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Geochemical implication of Eu isotope ratio in the anorthosite: a new evidence of Eu isotope fractionation by feldspar crystallization

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Rare earth element geochemistry is important for understanding the evolution of the crust-mantle system. Europium (Eu) exists in divalent and trivalent states, and Eu\(^{2+}\) can be substituted for Ca\(^{2+}\) during plagioclase feldspar crystallization in reducing magmas. This leads to positive Eu anomaly in Ca-plagioclase-rich anorthosite derived from the mantle and negative Eu anomalies in fractionated silica-rich crustal rocks. But while Eu anomalies are well known, Eu has only two stable isotopes (\(^{151}\)Eu and \(^{153}\)Eu), Eu isotope ratios have not been compared with Eu anomalies in igneous rocks. Here we report a systematic variation of the Eu isotope ratio (\(\delta^{153/151}\)Eu) from igneous rocks including anorthosite. This study finds a linear relationship between Eu anomalies and Eu isotope ratios in igneous rocks, with rhyolites and highly fractionated granites having large negative Eu anomalies and negative \(\delta^{153/151}\)Eu values but
anorthosites having large positive Eu anomalies and positive $\delta^{153/151}$Eu values. Particularly, in
the area of the highly fractionated igneous rocks with negative Eu anomaly, the Eu isotope
fractionation proceeds with different slope according to the degree of magmatic differentiation
in extrusive (volcanic) and intrusive (plutonic) rocks. Our finding reveals that Eu isotope
fractionation in igneous rocks will provide new information related to magmatic differentiation
and plagioclase feldspar fractional crystallization including anorthosite formation in the crust-
mantle.

Key words: Eu isotope fractionation, Eu anomaly, magmatic differentiation, feldspar
crystallization, anorthosite

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Rare earth elements (REEs) and their radiogenic isotope geochemistry (especially the $^{147}$Sm-$^{143}$Nd and $^{138}$La-$^{138}$Ce system) have provided abundant information for interpreting the geochemical evolution of Earth and extra-terrestrial materials as a result of their similar chemical behavior and continuously varying atomic masses of REEs. In particular, the geochemistry of chondrite-normalized REEs provides valuable petrogenetic information during the magma evolution processes such as partial melting from the mantle-derived rocks or crystallization from the magma (Coryell et al., 1963; Fowler and Doig, 1983; Masuda, 1962; Shearer and Papike, 1989; Weill and Drake, 1973). Most REEs have a stable (+3) state in natural systems; however, Eu can exist in both divalent and trivalent state under magmatic redox conditions, which indicates that the behavior of Eu during magmatic differentiation depends on the oxygen fugacity and crystallization of minerals (Burnham et al., 2015). Fractional crystallization is considered the dominant mechanism of magmatic differentiation and isolates crystallized-minerals from magma step by step (Bowen, 1928). Positive or negative Eu anomalies from the igneous rocks are produced by feldspar (particularly plagioclase) fractional crystallization with removal or accumulation, respectively, of plagioclase during magma evolution and have been interpreted as indicating the degree of differentiation of the source magma (Fowler and Doig, 1983; Shearer and Papike, 1989; Weill and Drake, 1973). For example, extremely large positive Eu anomaly in the anorthosite is due to concentration of Eu due to be substituted into the Ca site in plagioclase feldspar because the Ca$^{2+}$ site in feldspar readily accepts Eu$^{2+}$. However, highly fractionated granite and high-silica rhyolite shows extremely large negative Eu anomalies.
Eu has only two isotopes, $^{151}\text{Eu}$ (47.81\%) and $^{153}\text{Eu}$ (52.19\%) (Rossman and Taylor, 1998). Though $^{151}\text{Eu}$ decayed to $^{147}\text{Pm}$ by $\alpha$ decay with the half-life $T_{1/2}=5\times10^{18}\text{yr}$ (Belli et al., 2007), $^{151}\text{Eu}$ can be considered as a stable isotope in earth and solar system. In addition, recently, Lee and Tanaka (2021a) reported Eu isotope fractionation due to light Eu isotope enrichment ($^{151}\text{Eu}$) in highly fractionated granite and high-silica rhyolite with large negative Eu anomalies. The authors proposed that the heavier Eu isotope ($^{153}\text{Eu}$) might be enriched in anorthosite with large Eu positive anomaly due to Ca-feldspar crystallization.

At present, there have been no report on Eu anomaly and Eu isotope ratio in anorthosite including gabbro as well as the volcanic rocks such as andesite and trachyte. Therefore, here, we report the Eu isotope ratio and Eu anomaly among plutonic (intrusive) rocks such as anorthosites, gabbro and volcanic (extrusive) rocks such as andesite and trachyte, and compare the data of Eu isotope ratio from the igneous rocks such as basalt, rhyolite and granitoids.

The objective in this article is to find a possibility of a new tracer for studying the relationship between Eu anomaly in the chondrite-normalized REE pattern and the Eu isotope fractionation by comparing the magnitude of Eu anomaly and the degree of Eu isotope fractionation in various kinds of igneous rocks such as the extrusive rocks and intrusive rocks including anorthosite.

**SAMPLES AND EXPERIMENTAL METHODS**

*Samples*
In order to measure Eu isotope ratio of various kinds of igneous rocks, 49 igneous rock samples were used for Eu isotope ratio and REE abundance determination, of which 25 samples were geochemical reference materials purchased from the United States Geological Survey (USGS) and the Geological Survey of Japan (GSJ), while the others were anorthosites, granitoids and trachytes from Korea and Antarctica. The 25 geochemical reference materials in this study were as follows; Seven basalts (BCR2, BHVO2 and BIR1a purchased from the USGS; JB1a, JB1b, JB2 and JB3 from the GSJ), four andesites (AGV2 from USGS; JA1, JA2 and JA3 from GSJ), four rhyolites (RGM2 from USGS; JR1, JR2 and JR3 from GSJ), one diabase (W-2a from USGS), one dolerite (DNC1a from USGS), two gabbros (JGb1, JGb2 from GSJ), one syenite (STM2 from USGS), and five granites (G2 and GSP2 from USGS; JG1a, JG2 and JG3 from GSJ). The 24 rock samples from Korea and Antarctica are as follows; fourteen granites and five anorthosites from Korea, and five trachytes from Antarctica. Because there was no SRM trachyte, we collected five trachytes from Antarctica.

Sample digestion and determination of REE concentrations

The sample digestion procedure was based on the approach of Lee et al (2016). Approximately 100~200 mg of each sample powder was decomposed by a 2:1 mixture of 2~4 mL of concentrated HF (29M) and 1~2 mL of concentrated HNO₃ (16M) at ca. 160 ºC for more than 72 hours in 15 mL Savillex vial. After the addition of 0.1~0.2 mL of concentrated HClO₄, the decomposed sample solution was heated to dryness at ca. 180 ºC for more than 1 day. The cakes were re-dissolved by a mixture of 1 mL of concentrated HCl and 0.5 mL of concentrated HNO₃ at ca. 160 ºC for 1 day. Each sample solution was dried again, and diluted in 10 ml of 6 M HCl as a stock solution. Of this 10 ml stock solution, 0.5~1 ml stock solution was used to
determine the rare earth element (REE) concentrations, and the remainder was used for
determination of Eu isotope ratio.

Before Eu purification, we analyzed REE concentration of the sample using inductively
coupled plasma mass spectrometry (ICP-MS, NexION350, Perkin Elmer) at KIGAM.
Although Eu anomalies of the 25 geochemical reference rocks (USGS, GSJ) have previously
been characterized, we also reanalyzed their REE abundances for comparison. The analyzed
REE data from the geochemical reference sample powders (SRM) agreed with the
recommended values within 5~10%.

Experimental procedures for determination of Eu isotope ratio

Recently, Lee and Tanaka (2019, 2021b) developed a method for determining highly
precise and accurate Eu isotope ratio using Sm spike as an internal standard in combination
with standard-sample-standard bracketing mass bias correction (C-SSBIN). In addition, Lee
and Tanaka (2021a, 2021b) also showed that incomplete Eu purification from the geological
material lead to change in the Eu isotope ratio, that is, pseudo-fractionation of Eu isotope ratio.

In this study, Eu was separated from the obtained REE fraction using 0.12 M 2-
hydroxyisobutyric acid (HIBA) with the pH adjusted to ~4.60 (Lee and Tanaka, 2019, 2021b).
To minimize isobaric interference because we used Sm which was prepared from ultrapure
Sm$_2$O$_3$ produced by Alfa Aesar as a spike for normalization of Eu isotopes, we always checked
for tailing of both Gd and Sm.

Eu isotope ratios were measured using multicollector inductively coupled plasma mass
spectrometry (MC-ICP-MS; Neptune Plus, Thermo Fisher Scientific Ltd.) in static mode with
nine Faraday cups at KIGAM. The instrument was tuned to achieve high sensitivity while maintaining flattened square peaks and stable signals enough to ensure accurate measurements. The gain on each Faraday cup was monitored daily to ensure normalization of its efficiency.

Sample dilution for Eu isotope measurement by MC-ICP-MS was performed with 2% HNO₃ which was prepared from 60% ultrapure HNO₃ (Merck, Darmstadt, Germany) and DIW (Milli-Q system, Millipore, Milford, USA). We used a diluted solution of NIST 3117a (10,000 μg/mL, Lot No. 120705) as an in-house standard solution for comparison of the Eu isotope ratios.

The isotopes ¹⁴⁷Sm(L4), ¹⁴⁹Sm(L3), ¹⁵⁰Sm(L2), ¹⁵¹Eu(L1), ¹⁵²Sm(C), ¹⁵³Eu(H1), ¹⁵⁴Sm(H2), ¹⁵⁵Gd(H3), and ¹⁵⁷Gd(H4) were monitored simultaneously using nine Faraday cups for Sm normalization and Gd interference correction by the Gd matrix (Lee and Tanaka, 2021b).

Data acquisition consisted of 1 block of 50 cycles with an integration time of 4.194 seconds and a sample aspiration rate of 80-100 μL/min. Peak centering was performed at the beginning of each analysis and 250 s of washout time was used between sample measurements. Blanks were checked during, before, and after each sample measurement. Operating conditions and data acquisition parameters, including cup configuration, are the same as Lee and Tanaka (2021a, 2021b). In determination of Eu isotope ratio, we used ¹⁴⁷Sm/¹⁴⁹Sm (1.0868, Dubois et al., 1992) for normalization to obtain an optimum value of Eu isotope fractionation from the natural materials because of isobar matrix problem by ¹⁵⁴Gd due to incomplete separation from the geological rock during ¹⁵⁰Sm/¹⁵⁴Sm normalization (Lee and Tanaka, 2021a, 2021b). Eu isotope fractionation is represented in standard δ-notation in per mil relative to the NIST3117a Eu standard solution as follows: δ¹⁵³/¹⁵¹Eu = 1,000 × [(¹⁵³Eu/¹⁵¹Eu_sample)/(¹⁵³Eu/¹⁵¹Eu_NIST3117a)] – 1].
RESULTS

Rare Earth Element concentration in the extrusive rocks and intrusive rocks

In order to validate the accuracy of the REE data in this study, we determined REE concentrations of 25 geochemical standard reference materials (SRM) produced by USGS and GSJ. REE abundances of the geochemical reference materials from the United States of Geological Survey (USGS) and Geological Survey of Japan (GSJ) measured in this study are reported in Supplementary Table S1. In addition, REE concentrations of the local igneous rocks in Korea and Antarctica including anorthosite are presented in Table 1.

Fig. 1. Chondrite (McDonough and Sun, 1995)-normalized REE pattern of standard reference materials (SRMs) of USGS and GSJ. (a), (b) and (c) are SRMs for volcanic (extrusive) rocks whereas (d), (e) and (f) are SRMs for intrusive rocks such as gabbro, diabase and granitoids. In this paper, we classified dolerite and diabase as plutonic rocks rather than volcanic rocks. The REE abundances of all SRMs were re-measured from this study (see Table S1). REE patterns by solid black dots were drawn by recommended values for each SRM from USGS and GSJ.
Figures 1 and 2 are chondrite-normalized REE patterns for SRMs and Korea and Antarctic igneous rocks, respectively. In Fig. 1, REE patterns from the volcanic rocks such as basalt, andesite and rhyolite were drawn in Fig. 1a~1c whereas those from the plutonic rocks such as gabbro and granitoids were drawn in Fig. 1d~1f. The chondrite-normalized REE patterns from various kinds of igneous rocks in Figs. 1 and 2 clearly show variation of the magnitude of Eu anomaly due to feldspar crystallization during magmatic differentiation even though they are not cogenetic igneous rocks. Particularly, the anorthosites in Fig. 2a has strikingly large Eu positive anomaly.

Fig. 2. Chondrite (McDonough and Sun, 1995)-normalized REE pattern of Korean and Antarctic igneous rocks. Except (b) trachyte, the others are all collected from Korea. Trachyte was collected from Antarctica. The REE abundances of Korean anorthosites and Antarctic trachytes were re-measured from this study. REE patterns of Korean granites are from Lee et al. (2004, 2006, 2008, 2013).
Eu isotope ratio in the extrusive rocks and intrusive rocks

Eu isotope ratio and magnitude of Eu anomaly from various kinds of the igneous rocks in this study are presented in Table 2. For comparison, in Table 2, we divided the samples into SRM and local igneous rocks. The $^{153}/^{151}$Eu value of anorthosite all are positive, indicating that heavier Eu isotope ($^{153}$Eu) was enriched compared to lighter Eu isotope ($^{151}$Eu).

DISCUSSION

A major objective of this study is to examine the relationship between the magnitude of Eu anomaly due to feldspar crystallization during magmatic differentiation and Eu isotope differentiation. Therefore, we first compared the magnitudes of Eu anomalies with the $\delta^{153/151}$Eu values of the 49 samples to investigate the possibility that Eu isotope fractionation had occurred during magma differentiation (Fig. 3). Figure 3 illustrates three geochemical characteristics of Eu isotope fractionation as follows; 1) The $\delta^{153/151}$Eu values of the highly fractionated granites and rhyolites with extremely large negative Eu anomaly are negative, whereas the anorthosites with extremely large positive Eu anomaly show relatively large positive $\delta^{153/151}$Eu values. This contrast indicates that the highly fractionated igneous rocks, which are emplaced from felsic magma in an upper crustal environment, were enriched in the lighter Eu isotope ($^{151}$Eu), whereas Ca-plagioclase-rich anorthosite, which are derived from the mafic magma in a lower crustal environment, were enriched in the heavier Eu isotope ($^{153}$Eu). 2) The $\delta^{153/151}$Eu value in the igneous rock varies systematically with magnitude of the Eu anomaly. 3) Another interesting feature of the Eu fractionation trends in the volcanic and
plutonic rocks is that intrusive rocks (red symbols in Fig. 3) and extrusive rocks (green and blue symbols in Fig. 3) are distributed with different slopes.

Fig. 3. Variation of Eu isotope ratio according to magnitudes of Eu anomalies from igneous rocks. The error bars represent uncertainties (2SD) of the average δ$^{153/151}$Eu values from some of igneous rock samples.

Ismail et al. (1998) employed cation exchange chromatography and concluded that an isotope effect in the Eu$^{2+}$/ Eu$^{3+}$ exchange reaction may occur in aqueous solutions; specifically, they found isotope effects in which the heavier isotope $^{153}$Eu is enriched in Eu$^{2+}$ in the Eu$^{2+}$/Eu$^{3+}$ electron exchange system. The positive Eu anomaly in anorthosite can easily be explained by the substitution of Eu$^{2+}$ for Ca$^{2+}$ in plagioclase during differentiation of the anorthositic (primary) magma either in the upper mantle or at the lower crust. Therefore, we can suggest that the enrichment of heavier isotope $^{153}$Eu in the anorthosites with large positive Eu anomaly should be explained due to isotope effects in Eu$^{2+}$/Eu$^{3+}$ electron exchange system during Ca-plagioclase accumulation in the anorthositic magma. Moreover, the systematic
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al., 2013; Shollenberger and Brebbecka, 2020; Hu et al., 2021). This means that combined
information using chondrite-normalized REE pattern, radiogenic isotope geochemistry and δREE will provide new constraints for understanding more clearly the processes in our Earth and Planetary system such as redox conditions in the mantle and/or crust, early earth formation, and crust/mantle differentiation.

CONCLUSION

We compared the magnitude of Eu anomaly in the chondrite-normalized REE pattern from various kinds of igneous rocks such as the extrusive rocks and intrusive rocks including anorthosite and their Eu isotope ratio from the fractionation. The anorthosites having large positive Eu anomalies show a geochemical characteristic of a heavier Eu isotope (\(^{153}\text{Eu}\)) enrichment (i.e., positive \(\delta^{153/151}\text{Eu}\) value) whereas the rhyolites and highly fractionated granites having large negative Eu anomalies show a geochemical characteristic of a lighter Eu isotope (\(^{151}\text{Eu}\)) enrichment (i.e., negative \(\delta^{153/151}\text{Eu}\) value). Particularly, our results clearly showed that variation of the magnitude of Eu anomaly and Eu isotope fractionation in igneous rocks has systematic correlation, suggesting that Eu isotope fractionation in igneous rocks should be produced by feldspar crystallization during magma evolution. In addition, the Eu isotope fractionation in the highly fractionated volcanic and plutonic rocks was proceeded with different trend, implying that the Eu isotope fractionation from the intrusive and extrusive magma in the crustal environment may occur under different mechanism or geochemical environment.
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REFERENCES


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Fig. 2. Chondrite (McDonough and Sun, 1995)-normalized REE pattern of Korean and Antarctic igneous rocks. Except (b) trachyte, the others are all collected from Korea. Trachyte was collected from Antarctica. The REE abundances of Korean anorthosites and Antarctic trachytes were re-measured from this study. REE patterns of Korean granites are from Lee et al. (2004, 2006, 2008, 2013).

Fig. 3. Variation of Eu isotope ratio according to magnitudes of Eu anomalies from igneous rocks. The error bars represent uncertainties (2SD) of the average $\delta^{153/151}$Eu values from some of igneous rock samples.
<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Area</th>
<th>Sample Name</th>
<th>La (ppm)</th>
<th>Ce (ppm)</th>
<th>Pr (ppm)</th>
<th>Nd (ppm)</th>
<th>Sm (ppm)</th>
<th>Eu (ppm)</th>
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<td>Trachyte</td>
<td>Mt. Melbourne (Antarctica)</td>
<td>M17102801-3</td>
<td>78.42</td>
<td>190.5</td>
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Table 2. Eu isotope ratio from SRM and local igneous rocks in this study

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<th>Trachyte (Antarctica)</th>
<th>Rhyolite (SRM)</th>
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Intrusive (plutonic) rocks

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1) The samples of Bold character are SRMs of USGS and GSJ.
2) The magnitude of Eu anomaly is defined as the ratio $\text{Eu}_0/\text{Eu}^*$ where $\text{Eu}^*$ is $\sqrt[4]{\text{Sm}_{0.4} \times \text{Gd}_{0.4}}$.
3) Eu isotope ratio normalized by $^{147}\text{Sm}^{148}\text{Sm}$ isotope pair (Lee and Tanaka, 2021a, 2021b).
4) Eu isotope data (Bold Italic numbers) are from Lee and Tanaka (2021a)
Plutonic rocks
- SRM and Korean Granitoids
- Korean anorthosites
- SRM syenite
- SRM Gabbros
- SRM diabase
- SRM dolerite

Volcanic rocks
- SRM rhyolites
- SRM andesites
- SRM basalts
- Antarctic trachyte

\[ \delta^{153/151}\text{Eu} = 0.0578 \times \ln(\text{Eu}/\text{Eu}^*) - 0.0126 \]
\[ (R=0.729) \]

\[ \delta^{153/151}\text{Eu} = 0.1364 \times \ln(\text{Eu}/\text{Eu}^*) - 0.0275 \]
\[ (R=0.709) \]
Table S1. Concentrations of rare earth elements of standard reference materials (SRMs) measured in this study.

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<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
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[^1]: Units in ppm; error values shown in parentheses; samples measured in triplicate except as noted.

Note: Table entries with an asterisk (*) indicate that the measurement is reported in this study.

[^2]: BCR2 was measured as a quality control sample.

[^3]: AGV2 was measured as a quality control sample.
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1) The magnitude of Eu anomaly is defined as s the ratio Eu/Er where Er* is SQRT(Sm x Gd). The magnitude was calculated based on the values of Sm, Eu and Gd from the reference.

2) The bold number of this raw are recommended value by United States of Geological Survey (USGS) or Geological Survey of Japan (GSJ)