IOP Conference Series: Earth and Environmental Science

PAPER • OPEN ACCESS

Potential of Rare Earth Elements (REEs) in Gua Musang Granites, Gua Musang, Kelantan

To cite this article: Nor Shahida Shafiee *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **549** 012027

IOP Conf. Series: Earth and Environmental Science **549** (2020) 012027 doi:10.1088/1755-1315/549/1/012027

Potential of Rare Earth Elements (REEs) in Gua Musang Granites, Gua Musang, Kelantan

Nor Shahida Shafiee[1*], Arham Muchtar Achmad Bahar[1] and Mohamad Muqtada Ali Khan[1]

[1] Geoscience department, Faculty of Earth Science, Universiti Malaysia Kelantan, Jeli Campus, 17600 Jeli, Kelantan

E-mail: shahidashafiee@umk.edu.my

Abstract. Granitoid and some extrusive volcanic rocks are widely exposed in Kelantan. In Gua Musang area, the granites are characterized by slightly feldspar. One of the groups of elements found to be in association with granitic rocks is rare earth elements (REEs). The objective of the study is to investigate the distribution of REEs in different types of granitoid rocks in Gua Musang, Kelantan. For this purpose, 10 selected samples of granites were analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Light REE are predominant, consisting up to 448.00 ppm. Distribution of light REE in the majority of samples (e.g as shown in sample #001, #003,#008, #009 and #010) are up to 90%. Interestingly, one of the samples show a considerably high REE value than previously reported in literatures (i.e sample #002 with a value of 574.3858 ppm) suggesting a good potential for REE. As granitoid rocks are widely exposed in Malaysia, result of this study would give a basic knowledge to develop a more detail study especially in Rare Earth Elements (REE) potential in different types of granitoid rocks in Malaysia.

1. Introduction

Rare earth elements (REE), or rare earth metals (REM), are a set of seventeen chemical elements in the periodic table with atomic numbers from 57 lanthanum (57La) to 71 lutetium (71Lu) plus scandium (21Sc) and yttrium (39Y). Scandium and yttrium are considered as rare earth elements since they tend to occur in the same ore deposit as lanthanides and display similar chemical properties. REE can be divided into two, lanthanum group and terbium group. Lanthanum group or called as Light Rare Earth Elements (LREE) consists of La, Ce, Pr, Nd, Pm, Sm while Terbium group or called as Heavy Rare Earth Elements (HREE) consists of Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y. The rare earth elements are all metals, and the group is often referred to as the "rare earth metals." Since these metals have many similar properties, and that often causes them to be found together in geologic deposits. They are also referred to as rare earth oxides because many of them are typically sold as oxide compounds [1]. REE have been recognised as valuable because of their unusual chemical and physical properties. REE are mainly used in the production of permanent magnets, catalysts, super alloys, and car batteries which are critical in many green technologies. The increasing demand for rare earth elements is related to continuous development of technology that the elements are used in modern equipment.

Although rare earth elements are relatively abundant in the Earth's crust, they are rarely concentrated into mineable ore deposits. They are commonly concentrated related in carbonatite igneous rocks and sedimentary rocks [1]. REE are associated with alkaline igneous rocks and carbonatites, as well as in sedimentary rocks [1]. However, there is a significant value of REE deposits in association with granitic rocks and their related igneous bodies. The source of rocks are usually shallow magma sources. The enrichment of REE minerals occur during magma, late magma or hydrothermal stages of post magmatism. Granitoid and some extrusive volcanic rocks are widely exposed in Malaysia, including in Kelantan territory [3]. In Gua Musang are, two different granites are exposed, these are the grey granite with slightly fieldspar-phyric and the pink granite.

In this paper, geochemical analysis was carried out to describe and analyse the elements contained in granitoids. Elements in the rock are determined to an intermediate level of accuracy. The ICP-MS is used to analyse the rare earth elements and trace elements in geological materials like Ba, Cr, Cu, Nb, Ni, Rb, Zn and others in rock and sediment that more >1 ppm.

2. Methods

2.1 Sampling location

The study area is predominated by Middle Permian to Late Triassic Gua Musang Formation (Figure 1) and the details of sampling locations shown in Table 1 and Figure 2. The Gua Musang Formation is very well exposed in the northern part of the Gua Musang. This formation consists of Pre-Mesozoic metasediment i.e. shallow marine argillaceous facies made up phyllite, slate and hornfels.

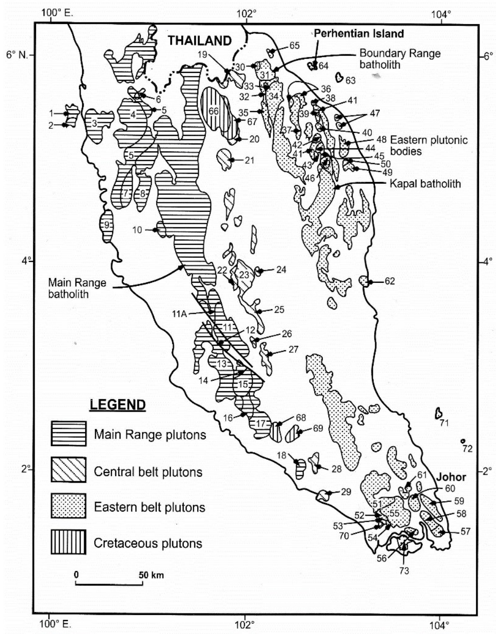

Figure 1. Map of Malaysia Peninsula showing the distribution of granitoids [11]

Table 1. List of Sample ID and coordinates of sampling point

Sample ID	Coordinates
#001	N04°53'51.3" /E101°52'25.8"
#002	N04°53'26.7"/E101°51'42."
#003	N4°54'4.21"/E101°53'44' 36.1"
#004	N04 53' 18.5"/E101° 58' 54.3"
#005	N04 53' 18.7"/E101° 58' 55.6"
#006	N04 53' 18.1"/E101° 58' 54.9"
#007	N04 53' 32.4"/E101° 58' 47.4"

Sample ID	Coordinates
#008	N04 57’13.3"/E101°55'20.49"
#009	N04 56’50.2"/E101°55'11.3"
#010	N04 58’33.8"/E101∘47' 29.2"

About 40% of granitoids formed on the land surface and as the bedrock of main mountain ranges. Granitic terrains in Peninsular Malaysia are exposed to intense and high degree of chemical weathering causing granitic rocks to breaking down into sands or red quartz-bearing clay (present in brown-orange colored). According to Heng [5] the geology of Kelantan central zone is composed of sediment and metasedimentary rocks that are bordered by Main Range granites to the west and Boundary Range granite to the east. The granite intrusive within the central zone is comprises of Senting batholiths, Stong Igneous Complex and Kemahang pluton.

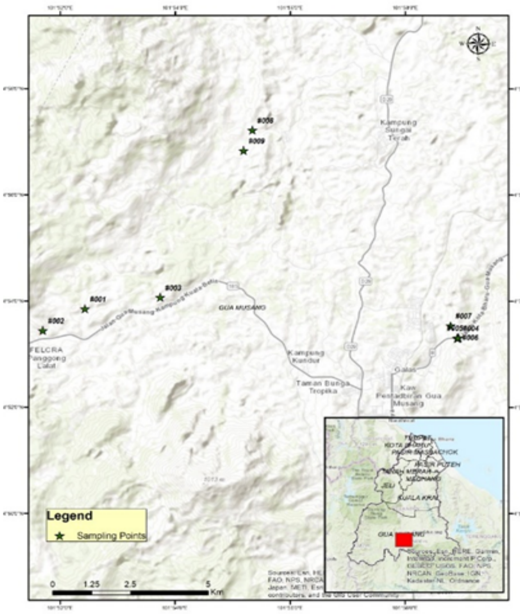

Figure 2. Map of study area showing the sampling location

2.2 ICP-MS

ICP-MS was used to determine the concentrations of 16 Rare Earth Elements (REEs) in the granitoids samples. ICP-MS is an analytical technique that allows more sensitive detection in determining a wide range of extremely low detection limit of atomic elements below one part in 10^{12} (part per trillion). Mass spectrometer will be detecting the ion that has been separated by ICP source [6]. This technique is highly recommended for trace elemental analysis as it offers a high speed of analysis, accurate detection limit and isotopic sensitivity potential [6]. Fresh granite samples were crushed to nearly powder size. Approximately 0.5 g dried samples were placed into digestion vessel of High-Performance Microwave Digestion System, Ultra wave digester, 6 ml of HNO_3 and 2 ml of H_2O_2 was added into the vessel. The vessel was closed and tightened. After that, the microwave was programmed and run. After digestion process completed, the solution was transferred into 50 ml volumetric flask and was diluted to mark with 2 % HNO_3. Samples then were analysed using Inductively Coupled Plasma Mass Spectrometer, 7500 series, Agilent. ICP-MS analysis of rock samples had been carried out at Central Laboratory, Universiti Malaysia Pahang (UMP).

3. Results and Discussion

3.1 REE Analysis

Rare Earth Elements data was obtained from ICP-MS analysis and after running the analysis on ten samples of granitoid rocks of #001, #002, #003, #004, #005, #006, #007, #008, #009 and #010. Light REE (La, Ce, Pr, Nd, Pm) and heavy REE (Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) was obtained except promethium (Pm) the rarest, only occurs in trace quantities in natural materials as it has no long-lived or table isotopes [11].The ICP-MS data indicates that the total REE elements in ten granites samples in Gua Musang is ranging from 88.00 ppm to 575.00 ppm. Although, the previous finding by [7]. indicates that the total REE in the Peninsular Malaysian granites is ranging from 85 to 414 ppm. As shown in Table 2, out of ten samples, seven samples have values of more than 100 ppm with sample #002 appear to be the highest value total REE of 574.3858 ppm followed by sample #006 with a value of 311.6130 ppm.

Figure 3 shows the light REE and heavy REE distributions in ten granitoid samples measured in ppm unit. The total light REE are generally high value with a range of 55.00 ppm to 450.00 ppm. While the total of heavy REE are generally low with value ranging from 2.00 ppm to 128.00 ppm. As expected, light REE are more abundance than heavy REE as the heavy REE are known to be less common and more valuable compare to light REE.

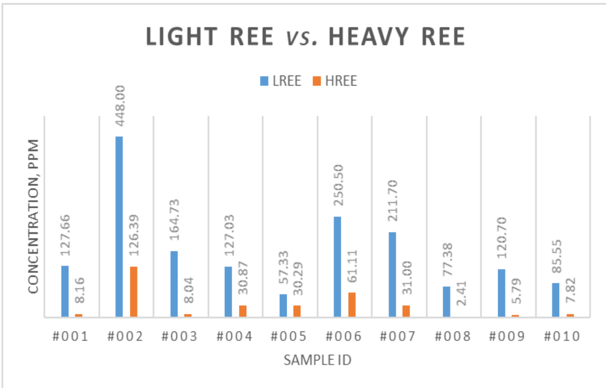

Figure 3. Total abundance of light REE *vs*. heavy REE in ppm unit

Table 2. Distribution of REE in ten granites samples in ppm unit *EE*

	#001	#002	#003	#004	#005	#006	#007	#008	#009	#010
(La)	28.5000	145.6000	41.5000	30.6000	1.6000	20.2000	53.2000	2.0000	28.7000	2.4000
(Ce)	62.1000	125.3000	82.1000	62.9000	33.9000	40.2000	106.2000	44.9000	59.5000	50.7000
(Pr)	0.7605	28.8000	0.9330	0.7282	0.4283	40.2000	1.2000	0.5832	0.6973	0.6470
(Nd)	30.3000	121.9000	34.2000	27.5000	17.4000	130.0000	43.2000	24.6000	27.0000	26.3000
(Sm)	6.0000	26.4000	6.0000	5.3000	4.0000	19.9000	7.9000	5.3000	4.8000	5.5000
(Eu)	0.0793	0.3872	0.0617	0.0500	0.0478	0.1410	0.0331	0.0932	0.0691	0.0797
(Gd)	5.3000	29.5000	5.2000	5.0000	4.1000	15.0000	6.7000	0.0046	4.0000	5.0000
(Tb)	0.0771	0.4123	0.0736	0.0809	0.0739	0.1850	0.0994	0.0648	0.0518	0.0727
(Dy)	0.4006	2.1000	0.3941	0.4736	0.4543	0.9053	0.5652	0.3362	0.2591	0.3797
(Ho)	0.0767	0.3768	0.0764	0.0966	0.0974	0.1694	0.1124	0.0638	0.0484	0.0736
(Er)	0.2035	0.8952	0.2066	0.2689	0.2761	0.4383	0.3043	0.1661	0.1274	0.1946
(Tm)	0.0278	0.1116	0.0285	0.0381	0.0413	0.0595	0.0435	0.0223	0.0173	0.0281
(Yb)	0.1714	0.6173	0.1733	0.2261	0.2630	0.3634	0.2629	0.1377	0.0993	0.1641
(Lu)	0.0244	0.0854	0.0245	0.0312	0.0387	0.0511	0.0366	0.0194	0.0145	0.0230
(Y)	1.8000	91.9000	1.8000	24.6000	24.9000	43.8000	29.8000	1.5000	1.1000	1.8000
∑ SUM	135.8213	**574.3858**	172.7717	157.8936	87.6208	311.6130	249.6574	79.7913	126.4842	93.3625

Distribution of light REE shows that Cecium (Ce), Neodymium (Nd) and Lanthanium (Ln) appears to be the most prominent elements within all ten samples. Referring to Figure 4, Sample #002 has the highest values of Ln element, sample #006 has the highest values of Nd element and sample #007 has the highest value of Ce elements with the values of 145.6000 ppm, 130.0000 ppm and 106.2000 ppm respectively. The distribution of Pr and Sm elements are generally low with a range of 0.4000 ppm - 29.0000 ppm and 4.0000 ppm – 27.0000 ppm, respectively. Theoretically, according to Zepf [10], the abundance of REE may relates to two main factors. The first is REE with even atomic numbers have an even atomic numbers have greater abundance than their odd numbered neighbours (Oddo-Harkins effect); and Secondly the lighter REE are more incompatible (because they have larger ionic radii and consequently more strongly concentrated in the continental crust than the REE with larger atomic numbers. The chemically similar nature (ionic radii and oxidation states) of the REE means they can substitute for one another in crystal structures. This results in the occurrence of multiple REE within a single mineral and a broad distribution in the Earth's crust. Nevertheless, this is not the case for some of the samples. For example, from the distribution, the concentration of Nd and La shows that Nd has higher concentration than La. This observation may be due to the atomic weight of Nd is higher than La. However, according to [9] it is also possible that La can eu higher than Nd due to the atomic radii of La is bigger than Nd makes La is more easily to aggregate with the rocks.

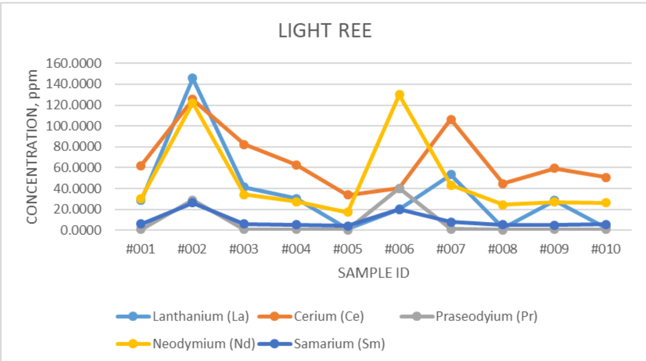

Figure 4. Distribution of light REE in ppm unit

For heavy REE, the most abundance elements within all samples are Yttrium (Y) and Gadolinium (Gd) ranging from 1.00 pm – 92.00 ppm and 0.04 ppm – 30.00 ppm respectively. Other samples however show the same REE distribution and are considerably below than <1.00 ppm. Based on the Figure 5. Thulium (Tm) and Lutetium (Lu) show the lowest distribution reading as they are the two least abundances of Rare Earth Elements.

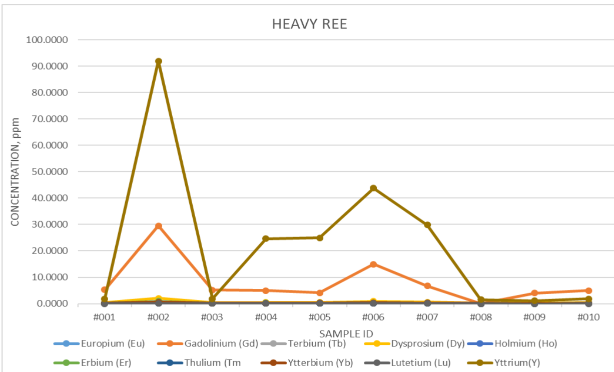

Figure 5. Distribution of heavy REE in ppm unit

4.Conclusions

Light REE that was obtained by the ICP-MS analysis are Lanthanium (La), Cerium (Ce), Praseodyium (Pr), Neodymium (Nd) and Samarium (Sm). This shows that only 5 out of 6 light REE present in the granite of Gua Musang with Ce appeared to be the most abundance in the majority of all samples. For heavy REE, there are 10 elements that appears in all granite samples which are, Europium (Eu) Gadolinium (Gd) Terbium (Tb) Dysprosium (Dy) Erbium (Er) Thulium (Tm) Ytterbium (Yb) Holmium (Ho) Lutetium (Lu) and Yttrium (Y). Among all these, Gd and Y appeared to be most abundance in the majority of all samples. As expected, light REE are more abundance than heavy REE as the heavy REE are known to be less common and more valuable compare to light REE. The abundance of light REE compare to Total REE in the majority of samples are up to 90% (e.g #001, #003,#008, #009 and #010). Total REE in granite sample of Gua Musang shows highest concentration in sample #002 > followed by #006> #007> #003> #004> #001> #0010> #008 > #005. With the highest concentation is 574.3858 ppm and the lowest is 79.7913 ppm. Reported range of total REE indicates that the total REE in the Peninsular Malaysian granites is ranging from 85 to 414 ppm and ranging from 85 to 327 for the East Coast granites. Thus Sample from #002 with total REE of 574.3858 ppm might be consider as a good potential of REE since the abundance of REE is exceed the reported range.

Acknowledgements

We thank University Malaysia Kelantan for funding this research activities and providing the equipment and facilities for this project. We also thank staff and students of Department of Geoscience for their contributions and continuous support during this work. We appreciate the contributions from two anonymous reviewers whose comments and suggestions greatly improved the manuscript. We acknowledge the great help and enthusiasm we received from the editor.

References

[1] Haxel G B, Hedrick J B and Orris G J 2002 *Rare earth elements—Critical resources for high technology*. USGS Fact Sheet 087-02, http://geopubs.wr.usgs.gov/fact-sheet/fs087-02/

[2] Long K R, Van Gosen B S, Foley K and Cordier D 2010 Geology of Rare Earth Elements. Republished from: *The Principal Rare Earth Elements Deposits of the United States, USGS Scientific Investigations Report* **2010-5220**.

[3] Ng S W P, Whitehouse M J, Searle M P, Robb L J, Ghani A A, Chung S L, Oliver G J H, Sone M, Gardiner N J and Rosele M H , 2015. *GSA Bulletin*, doi:10.1130/B31214.1

[4] Metcalfe I 2011 Tectonic framework and Phanerozoic evolution of Sundaland: *Gondwana Research*, v. **19**, p. 3–21, doi: 10 .1016 /j .gr .2010 .02 .016 .

[5] Heng G S, Hoe T G and Hassan W F W 2006 *Geological Society of Malaysia Bulletin*.

[6] Pinto F J, Junior R E and SaintPierre T D 2012 *Analytical Letters* - **45**

[7] Batsala M, Chandu B, Sakala B, Nama S, Domatoti S, Bosco D, Pradesh A 2012 *International Journal of Research in Pharmacy and Chemistry*, **2(3),** 671–680.

[8] Castor S B, and Hedrick J B 2006 *Rare Earth Elements. In: Kogel* J E, Trivedi N C, Barker J M, and Krukowski S T. Industrial Minerals and Rocks: Commodities, Markets, and Uses, 7th edition. SME. p1568.

[9] Wan Hassan W F and Hamzah M S 1999 *Bulletin of the Geological Society of Malaysia,* Volume **43**, pp. 513 – 528

[10] Zepf V 2013 Rare Earth Elements: What and Where They Are. Doi:10.1007/978-3-642-35458-8_2.pp.11-39

[11] Ghani, A. A., 2009. Plutonism, in Hutchison, C.S. and Tan, D.N.-K., eds., *Geological Society of Malaysia*, p.211-232.