Rare Earth Elements on the A-type Unggan Granite and Its Comparison to the A-type Section of Sibolga Granite

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Abstract. Rare earth elements are often correlated to A-type granite. Unggan Granite is A-type granite which is located in Sijunjung Regency, West Sumatra. This study discusses the rare earth elements composition on A-type Unggan Granite and compares the element abundance to the nearest A-type granite from Sibolga. Total REE of the studied location in the part of Solok Quadrangle is averagely 860 ppm. XRF and ICP-MS at Center for Geology Survey were applied to measure the composition of major oxides, trace elements, and rare earth elements in the selected granite. Megascopically, the samples are dark red and coarse grain granites with quartz and feldspar as major minerals. Major oxides content of the samples affirms the samples as granite based on geochemistry composition. Ga, Nb, and Y amounts in the granites reveal the A-type affinity. The average REE abundance of Unggan Granite is higher than the A-type section of Sibolga Granite. The selected rock are classified in shoshonitic series with lanthanum and neodymium as the major REE. Negative Ce and negative Eu anomalies in normalized spider plot are detected in the samples. The granite characters are worth to be explored more for national income from rare earth elements resource.

1. Introduction

Rare Earth Elements is a set of chemical elements, especially the lanthanides, and were considered rare and isolated in the 19th century. The development of earth science uncovered that some parts of the REE are more abundant than silver (Ag), lead (Pb), copper (Cu), and mercury (Hg) in the Earth’s crust (Castor and Hedrick, 2006). Scandium (Sc, Z = 21) and yttrium (Y, Z = 39) are sometimes considered rare earth elements because they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties (i.e. Zepf, 2013; Migaszewski and Galuszka, 2015). This suite of elements is required in a variety of high-tech industries, such as permanent magnets, superconductors, rechargeable batteries, mobile phones, and security system devices. In Indonesia, REE has not become a major focus for both the government and industry although it is proven to be a strategic resource (Irzon et al., 2014).

Advanced analytical instruments are required along with careful preparation procedures to measure the REE content in any samples precisely. The integration of Instrumental Neutron Activation Analysis (INAA) with Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) was used in the study of soil samples (Salvini et al. 2006) while the Multi Collector (MC)-ICP-MS isotope dilution
device was applied on analysing the REE abundance in various certified reference material (CRM) (Kent et al., 2004). ICP-MS at the Geological Laboratory of the Center for Geological Surveys has been frequently utilized to identify, characterized, and predict the REE mobility in Indonesia. REE in the parent granite, weathered horizons, and tin mining tailings in Lingga Regency was studied using the Thermo Elemental X-Series ICP-MS device (Irzon et al., 2014; Irzon, 2015; Irzon et al., 2016). Although ultramafic rocks are not the primary domain of the REE, the differences between lherzolite and olivine-hornblende-pyroxenite rocks in North Konawe were portrayed on the spider diagram patterns (Irzon and Baharuddin, 2016).

The most abundant intrusive rock in upper continental crust, phaneritic, granular, and consist of three major minerals (feldspar, quartz, and mica) is the character of granitoid. The rock range from diorite to granite (i.e. Kurniawan, 2014; Hutabarat et al., 2016). Granitoids are interested to be explored because of their REE content, especially Light-REEs (i.e. Castor and Hedrick, 2006; Sahoo et al., 2011). Sumatra-Peninsular Malaysia is a complex tectonic region and was developed by several microplates (Pulunggono, 1985). Various granitoid locations were outcropped in the West Sumatra Province and tend to be emplaced in 122 ± 24 Ma (Katili, 1968). Granitoids in Sumatra and Peninsular Malaysia are generally grouped on four provinces: Eastern, Main Range, Western, and Volcanic Arc (Cobbing, 2005). The plutons in this study are situated on Volcanic Arc Province and are adjoining the Bukit Barisan Mountains as shown in figure 1.

Geochemistry uses the tools and principles of chemistry to explain the mechanisms behind geological systems. The combination of chemical and geological concepts have been applied in exploring the genesis of rocks and/or formations, trace mineral deposits, and even environmental pollutions. Geochemistry including REE, the characterization of granitoids from Unggan, Sijunjung Regency - West Sumatra Province, is the aim of this study. The REE abundance on Unggan Granite is then compared to the nearest A-type granite from Sibolga (Setiawan et al., 2017). The geochemistry composition is then utilized in chemistry based diagrams to understand about the granitoids more broadly. REE identification might encourage further exploration activities as a strategic resource.

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**Figure 1.** Studied granitoids are located in Unggan on the Volcanic Arc Province (modified from Cobbing, 2005). ★ = studied location
2. Material and Methods

Two granitoid samples were taken during fieldwork at Unggan, Sumpur Kudus – West Sumatra. The first rock, P-30, was obtained near the roadway and was described as reddish brown, granular, very coarse grain, and slightly weathered granitoid. P-31 is brighter but smaller grain pluton just near a small river in Unggan. Megascopically, the rocks are majorly composed of quartz and K-feldspar. Some field conditions are illustrated in figure 2.

The selected samples were analyzed in Geological Laboratory – Center for Geological Survey. Prior to chemical preparation, the samples were dried under direct sunlight and then were crushed to 200 mesh grain size to simplify the destruction process because the area of the reaction is directly proportional to the speed of reaction. One gram of sample that was transformed into pressed pellets then was analyzed using XRF to determine the major oxides contents. The Loss on Ignition (LOI) was measured to determine the amount of volatile material in samples such as hydrate compounds, hydroxy compounds, and carbon dioxide. Only 0.1 gram of rock was needed for subsequent destruction with three types of acids prior to ICP-MS analysis: nitric acid (HNO3, ultra-pure grade), formic acid (HCOOH, ultra-pure grade), and perchloric acid (HClO4, pro analysis grade). The blank solution and five levels of the calibration solutions (0.1 ppb, 1 ppb, 5 ppb, 10 ppb, and 50 ppb) were prepared to be measured together with the selected samples. Geochemistry components of the samples were obtained by comparing the count per second (CPS) of the calibration solution series against the sample solutions.

ICP-MS should be tuned up before analyzing element concentration in the samples to gain its good stability and the detection capabilities which affect the measurement result. Sample introduction to ICP-MS device begins with the pumping process and ends in a mass spectrometer which detects the element concentration of the sample (Irzon, 2010). The sample solution is nebulized toward sample injector and then is transformed into plasma with the argon gas in the plasma torch. The computer program converts CPS of the samples from the mass spectrometer to become element abundance based on a comparison of the calibration solution curve.

3. Result and Discussion

The composition of major oxides in the two Unggan Granite samples is not much different. The rocks show felsic character on the high SiO2 content (> 68%). The abundance of Fe2O3 is lower than K2O and Al2O3 of 2.61%, 5.18%, and 16.7% respectively. The significant difference between the two examples is that the composition of CaO at P-31 (1.6%) is almost twice that of P-30 (0.88%). Although the amount of Na2O in P-31 was detected lower than P-30, the first sample contains more TiO2, MgO, and P2O5 than the later one. Higher LOI in P-30 is parallel to the megascopic description
that the rock tends to be more weathered. The major oxide, rare elements, and REE compositions in
the examples of the study are summarized in Table 1.

Based on the geochemical composition, the two samples belong to the granite group in De la Roche
et al. (1980) diagram as shown in figure 3a. P-30 and P-31 are derived from the same magma series
(shoshonite) with reference to the SiO$_2$ versus K$_2$O diagram (Peccerillo and Taylor (1976)) (figure
3b). On the other hand, the A-type section of Sibolga Granit depicts high-K calc-alkaline alkali
feldspar granite characters. The peralkaline rock is indicated on smaller aluminum oxide content than
sodium oxide plus potassium oxide. High Al rocks were further classified into two groups:
metaluminous with Al$_2$O$_3$ <(CaO + Na$_2$O + K$_2$O) and peraluminous with opposite conditions (Shand,
1943). Both of Unggan Granite and the A-type section of Sibolga Granite are peraluminous based on
A/CNK - A/NK diagrams (Shand, 1943) as shown in figure 3c.

The high contents of SiO$_2$, Na$_2$O+K$_2$O, Nb, Ta, Y, Cs, Ga, U, Th, and REE are the A-type granite
characters. However, the abundances of MgO, CaO, Ba, Sr, P, Ti, Ni, Cr, Co, V in this type of pluton
tend to be low (i.e. Singh and Vallinayagam, 2012; Irzon, 2017; Setiawan et al., 2017). Grouping the
two samples as A-type granite samples are supported by the high sodium oxide plus potassium oxide contents
(Table 1 and Figure 4b) of 8.15% - 9.04%. The A-type granite is attractive to be explored in
correlation to the economic REE content as previous studies stated that REE is more concentrated in
this type of pluton (i.e. Irzon, 2017). The number of REE in the Unggan Granite samples is 1,369 ppm
(P-30) and 355 ppm (P-31). This REE composition is much higher than the average of the B facies of
this type of pluton (i.e. Irzon, 2017). The number of REE in the A-type section of Sibolga Granite are supported by the high sodium oxide plus potassium oxide contents
in the previous study (Setiawan et al., 2017).

REE numbers should be normalized to a certain parameter to eliminate the Oddo-Harkins effect,
and make it easier to be studied (i.e. Irzon and Baharuddin, 2016). The abundance of REE in this study
was normalized using the primitive mantle value (McDonough, 1995). All REE in both samples is
very high, 10-800 times than the primitive mantle as shown in figure 5. In the spider diagram, similar
patterns are detected: a fairly sharp subduction of the Light-REE and the relatively flat pattern flat on
Heavy-REE to conclude that the rocks formed


| Major Oxides (%) | P-30 | P-31 | Trace Elements (ppm) | P-30 | P-31 | REE (ppm) | P-30 | P-31 |
|------------------|------|------|----------------------|------|------|-----------|------|------|
| SiO$_2$          | 68.50| 68.80| Sc                   | 3.86 | 4.42 | La        | 435  | 105  |
| TiO$_2$          | 0.26 | 0.34 | Ga                   | 37   | 25.3 | Ce        | 94.6 | 80.7 |
| Al$_2$O$_3$      | 17.10| 16.30| Sr                   | 125  | 184  | Pr        | 106  | 22.9 |
| Fe$_2$O$_3$      | 2.32 | 2.90 | Y                    | 233  | 34.8 | Nd        | 401  | 89   |
| MnO              | 0.04 | 0.04 | Nb                   | 25.4 | 24.9 | Sm        | 88.9 | 17   |
| CaO              | 0.88 | 1.60 | Cs                   | 5.16 | 4.05 | Eu        | 6.37 | 1.88 |
| MgO              | 0.46 | 0.59 | Ba                   | 676  | 615  | Gd        | 32.5 | 6.62 |
| Na$_2$O          | 3.59 | 3.24 | Ta                   | 2.07 | 1.33 | Tb        | 10.7 | 1.74 |
| K$_2$O           | 5.45 | 4.91 | Ti                   | 6.57 | 4.19 | Dy        | 82.5 | 12.8 |
| P$_2$O$_5$       | 0.10 | 0.12 | Ho                   | 15   |      |          | 2.36 |
| SO$_3$           | 0.02 | 0.02 | Er                   | 42.8 |      | Tm        | 5.8  | 0.92 |
| LOI              | 1.50 | 0.98 | Yb                   | 44   |      | Lu        | 4.26 | 0.67 |

REE patterns are detected: a fairly sharp subduction of the Light-REE and the relatively flat pattern flat on
Heavy-REE to conclude that the two samples are originated from the similar magma source.

Subsequent uniformity is the negative Ce and negative Eu anomalies to explain that the rocks formed
in the previous study (Setiawan et al., 2017).

REE composition in Unggan Granite is relatively higher than the Sibolga Granite. The next difference
between the two plutons is the occurrence of positive Tm anomaly which might reflect the Tm-bearing
mineral in the A-type section of Sibolga Granite.

Tabel 1. Major oxides, trace elements, and REE composition of the two Unggan Granite samples.
Figure 3. Geochemistry based diagrams: a) R1-R2 classification (De la Roche et al., 1980); b) Tectonic diversification of Peccerillo and Taylor (1976); and c) A/CNK-A/NK diagram (Shand, 1943). ▲ = Unggan Granite and ● = A-type section of Sibolga Granite.

Figure 4. Samples plot on Whalen et al. (1987) discriminations that show A-type granite characters: a) 1000*Ga/Al vs. Ce; b) 1000*Ga/Al vs Y; and c) 1000*Ga/Al vs Nb. ● = P- 30 and ▲ = P- 31.
Figure 5. REE spider diagram which is normalized to primitive mantle value of Sun and McDonough (1995). Symbols are the same as figure 3. Positive Tm anomaly is detected on Sibolga Granite.

4. Conclusion
The combination of chemical and geological based analysis is very useful in understanding the natural process. The composition of major oxides, trace elements, and REE of the two pinkish granitoid rocks from the Unggan region was measured using XRF and ICP-MS devices. The rocks are categorized as granite, formed on the shosonite series, and are peraluminous based on their geochemical composition. The samples are relatively fresh refer to LOI of 0.98% -1.5%. REE in the samples is 355 ppm and 1,369 ppm with lanthanum and neodymium as the most abundant elements. The high contents of SiO$_2$, Na$_2$O + K$_2$O, Ga, Y, and REE amplify A-type granitoid character. Rocks were mostly formed in the oxidative state of a parental magma which experienced plagioclase reduction during the differentiation process. The REE content in Unggan Granite is relatively higher than the A-type section of Sibolga Granite which indicates positive Tm anomaly.

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