International Journal of Engineering and Science Applications ISSN: 2406-9833 @2016 PPs-UNHAS



Petrology and Geochemistry of Granitoid from South Sulawesi, Indonesia: Implication for Rare Earth Element (REE) Occurrences

A.Maulana¹, K. Watanabe², K. Yonezu²

¹Department of Geology Engineering, Faculty of Engineering, Hasanuddin University, 90245, Makassar, Indonesia

²Department of Earth Resources Engineering, Kyushu University, Fukuoka 819-0395, Japan

Email: adi-maulana@unhas.ac.id

ABSTRACT

This study reports petrology and geochemistry of potential rare earth elements (REE) bearing granitoid from South Sulawesi. The granitoid consists of monzogranite, granodiorite and diorite with subordinate of quartz monzonite, monzodiorite and syenite. Major and trace element analysis were determined using XRF method while trace element and rare earth element composition were determined by ICP-MS method. Geochemical study suggested that the granitoid were metaluminous series and "I-type" granitoid. They were furthered classified as calc alkaline series in AFM diagram. The total REE concentration in the granitoids range from 279 ppm to 400 ppm whereas total REE + Y contents up to 305 ppm for Polewali and 428 ppm for Masamba granitoid. Chondrite normalized REE patterns were characterized by enrichment of LREE with the depletion of heavy HREE. REE-bearing mineral were detected as zircon, apatite and monazite as shown by the positive correlation between Zr and P_2O_5 contents in bulk rock with REE content.

Keywords: Petrology, geochemistry, granitoid, rare earth element, Sulawesi Article history: Received 21 May 2016, last received in revised 28 May 2016.

1. INTRODUCTION

Environmental application of Rare Earth Element (REE) has significantly increased over the past three decades. REE are essential and crucial to every aspect of green economy from wind turbine to electric vehicle to energy vehicle lighting. The use of several REE in automobile technology such as automotive pollution-control catalyst converter will eventually reduce CO2 emission. In addition, large application of magnetic refrigeration technology also could significantly reduce energy consumption as well as CO2 emission. Nowadays, source of REE is heavily dependent on some weathered crust deposits in China (ex. Bayan Obo Deposit and highly weathered granitic rock from Southern China) which has recently imposed restrictions on their import. This condition has led to the growing concern that the world may soon face a shortage of rare earth elements resources. Therefore, other sources of rare earth elements are expected to be developed in order to balance supply and demand of them. Rare earth elements mineralization occur in some deposit types; e.g. carbonatite rock formation, granitoid, manganese deposit hydrothermal iron-ore deposit, placer deposit, lateritic soil, ion adsorption weathering crust and uranium deposit [1-2].

One of the most promising sources of these elements is in granitoid as reported by previous studies [3-5]. These rocks are widely distributed in Sulawesi Island which located in the central part of the Indonesian archipelago. This paper reports the geochemical characteristic of rare earth elements (REE) bearing granitoids in Polewali and Masamba area, South Sulawesi, Indonesia.

2. METHODOLOGY

Sixteen fresh granitoid samples were randomly taken from the outcrops in both Polewali and Masamba areas. The samples were prepared and studied petrographically determine rock to types, mineral assemblages, fabric and textural relations. They were later crushed and pulverized and approximately 1 kg were crushed and milled to 200 mesh and then thoroughly mixed using a swing mill. Major and trace elements compositions were analysed at Dept. of Earth Resources Engineering, Kyushu University and ALS Chemex, Vancouver, Canada, respectively. Major compositions were determined on fused disc and pressed powder using X-ray fluorescence spectrometer Rigaku RINT-300 whereas rare earth element and trace element were determined by ICP-MS method.

3. RESULT AND DISCUSSION

A. Geology

The study areas were located in the northern part of the west region of the island, particularly in Polewali and Masamba area which more than 300 km and 400 km to the Makassar northward of in distance. respectively (Fig.1). Both areas are separated by mountainous topography and consist of Tertiary and Quaternary volcanic rocks. The Polewali granitoid consist of granite to diorite in composition [6]. However, Sukamto [7] classified these rocks as intrusive rocks groups, consisting of granodiorite and recent report from Djuri et al. [8] reported these rocks as intrusive rocks group consisting of generally acid to intermediate in composition, such as granite, granodiorite, diorite. syenite, quartz monzonite and rhyolite. They further concluded the age of these rocks to be Pliocene since the Unit intruded the Mio-Pliocene Walimbong Volcanic rocks.

Elburg and Foden [9] reported that the intrusive body from this area consists of granodiorite, syenite and rhyodacite and dated as 5.7 to 8 Ma. Simanjuntak et al. [10] reported the occurrence of Masamba granitic rock and classified them into Kambuno Granitic group consisting of granite, granodiorite and gneiss rocks. The age of these groups were interpreted as Tertiary as they intruded the Bonebone Formation which is Tertiary in age.

Fig. 1 Map of Sulawesi Island and studied area

B. Petrography

In Polewali, a series of small plutons consist of monzogranite and granodiorite, intruded into the Upper Cretaceous sedimentary Latimojong Formation. The monzogranite, represented by sample POL-ST3, shows porphyritic texture and contains plagioclase as phenocrysts set in a of plagioclase groundmass (40%), hornblende (25%), biotite (15%), quartz (10%), and K-feldspar (5%), with accessory titanite, apatite and opaque oxide. In another monzogranite (POL-ST1), plagioclase occurs as phenocrysts, up to 8 mm in length, showing polysynthetic twinning and containing abundant inclusions of quartz and biotite. Granodiorite (POL-ST2) consists mainly of plagioclase (50%), quartz (15%), hornblende (15%), biotite (10%), K-feldspar (<5%), and some accessory minerals (e.g. titanite, zircon and opaque oxide).

A composite pluton composed of granodiorite, quartz monzonite and syenite is found in Mamasa, approximately 60 km NE of Polewali Pluton. Granodiorite (MA-41BA) consists of plagioclase (60%), quartz (10%), hornblende (15%), biotite (10%), and accessory minerals (titanite, apatite and opaque oxide), whereas quartz mononite (MA-45) shows a granular texture, consisting plagioclase (50%), quartz of (15%)hornblende (15%), biotite (15%), and Kfeldspar (<3%), with some accessory minerals (e.g. titanite, opaque oxide and zircon) (Fig. 2a). Monzogranite (samples MA-48 and MA-46) is mainly composed of plagioclase (45%), quartz (30%), K-feldspar (10%), biotite (10%), and hornblende (5%), with accessory mineral of titanite and opaque oxide (Fig. 2b).

IJEScA

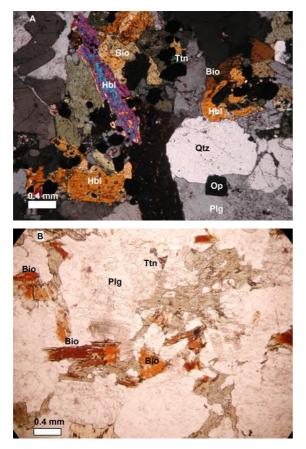


Fig. 2. a) Photomicrograph of granodiorite (MA-45) from Mamasa consisting mainly of plagioclase, quartz, hornblende and biotite. Accesory of titanite and opaque oxide are common (cross-polorized). b) Biotite in monzogranite (MA-41) showing reddish brown color (plane-polarized).

C. Major and Trace elements

Major element and trace compositions of representative lithologies are presented in Table 1 & Figs. 3. The granitoid are vary in silica contents between 56 and 76 wt% and were plotted in the field of granite, granodiorite and diorite with subordinate quartz monzonite and monzodiorite in Total Alkali Silica (TAS) diagram of Le Bas [11]. All the samples were plotted in calc-alkaline series in AFM diagram. Excepting Na2O and K2O, the major element oxide vs. SiO2 diagrams displays linier trends, indicating fractional crystallization process (Fig. 4). The trace element data are also commensurate with fractional crystallization with lower Sr, Rb and Ba relative to an increase of the SiO2.

D. Rare earth element

Total REE contents of Polewali granitoid range from 191 to 277 ppm whereas those from Masamba granitoid ranges from 47 to 399 ppm (Table 1).

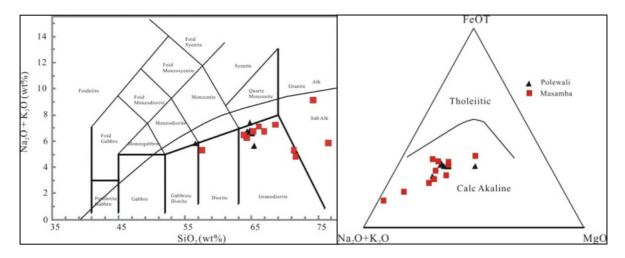


Fig. 3. Major composition of samples from Polewali and Mamasa area plotted in TAS and AFM diagram

Variations in total REE among individual samples may reflect variable crystallization of zircon, apatite, monazite and allanite. All of the analysed sample have right-inclined, chondrite-normalised REE pattern, showing significant light rare earth element (LREE) enrichment (Fig.5). They also show pronounced negative Eu anomaly, indicating early fractionation of plagioclase. The Polewali granitoid behave homogeneously on the chondrite-normalised REE [12] plots, with LaN: YbN = 8 - 19.8, fairly flat HREE from Dy to Lu and negative Eu anomaly. The Masamba granitoid shows two groups in chondrite-normalised REE plots. The first group show higher LREE content compare to Polewali samples with LaN:YbN ranges from 15 - 51 whereas the second groups show lower value of LaN:YbN (less than 5). All samples resemble upper continental crust composition from Rudnick and Gao [13]. The ASI (Aluminium Saturation Index), molar Al2O3/Na2O+K2O+CaO for all but three samples is < 1, and molar Al2O3/Na2O+K2O is higher than one, indicating that most samples are metaluminous I-type granitoid.

4. DISCUSSION

A. Rare earth elements enrichment

The granitoid from Polewali and Masamba area were highly fractionated as shown by the strong negative Eu anomaly. However, one samples from Masamba area show positive Eu anomaly suggesting the K-Feldspar fractionation in magma chamber. Discrimination diagram of SiO2 vs $\sum REE, \sum$ LREE, \sum HREE and \sum REE + Y (Fig.6) composition show relatively negative correlation suggesting that REE were depleted by the magmatic differ entiation. However, the diagram show that the samples with has SiO2 ranging from 60 to 65 wt% tend to contain higher REE than other samples. This is in contrast to granitoid from southern China [14] which showed an increasing pattern of REE with SiO2 enrichment, especially HREE.

The depletion of REE along with enrichment of SiO2 suggests that REE mineral crystallize before the quartz crystallization in highly fractionated magma. Rare earth elements in granitoid are hosted by some accessories minerals. In Polewali and Masamba granitoid, the accessories mineral which responsible for the occurrences of these elements are zircon, apatite and monazite which supported by the positive correlation of Zr element and P2O5 content in bulk rock with REE content (Fig.7). The high ratio of HREE/LREE indicates that the enrichment of HREE is not pronounced from these samples. Overall, the content of REE in granitoid from Polewali and Masamba area are low to moderate in scale.

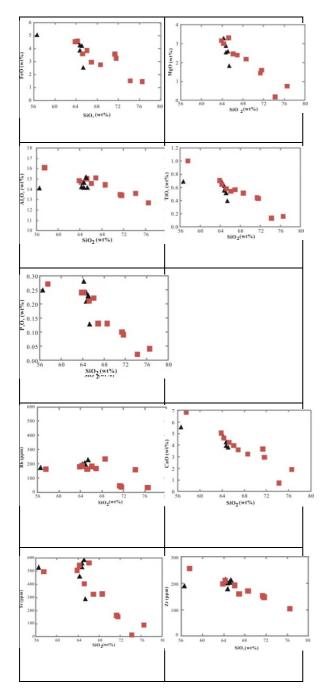


Figure 4. Variation diagram of major and trace element vs SiO_2

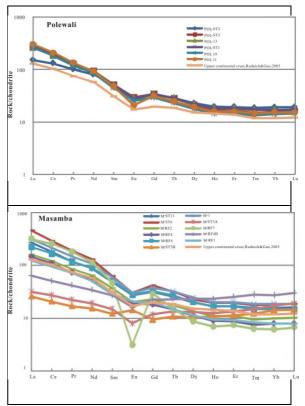


Figure 5. Chondrite normalized REE pattern of Polewali and Masamba samples. Upper continental crust composition shown as comparison.

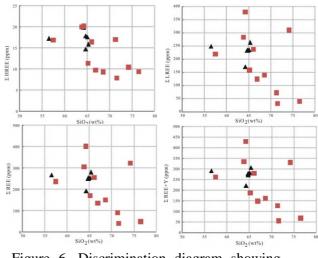


Figure 6. Discrimination diagram showing (a) SiO_2/Σ HREE, (b) SiO_2/Σ LREE, (c) SiO_2/Σ REE, (d) SiO_2/Σ REE + Y. Symbol as shown in Fig.2

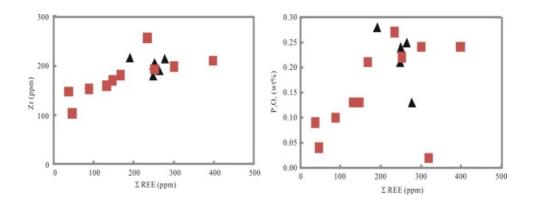


Figure 7. Diagram showing (a) Zr / Σ REE, (b) P₂O₅/ Σ REE. Symbol as shown in Fig.2

5. CONCLUSIONS

The granitoid from Polewali and Masamba area are dominated by granodiorite with granite, diorite, quartz monzonite and monzodiorite in composition. Most samples were plotted into metaluminous field, calc alkaline affinity and further classified as Itype granitoid. The total REE for Polewali samples range from 191 to 279 ppm (average of 249) whereas those from Masamba ranges from 47 to 399 ppm (average of 194). All samples show enrichment of LREE relative The REE-bearing minerals to HREE. detected from the rocks are zircon, monazite apatite shown chemical and as by composition.

6. ACKNOWLEDGEMENT

The first author is thankful to the MEXT Scholarship. Financial support from Global-Center of Excellent program of Kyushu University is gratefully acknowledged.

7. REFERENCES

- Wu, C.Y. 2008. Bayan Obo controversy: Carbonatite versus iron oxide-Cu-Au-REE. Resources Geology, 58, 4, 334-347.
- Wall. F., Mariano A.N., 1996. Rare [2] mineral in Carbonatite, earth Α discussion centred on the Kangankunde carbonatite, Malawi, In In Jones, A. P., Wall, F. and Williams, C. T. Rare Earth (eds.) Minerals: Chemistry, Origin, and Ore Deposits. Mineralogical Society Series 7, Chapman & Hall, London. 193-225.
- [3] S. Ishihara, R. Hua, M. Hoshino, H. Murakami, 2008. "REE abundance and REE minerals in granitoid in the Nanling Range, Jiangxi Province, Southern China, and generation of the REE rich weathered crust deposits", Resource Geology, 58 (4), 355 372.
- [4] Wu, C., Yuan, Z. and Bai, G. 1996.Rare earth deposits in China, In Jones,A. P., Wall, F. and Williams, C. T. (eds.) Rare Earth Minerals: Chemistry,

Origin,andOreDeposits.MineralogicalSocietySeries7.Chapman & Hall, London,281-310.

- [5] Imai, A., Sanematsu, K., Ishida, S., Watanabe, K., Boosayasak, J. 2008. Rare earth elements in weathered crust Sn-bearing Granitoid in Southern Thailand. Proceeding of the International Symposia on Geoscience Resources and Environments of Asian Terranes (GREAT 2008), 4thIGCP and 5th APSEC., Bangkok, Thailand. 232 – 237.
- [6] Djuri & Sudjatmiko. 1974. Geology map of the Majene and western part of the Palopo quarangles. 1 : 250.000 in scale. Geology Research and Development Centre. Bandung.
- [7] Sukamto, R., 1975. Geological map of Indonesia, Ujung Pandang sheet - scale
 1:1,000,000. *Geological Survey of Indonesia*.
- [8] Djuri, Sudjatmiko, Bachri, S., Sukido, 1998. Geology map of the Majene and western part of the Palopo quarangles.
 1 : 250.000 in scale (2nd edition). Geology Research and Development Centre. Bandung
- [9] Elburg, M. & Foden, J., 1998. Temporal change in arc magma geochemistry, northern Sulawesi, Indonesia. *Earth and Planetary Science Letters*, 163, 381-398Elburg, M. & Foden, J., 1999. Geochemical

response to varying tectonic setting; An example from Southern Sulawesi (Indonesia). *Geochimica et Cosmochimica Acta*, **63**(7/8), 1155-1172.

- [10] Simanjuntak, T.O., Rusmana, E.,
 Surono, Supandjono, J.B. Geology
 map of Malili Qaudrangle, Sulawesi.
 1: 250.000 in scale. Geology Research
 and Development Centre, Bandung.
- [11] Le Bas, M.J., Le Maitre, M.W., Streckeisen, A. Zanettin. B. 1986. A Chemical Classification of Volcanic Rocks Based on the Total Alkali-Silica Diagram. Journal of Petrology 27, 745 -750.
- [12] Sun, S.S., and McDonough, W.F. 1989.
 Chemical and isotopic systematic of oceanic basalts: implication for mantle composition and process. In: *Magmatism in Ocean Basins*. Eds. Saunders, A. D. & Norry, M. J., Geol. Soc. London Spec. Publ. 313-345.
- [13] Rudnick, R.L. and Gao, S. 2003. The Composition of the Continental Crust, In The Crust, Ed. R.L. Rudnick Vol. 3, Treatise on Geochemistry (eds. H.D. Holland and K.K. Turekian), Elsevier-Pergamon, Oxford, 1-64.
- [14] Wu, C., Huang, D-H., Guo, Z-X. 1989.
 REE geochemistry in the weathering process of the granites in Longnan County, Jiangxi province. Acta Geologica Sinica, 4,349-362 (in Chinese with English abstr.).