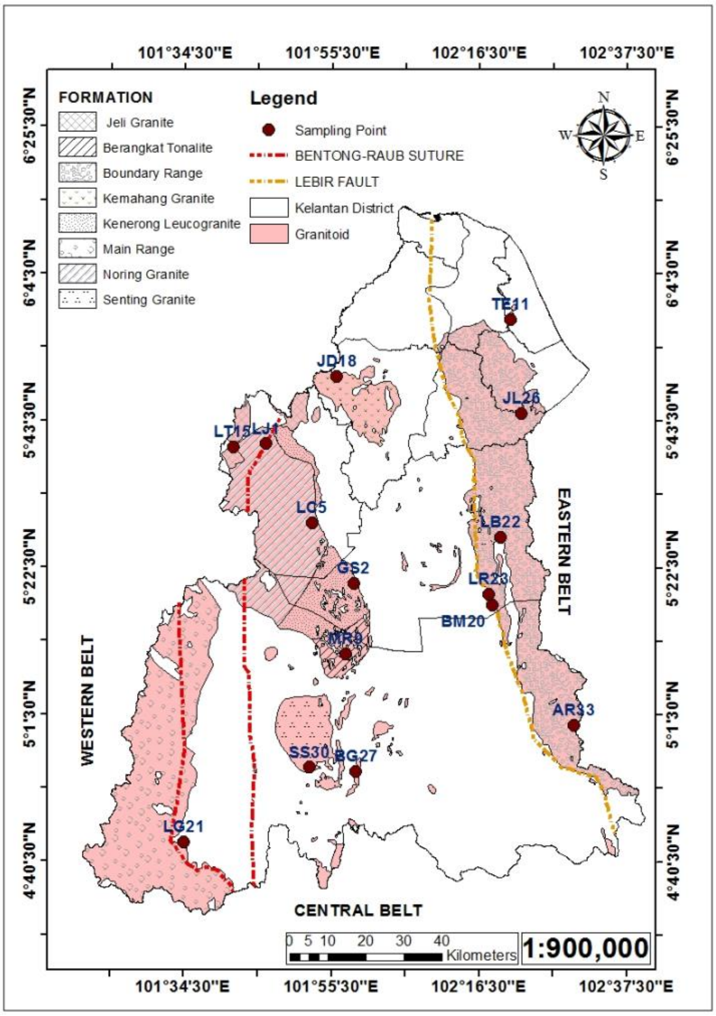

Figure 2. Sampling Point Map

3.2 Inductive Coupled Plasma Mass Spectrometer (ICP-MS)

ICP-MS analysis has been done using ICP-MS, 7500 series, Agilent at Central Laboratory, Universiti Malaysia Pahang (UMP). ICP-MS is used to determine the concentration of the 17 Rare Earth Element (REE) in granitoids sample. 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). A mass spectrometer will detect the ion that has been separated by the ICP source. Fresh rock crushed until nearly powder size. Approximately 0.5 g dried samples were paced into the digestion vessel of High Performance Microwave Digestion System, Ultra wave digester, 6ml of NHO_3 and 2 ml of H_2O_2 was added into the vessel, closed and tightened then later on, the microwave will be programmed and run. After finish, the solution was transferred into 50 m volumetric flask and diluted to mark 2% of HNO_3.

4. Result and Discussion

4.1 REE Analysis

Rare Earth Element data of 15 samples of granitoid rocks was obtained from ICP-MS analysis as shown in the Table 2. Light REE (La, Ce, Pr, Nd, Sm) and heavy REE (Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc) was obtained except promethium (Pm) which is the rarest, only occurs in trace quantities in natural materials as it has no long live or table isotopes [9]. The ICP-MS data indicates that total REE elements in fifteen granitoid samples in Kelantan ranging from 0.049 ppm to 2209.00 ppm. Hence, previously Shafiee et al. [5] mention that REE distribution in Gua Musang area range from 0.004 ppm to 145.60 ppm. Table 2 show that from 15 sample that been tested, out of 15 sample, there are 11 sample have value of more than 100 ppm and LT15 tend to be the highest value of total REE with 3164.93 ppm followed by MR9 with 1036.66 ppm.

Figure 3 shows the distribution of light REE and heavy REE in all samples in ppm unit. Total value of light REE tend to be high than heavy REE which is range from 23.78 ppm to 3148.50 ppm, while heavy REE range from 8.17 ppm to 969.44 ppm. This kind of results are as expected due to light REE are more abundance compare to heavy REE as heavy REE commonly less in volume but more economic and valuable than light REE.

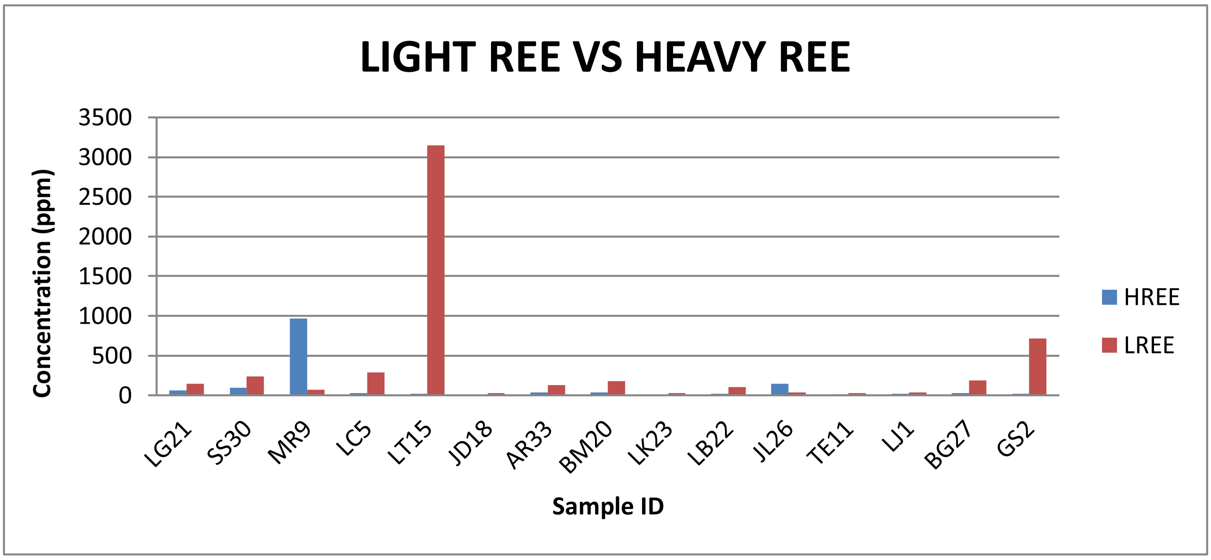

Figure 3. Total abundance of light REE vs. heavy REE in ppm unit

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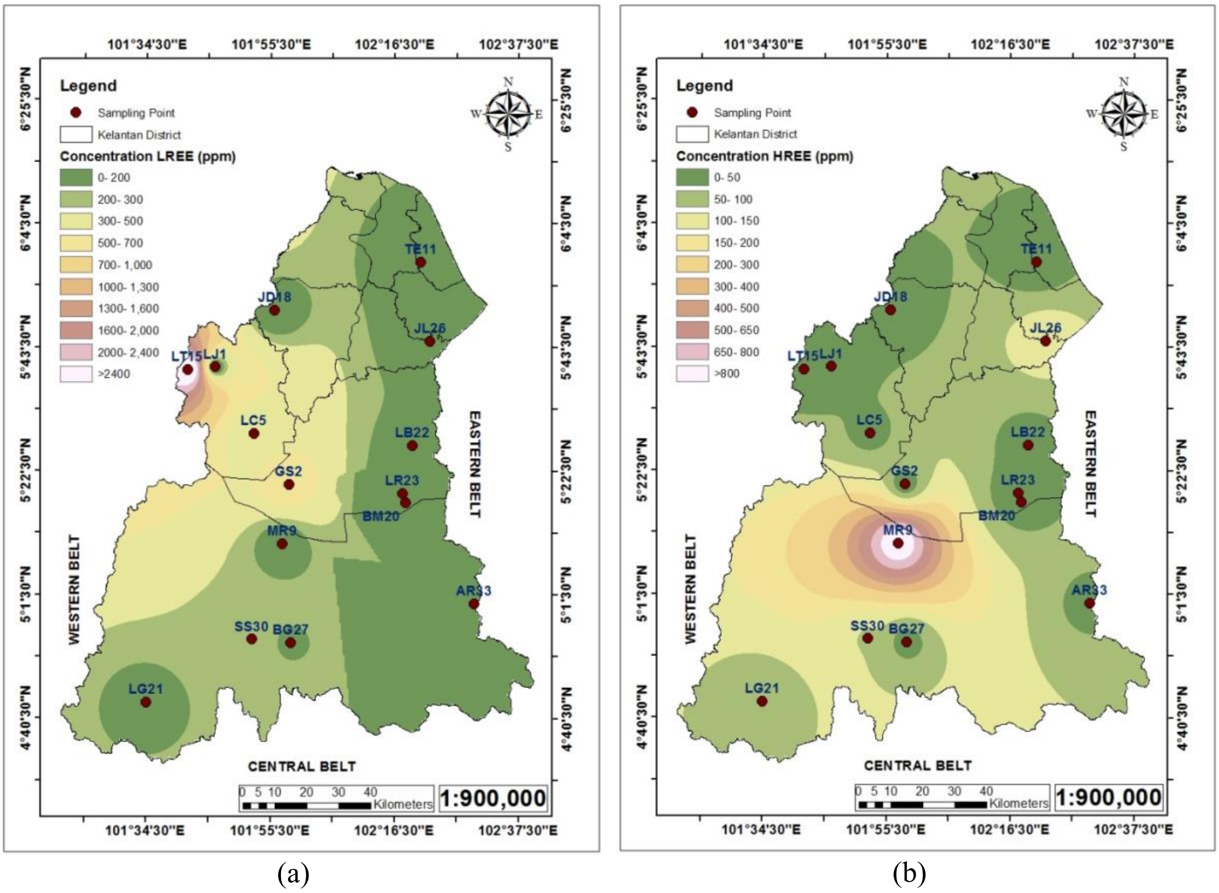

Figure 4. Concentration of (a) Light Rare Earth Element (LREE) and (b) Heavy Rare Earth Element (HREE)

Distribution of light REE shows that Cerium (Ce) appears to be the most prominent with value 2209.00 ppm and Samarium (Sm) is the most distant elements with value 0.64 ppm within all fifteen samples (Figure 4 and Figure 5). Respectively, Ce from LT15 and Sm from JD18. Theoretically, according to Zepf [10], the abundance of REE may relate to two main factors. The first is REE with even atomic numbers have greater abundance than their odd number neighbours (Oddo-Harkins effect). The second factor is due to light REE are more contradictory (since they have bigger atomic radii and subsequently more concentrated in the continental crust than the REE bigger atomic numbers). The chemically comparative nature (ionic radii and oxidation state) of REE implies they can substitute with one another in crystal structure. This clarifies why the event of numerous REE inside a single mineral and wide dispersion in Earth crust.

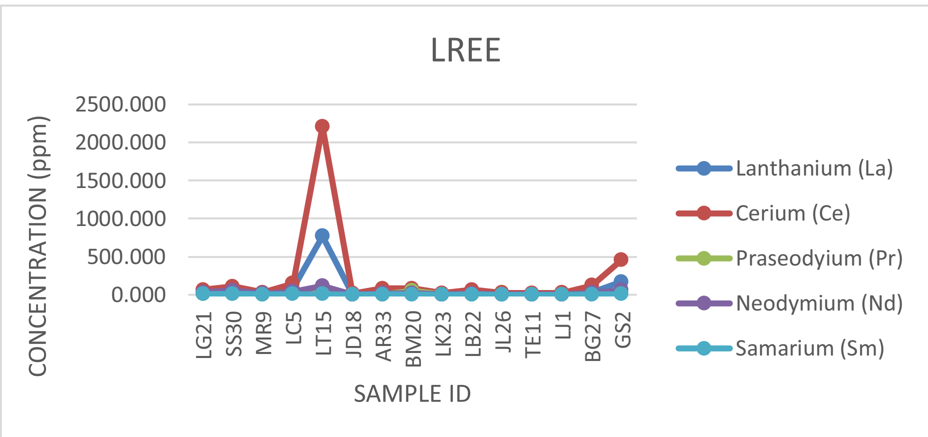

Figure 5. Distribution of light REE in ppm unit

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Table 2. Distribution of REE in fifteen Granites Samples in ppm Unit

	LG21	**SS30**	**MR9**	**LC5**	**LT15**	**JD18**	**AR33**	**BM20**	**LK23**	**LB22**	**JL26**	**TE11**	**LJ1**	**BG27**	**GS2**
Scandium (Sc)	11.09	14.98	1.47	4.19	2.67	0.46	2.67	5.72	1.47	2.84	0.20	0.99	1.80	2.66	2.84
Ytirium (Y)	30.84	45.24	7.91	12.48	5.04	4.63	18.00	14.66	3.75	10.32	5.24	7.57	9.46	11.89	7.46
Lanthanium (La)	31.77	46.81	12.55	81.90	768.20	4.13	21.90	18.10	4.83	18.20	5.75	3.87	6.71	29.23	167.83
Cerium (Ce)	65.50	109.52	31.60	146.56	2209.00	15.02	83.30	81.52	19.85	65.63	23.38	19.38	24.96	119.63	458.28
Praseodyium (Pr)	7.65	13.31	4.02	14.31	48.56	0.85	4.40	51.45	1.23	3.45	1.24	1.12	1.37	6.82	18.72
Neodymium (Nd)	29.64	55.60	16.12	42.87	115.30	3.14	15.27	21.45	4.68	12.18	4.54	4.63	4.81	25.30	59.67
Samarium (Sm)	6.82	12.81	2.93	5.58	7.44	0.64	3.20	4.64	0.97	2.44	1.05	1.13	1.07	4.56	6.82
Europium (Eu)	0.75	2.50	662.18	0.75	0.79	0.33	0.33	0.81	0.22	0.38	132.90	0.10	0.22	0.49	0.75
Gadolinium (Gd)	7.11	11.64	2.29	4.13	5.31	0.70	3.00	3.83	0.90	2.17	1.00	1.28	1.26	3.64	3.94
Terbium (Tb)	1.09	1.66	292.11	0.48	0.34	0.13	0.49	0.55	0.13	0.32	0.15	0.22	0.23	0.49	0.37
Dysprosium (Dy)	5.86	9.07	1.57	2.46	1.12	0.79	2.92	2.83	0.75	1.88	0.85	1.30	1.48	2.56	1.64
Holmium (Ho)	1.12	1.79	0.29	0.44	0.17	0.17	0.66	0.54	0.14	0.39	0.18	0.29	0.32	0.48	0.29
Erbium (Er)	2.97	4.50	0.82	1.19	0.49	0.45	1.97	1.52	0.39	1.05	0.49	0.80	0.96	1.23	0.72
Thulium (Tm)	0.39	0.66	0.10	0.18	0.06	0.06	0.31	0.22	0.06	0.15	0.07	0.11	0.15	0.17	0.09
Ytterbium (Yb)	2.18	3.80	0.61	1.14	0.38	0.39	2.09	1.51	0.40	0.91	0.48	0.77	0.89	1.03	0.61
Lutetium (Lu)	0.29	0.52	0.08	0.16	0.06	0.05	0.32	0.22	0.05	0.12	0.07	0.12	0.13	0.15	0.08
TOTAL	205.07	334.39	1036.66	318.81	3164.93	31.95	160.83	209.57	39.81	122.43	177.58	43.66	55.82	210.33	730.10

For heavy REE, it shows that Europium (Eu) appears to be the most prominent with value 662.180 ppm and Lutetium (Lu) is the most distant element with value 0.05 ppm within all fifteen samples. Respectively, Eu from MR9 and Lu from JD18. Other samples also show the same REE distribution with a concentration below than >1.00 ppm. Based on Figure 6, Thulium (Tm) and Lutetium (Lu) show the lowest distribution reading as they are the two less abundance of REE.

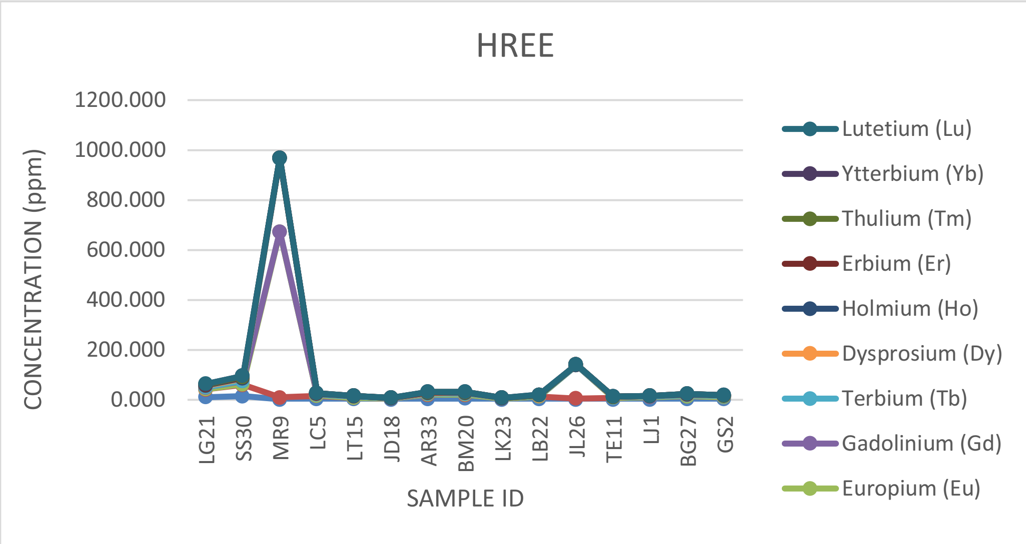

Figure 6. Distribution of heavy REE in ppm unit

5. Conclusion

Concentration or enrichment of REE strongly related to the parent rock genesis factors such as fault zone, rock formation, mineral composition and others. The results of this study indicate the light REE found were Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd) and Samarium (Sm). Based on the results, all 15 samples show the value of 5 out of 6 light REE with the Ce become the most abundant element appeared in the samples tested with a total of 3473.13 ppm and Sm is the lowest with a total of 62.10 ppm. However, in all 15 samples tested show all 11 heavy REE element appeared which are Scandium (Sc), Yttrium (Y), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb) and Lutetium (Lu). As shown in Table 1, Eu is the most abundant element that appeared with a total of 803.49 ppm and Lu is the lowest with a total of 2.43 ppm. As expected, light REE will appeared as the most abundant element compare to heavy REE as the heavy REE is very limited and economic compare to light REE. Distribution of light REE in all samples up to 78% and the rest 22% is heavy REE. Besides that, highest concentration of light REE is LT15 followed by GS2> LC5> SS30> BG27> BM20> LG21> AR33> LB22> MR9> LJ1> JL26> LK23> TE11> JD18. Hench, for heavy REE MR9 is the highest concentration followed by JL26> SS30> LG21> AR33> BM20> LC5> BG27> LB22> GS2> LJ1> LT15> TE11> LK23> JD18. These findings have significant implications for the understanding of how the distribution of REE correlates with the granitoid distribution in Kelantan, which are both prominent light REE and heavy REE from Central Belt, especially at Jeli Granite and Berangkat Tonalite.

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