Gd matrix effects on Eu isotope fractionation in geological rocks using MC-ICP-MS: Optimizing Europium isotope ratio measurements in geological samples

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Abstract

Eu has only two isotopes (^{151}Eu and ^{153}Eu). Eu and Gd are one of the rare earth elements that are very difficult to completely separate from each other. Eu isotope ratio can be determined by MC-ICP-MS using internal Sm or Gd spikes to correct for mass discrimination. NIST3117a ultrapure chemical reagent shows almost no Eu isotope fractionation regardless of the kind of normalization isotope pair. However, Eu isotope ratio in the silicate rocks was effected by Gd matrix during MC-ICP-MS measurement if a trace amount of Gd impurity remains in the purified Eu fraction. In this report, we tried to determine optimizing conditions for precise and accurate Europium isotope ratio measurements in geological samples using MC-ICP-MS. The pure Eu fraction with almost no Gd matrix separated from geological samples and NIST3117a ultrapure chemical reagent show almost same degree of Eu isotope fractionation regardless of the kind of normalization isotope pair. However, Eu isotope ratio in the silicate rocks was effected by Gd matrix during MC-ICP-MS measurement using if ^{154}Gd interference relative to ^{154}Sm as internal standard is more than ca. 0.1%. Particularly, highly fractionated granite and high silica volcanic rock with extremely low Eu concentration compared to Gd require high –purity Eu separation with a high recovery rate to obtain the true value of the Eu isotope fractionation in the geological rocks.

Key words: Geological rocks, Eu isotope fractionation, Sm and Gd internal standard, Gd matrix, MC-ICP-MS

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1. Introduction

Abundances and isotopic ratios of REEs provides valuable information to the evolution of Earth and other planetary systems. Among the REEs, Eu holds considerable potential as a geochemical tool because it can assume both divalent (+II) and trivalent (+III) oxidation states. Most rare earth elements exist only in the trivalent state (+III) in nature. The divalent oxidation state of Eu may cause elemental fractionation during magmatic evolution and may specifically indicate oxygen fugacity of the magmatic system [1-2]. Dauphas et al. [3] proposed a possibility of Eu isotope variation in bulk rocks and individual minerals due to redox condition in the mantles of Earth and other planets. Therefore, precise and accurate determination of Eu isotope ratio in the geological materials is challenging subject to demonstrate Eu isotope fractionation during the evolution of the Earth and solar system.

The development of MC-ICP-MS methodologies, which can precisely and accurately measure isotopic ratios for a broad range of elements, has allowed for more detailed investigation of different geochemical and cosmochemical proxies. Since Moynier et al. [4] reported Eu isotope ratio from some meteorites, several researchers have developed analytical methods to measure stable isotope ratios of rare earth elements [4-11] using MC-ICP-MS and TIMS. Moynier et al. [4] had reported Eu isotope ratios in chondritic and environmental materials determined using a Sm isotope pair (^{147}Sm-^{149}Sm spike) as an internal standard. Eu isotope ratio can be determined by SSB (standard-sample-bracketing, [11]) or C-SSBIN (Combined Standard-Sample-Bracketing Internal Normalization, [4, 9, 10]) method. Particularly, Lee and Tanaka [10] reported a method to determine Eu isotope ratio of high-purity commercial Eu reagents precisely and accurately by MC-ICP-MS using Sm internal standard. The authors also determined Eu isotope ratios from some geochemical reference materials (Table 1). In Table 1, except JG1a, the value of $\delta^{151/153}$Eu$_{NIST3117a}$ do not show large difference though the stability of the data is that C-SSBIN method is better than SSB method. However, JG1a seems to indicate that Eu isotope ratio varies depending on the measurement method (C-SSBIN and SSB).

Analysis of Eu isotopic values from geological or meteoritic materials requires purification of Eu to prevent interference by coexisting elements. Gadolinium (Gd) especially can interfere with detection of Sm peaks that serve as an internal standard during measurement. Li et al. [12] reported that the distribution coefficient of Gd and Eu between

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64HIBA and AG50W-X8 resin during column chromatography overlapped, suggesting that 65both elements should elute together during the HIBA chemistry. Lee and Tanaka [10] 66described Eu separation method from REEs using 2-hydroxyisobutyric acid (HIBA, 0.12M) 67as an eluant. However, we recently noticed that Eu isotopic determination method by MC-68ICP-MS using Sm isotope spikes developed by Lee and Tanaka [10] carry the risk of Gd 69matrix effects due to interference of ^{154}Sm and ^{154}Gd isobars in the high silica igneous ricks.

70   In this research, we checked Gd matrix effects during Eu isotope ratio determination by 71MC-ICP-MS using a Sm internal standard and suggest an optimal method for determining Eu 72isotope ratio from the geological rocks precisely and accurately. We used a commercial 73geochemical reference materials to compare Eu isotopic ratio estimates normalized according 74to different ratio pairs, ^{147}Sm-^{149}Sm, ^{147}Sm-^{152}Sm, ^{147}Sm-^{154}Sm, ^{149}Sm-^{154}Sm, ^{150}Sm-^{154}Sm and 75^{155}Gd-^{157}Gd. The objective was to identify an optimal normalizing pair to minimize ^{154}Gd 76interference with ^{154}Sm signals used to normalize Eu isotopic ratios. This research also found 77that Eu isotopic ratio estimates depend on thorough separation of Gd prior to mass spectral 78analysis.

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802. **Experimental Procedures**

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822.1. Reagents and methods

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84   The procedures used here followed those published in Lee and Tanaka [10]. Sample 85solutions for Eu isotopic measurements by MC-ICP-MS consisted of 2% HNO_3 prepared 86from 60% ultrapure HNO_3 (Merck, Darmstadt, Germany) and deionized water (Milli-Q 87system, Millipore, Milford, USA). NIST3117a was used as an in-house standard solution for 88determining Eu isotope ratios from geochemical reference materials. An in-house Sm 89solution was prepared from ultrapure Sm_2O_3 produced by Alfa Aesar. This, along with 90NIST3118a (Lot: 992004), was used as an in-house Gd spike for normalizing Eu isotopic 91ratios. The aforementioned Gd standard reagent was also used to investigate ^{154}Gd isotope 92interference with the ^{154}Sm spike used to measure Eu isotope ratio by MC-ICP-MS.

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942.2. Geological samples

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96   This study used well-known geochemical reference rocks BCR2, BIR1a, AGV2 and GSP2

97curated by the U.S. Geological Survey and JB3, JG1a and JGb2 curated by the Geological

98Survey of Japan the U.S. Geological Survey. These are three basaltic rocks (BCR2, BIR1a

99and JB3), two granitic rocks (GSP2, JG1a), one gabbro (JGb2) and andesite (AGV2). Sample

100digestion procedures followed those described in Lee et al. [13, 14]. Commercially available

101ultrapure HF, HNO_3 and HCl along with sub-boiled, high-purity $HClO_4$ (Merck) were used

102throughout analytical procedures including sample dissolution steps. Samples consisted of

103100-200 mg of powder weighed and digested in PFA Savillex with a 2:1 mixture of

104concentrated HF and HNO_3 at ca. 160ºC for more than 48 hours. After addition of 0.1 ml

105concentrated $HClO_4$, the sample solutions were dried at ca. 180ºC for more than a day. After

106drying, the cake was treated by aqua regia and dried again. Finally, the cakes were re-

107dissolved in 4 ml of 2M HCl for column chromatography. Before column chromatography,

108the solutions were checked for visual clarity to ensure total decomposition of the sample.

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110*2.3. Column chemistry for Eu separation*

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112   Complete separation of Eu from other REEs is essential for precise determination of Eu

113isotopic ratios. Separation becomes even more critical for downstream analytical procedures

114that use neighboring elements (e.g., Sm and Gd) to constrain Eu concentrations. In this study,

115we used a quartz glass (ø 3 mm, length 98 mm) chromatographic column packed with 0.8 mL

116of a cation-exchange resin (Biorad AG 50WX-8, 200–400mesh) and 2-hydroxyisobutyric

117acid (HIBA, Tokyo Chemical Industry, Japan) as an eluant. This method by Lee and Tanaka

118[10] is optimized to achieve the best separation of Eu from other REEs and provides better Eu

119recovery than that provided by the previous methods of de Carvalho et al. [9].

120   Due to the importance of Eu separation in generating precise and accurate results, a

121detailed description of this part of the procedure is provided. Eu was separated from other

122elements using two-step cation exchange column chromatography. A Biorad AG50W X-8

123resin (200–400 mesh stationary phase) was used in the column. After loading 4 ml of the

124sample onto the pre-cleaned column, matrix was removed with 40 mL of 2N HCl. The REE

125fraction was eluted from the resin using 30 mL of 6N HCl. Next, the REE fraction was

126injected onto a quartz glass column (ø 3 mm, length 98 mm) filled with 0.8 mL of the cation-

127exchange resin (Biorad AG 50WX-8, 200–400mesh). Eu was separated using 2-

128hydroxyisobutyric acid (HIBA, 0.12 M) as an eluant (Fig. 1). The eluant came from a 2M

129 stock solution of HIBA adjusted to pH 4.55 using ultrapure NH_4OH (Tamapure chemicals,

130 Kawasaki, Japan). Prior to drying of the eluted Eu fraction, its purity was checked by ICP-

131 MS (NexION 350, Perkin Elmer) or MC-ICP-MS. After the purity check, the Eu solutions

132 were dried at 160°C and re-dissolved in a 2% HNO_3 solution containing Sm or Gd internal

133 standard spikes for Eu isotope ratio measurement.

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135 *2.4. Mass spectrometry*

136   Eu isotopic measurements were performed on a Neptune Plus MC-ICP-MS (Thermo

137 Fisher Scientific Ltd.) with nine Faraday cups and operated under wet plasma conditions at

138 the Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon, Korea. An

139 aliquot of the NIST3117a standard used by Lee and Tanaka [10] was used as a reference.

140 Measurements were performed in low-resolution mode with the Ni normal- sampling cone

141 and Ni X-skimmer cones.

142   The typical sample aspiration rate was 80-100 µL/min. The gain on each Faraday cup was

143 monitored on a daily basis to ensure normalization of its efficiency. Table 2 summarize the

144 cup configuration and other operating parameters of Neptune Plus MC-ICP-MS. Previous

145 research efforts [10] used seven Faraday cups but this study used nine Faraday cups to

146 measure ^{147}Sm and ^{157}Gd.

147   Each sample was subjected 50 cycles (50cycles/block) with a 4.19 s integration interval.

148 Blanks were analyzed before and after each sample measurement.

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150 *2.5. Use of Sm and Gd internal standards for measuring Eu isotopic ratios in geological*

151 *samples*

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153   Lee and Tanaka [10] used ^{150}Sm and ^{154}Sm as internal standard reference peaks for Eu

154 isotope ratio measurements. Most geological or meteoritic samples contain Sm and Gd at

155 concentrations about three times higher than those of Eu. Even though Eu analytes had been

156 purified to 99.9%, detectable fractions of Sm and Gd remained in samples probably due

157 incomplete column chromatography. While they are expected even for state-of-the-art

158 separation procedures (described above), Gd impurities in the matrix include ^{154}Gd which acts

159 as an isobar to ^{154}Sm and therefore interferes with peaks needed to normalize Eu signal.

160   In this study, we systematically analyzed Gd interference with Sm spikes during Eu

161isotopic ratio determination. We specifically investigated Eu measurement stability for Sm

162isotope pairs ^{147}Sm-^{149}Sm, ^{147}Sm-^{152}Sm, ^{147}Sm-^{154}Sm, ^{149}Sm-^{154}Sm and ^{150}Sm-^{154}Sm. We also

163measured Eu isotopic ratios using ^{155}Gd and ^{157}Gd as internal reference peaks to determine

164variation they may introduce to measurements.

165   Eu isotope ratios are reported in standard delta notation (‰) relative to the NIST3117a Eu

166standard solution:

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168    $$\delta \, ^{151}_{153} Eu_\square (\text{‰}) = ¿ \qquad\qquad (1)$$

169   where $¿$ and $¿$ are the mass bias corrected ratios of the sample and NIST 3117a,

170respectively.

171   Using the methods described above, we examined the $\delta^{151/153}$Eu ratios for the NIST3117a

172and the geological reference materials listed above.

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174*2.6. Mass-dependent isotopic fractionation*

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176   As with similar analytical techniques, internal isotopic fractionation, referred to as mass

177discrimination (i.e., mass bias) occurs during MC-ICP-MS analysis [15-20]. Mass

178discrimination can arise due to space charge effects in the plasma or from vacuum effects [6,

17917]. Lee and Tanaka [10] used an ^{150}Sm-^{154}Sm isotope pair to correct for mass-discrimination

180effects among Eu isotopes during MC-ICP-MS analysis. The authors used because these

181nuclides at masses 150 to 154 bracket Eu's own mass numbers of 151 and 153. Approaches

182using different isotope pairs are described in Moynier et al. [4] and de Carvalho et al. [9]. All

183of these studies found consistently detectable degrees of Eu isotope fractionation in

184geological materials. However, normalization using a pair of isotope spikes (or a spike of

185isotope pairs) may suffer from unresolved peaks for the heavier isotope in the pair or isobaric

186interference with either isotope in the pair due to poor purification during sample preparation.

187Comparing results produced by different isotope pairs can help identify the pair that

188minimizes measurement uncertainties introduced by these effects.

189   This study compared and corrected mass-discrimination effects on Eu isotopes using an

190external correction technique that assumes an exponential relationship between unknowns

191and the reference isotope pair (^{147}Sm-^{149}Sm, ^{147}Sm-^{152}Sm, ^{147}Sm-^{154}Sm, ^{149}Sm-^{154}Sm, ^{150}Sm-

192^{154}Sm and ^{155}Gd-^{157}Gd).

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194   The correction was as follows:

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196    $(^{151}Eu/^{153}Eu)_{corr}$ =

197    $(^{151}Eu/^{153}Eu)_{meas}[SI_{nor}/SI_{meas}]^{\ln(Mass151Eu/Mass153Eu)/\ln(SI_{Mass1}/SI_{Mass2})}$

198(2)

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200   where the subscripts 'meas' and 'corr' denote the measured and corrected isotope ratios, 201respectively. SI_{nor} and SI_{meas} indicate the normalization value and measured value of the spike 202isotope, respectively. The terms 'Mass151Eu', 'Mass153Eu' respectively refer to the atomic 203mass of ^{151}Eu and ^{153}Eu, while 'SI_{Mass1}' and 'SI_{Mass2}' refer to lighter and heavier members of 204the spike isotope pairs, ^{147}Sm-^{149}Sm, ^{147}Sm-^{152}Sm, ^{147}Sm-^{154}Sm, ^{149}Sm-^{154}Sm, ^{150}Sm-^{154}Sm and 205^{155}Gd-^{157}Gd.

206   In a previous report [10], we assumed a natural abundance of $^{150}Sm/^{154}Sm$ = 0.3244 which 207represented a rounded average of values reported by Hidaka et al. (0.324395, [21]) and by 208Mass and McCulloch (0.324401, [22]). This study however used natural abundance ratios of 209samarium reported by Dubois et al. [23] to perform mass bias corrections. These values were 210determined by the total vaporization method using Johnson & Matthey Sm oxides and as 211follows; $^{147}Sm/^{154}Sm$ = 0.6626506, $^{147}Sm/^{149}Sm$ = 1.0868, $^{147}Sm/^{152}Sm$ = 0.562992, 212$^{149}Sm/^{154}Sm$ = 0.609726 and $^{150}Sm/^{154}Sm$ = 0.325396. Previously assumed values of 213$^{150}Sm/^{154}Sm$ =0.3244 [10] and $^{155}Gd/^{157}Gd$=0.947645 [23] also were used in spike isotope 214normalization for comparison. We could confirm that the calculated value of Eu isotope 215fractionation ($\delta^{151/153}Eu_{NIST3117a}$) is the same regardless of the number ($^{150}Sm/^{154}Sm$ =0.3244 or 2160.325396).

217   Elements in the sample matrix may result in doubly charged or polyatomic ions [24-29] 218that interfere with signals of interest. The mass range that includes ^{151}Eu and ^{153}Eu spans from 219^{150}Sm to ^{154}Sm and includes both ^{152}Sm and ^{152}Gd. This set of peaks makes Eu isotopes 220difficult to resolve and their proximity to the peaks of interest makes interfering peaks more 221difficult to isolate. In addition, ^{150}SmH, ^{152}SmH and ^{152}GdH can also interfere with ^{151}Eu and 222^{153}Eu during MC-ICP-MS analysis. We did not detect this interference however during 223analysis of Eu isotopes from NIST3117a or an in-house Sm standard.

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3. Results and Discussion

3.1. Variation in Eu isotope ratio estimates with different internal spike isotope pairs

Table 3 summarizes Eu isotope ratio estimates of NIST3117a for different Sm and Gd isotopic pairs used as an internal standard during MC-ICP-MS analysis. Table 4 and Fig. 3 show clearly that, in NIST3117a Eu standard reagent, different Sm isotope pairs used for normalization give highly similar Eu isotope ratio estimates. These results suggest that ultrapure Eu fraction without Gd matrix provide the same value of Eu isotope ratio regardless the kind of Sm isotope pair for normalization. In addition, in Table 3 and Fig. 3, Eu isotope ratio normalized by Gd isotope pair (^{155}Gd-^{157}Gd) appeared to have more mass discrimination and instability compared to Sm normalization. However, because it appears to have a slight isotope fractionation of Eu isotopes, Eu isotope determination by Gd isotope normalization needs more study.

3.2. Recovery rate of Eu, Sm and Gd in igneous rocks

Though de Carvalho et al. [9] mentioned that Sm and Gd do not significantly affect Eu isotopic measurements given standard separation and analytical methods, their data (see Table 4 of [9]) showed slight, systematic variation of Eu isotope ratio (for example, -0.16 ‰ to 0.02‰ for SSB methods and of -0.09‰ to 0.04‰ for C-SSBIN methods with Gd concentrations ranging from 1.0 to 5.0 μg/ml). Many studies have noted systematic isotopic bias introduced by incomplete separation [28, 29]. Lee and Tanaka [10] also emphasized the importance of complete separation of Eu from Sm and Gd when these latter elements are used as spikes. However, Lee and Tanaka [10] did not establish the degree of Eu isotope fractionation introduced by Gd matrix with Sm normalization or by Sm matrix with Gd normalization. This study estimated the extent to which incomplete separation of Sm, Eu and Gd influences Eu isotope ratio estimates for different Sm and Gd isotopic pairs used in standardization.

Table 4 summarize the purification results of Sm, Eu and Gd from some igneous rocks in this study based on HIBA column chromatography of Fig. 1 in this study. Table 4 also includes the concentration ratio between Eu and Gd from each reference material, which was calculated based on the recommend values of the concentration by USGS and GSJ. We also measured the REE concentration of all geochemical reference materials and confirmed that

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257our measured REE concentration values were consistent with recommend REE concentration

258values around 5%.

259   In Table 4, the recovery rate of Eu in most samples were over 99.7% except JG2. The

260relatively low recovery rate (97. 46 %) of Eu in JG2 is because, like the rate of Gd impurity

261in the Eu purified fraction, the large concentration difference and overlapped distribution

262coefficient of Gd and Eu between HIBA and AG50W-X8 resin during column

263chromatography make it very difficult to completely remove the Gd impurity in the Eu

264fraction.

265   Table 4 apparently seems to indicate that the purification among Eu, Gd and Sm is good in

266all geological samples. However, in JG2, we can notice that Eu concentration in the eluted

267solution is only 3 times higher than that of Gd impurity. In this case, apparently, although the

268separation of Eu seemed very good, when measuring the Eu isotope ratio by MC-ICP-MS,

269the interference of ^{154}Gd or ^{152}Gd to ^{154}Sm or ^{152}Sm, respectively, is severe, resulting in false

270Eu isotope. The experimental results related to will be described later. Lee and Tanaka [30]

271proposed a possibility of pseudo-fractionation of Eu isotope ratio from due to interference of

272Gd impurity in the highly fractionated granite and high silica rhyolite. Particularly, like JG2

273in Table 3, the geological samples with extremely lower Eu concentrations, relative to other

274REEs including Sm and Gd, may experience pseudo-fractionation of Eu isotopes due to Sm

275isotope normalization that Sm spike isotopes (^{152}Sm and ^{154}Sm) for determination of Eu

276isotope ratio are effected by Gd impurity (^{152}Gd and ^{154}Gd).

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278*3.3. Gd matrix effect during Eu isotope ratio determination in NIST3117a by MC-ICP-MS*

279*using Sm internal spike*

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281   Table 5 and Fig. 3 summarize Eu isotope ratios of NIST3117a corrected using various Sm

282isotope pairs in the artificial samples with different degrees of ^{154}Gd matrix effects in

283NIST3117a Eu standard solution. In Figure 2, we confirmed that the Eu isotope ratio of

284NIST3117a without Gd matrix was almost the same regardless of the type of Sm isotope pair

285for Sm normalization during Eu isotope ratio determination by MC-ICP-MS. However, Table

2865 and Fig. 3 show that Eu isotope ratio of NIST3117a varies with increasing Gd matrix

287regardless of Sm internal isotope pair except ^{147}Sm-^{149}Sm pair. Particularly, different Sm

288isotope pairs from samples containing more than ca. 1% of ^{154}Gd interference against ^{154}Sm

289produced the decreasing trends (a)-(c) or the steady to increasing trends (d)-(e) shown in Fig.

2903. It means that isotope pairs selected for mass bias correction can produce small but

291significant variation in Eu isotope ratio estimates due to Gd matrix. It suggests that Sm

292isotope pairs can specifically create apparent enrichment of ^{151}Eu or ^{153}Eu in natural samples.

293As a result, pseudo-fractionation of Eu isotope ratios occurs for any Sm isotope pair with

294more than ca. 0.1% of ^{154}Gd interference relative to ^{154}Sm.

295   Lee and Tanaka [10] used ^{150}Sm-^{154}Sm isotope pair for Sm normalization during Eu isotope

296ratio determination by MC-ICP-MS because the Sm mass number of 150 and 154

297conveniently and symmetrically bracket the Eu mass numbers of 151 and 153. And, Figure 2

298revealed that the kind of Sm isotope pair for normalization did not effect in precise and

299accurate determination Eu isotope ratio of ultrapure Eu chemical reagent such as NIST3117a

300determination. Figure 2 also suggests that Eu isotope ratio determined using Sm isotope pair

301such as ^{150}Sm-^{154}Sm and ^{147}Sm-^{154}Sm bracketing ^{151}Eu and ^{153}Eu does not show isotope

302fractionation. However, Table 5 and Fig. 3 seems to suggest that Eu isotope ratio normalized

303by ^{147}Sm-^{149}Sm was less affected compared to those normalized by other Sm isotope pairs in

304solutions containing Gd matrix.

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306*3.4. Comparison of Eu isotope ratio estimates from geochemical reference rocks*

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308   Previous studies have established Eu isotope ratio results for geological materials and some

309meteorites using MC-ICP-MS [4, 9-11]. Of these, Lee and Tanaka [10] detected a possible

310Eu isotope fractionation in geological samples. Hu et al. [11] also reported Eu isotope ratio

311variation from meteorite samples and mentioned that Eu isotopic variations correlate with

312mass-dependent Sr isotopic variation. However, in this study, we noticed that there might

313occur pseudo-Eu fractionation due to a trace of Gd matrix in purified Eu fraction from

314geological materials.

315   Tables 6-10 and Figs. 4-6 summarize Eu isotopic ratio data from four geochemical

316reference rocks measured by a Neptune plus MC-ICP-MS and using various Sm isotope pairs

317for mass bias correction.

318   Figs. 4-6 clearly indicate that determination method of Eu isotope ratio using Sm isotope

319normalization (C-SSBIN) provide more stable data than that by conventional SSB method

320even though the purified sample include a little of matrix. We can also notice that JG2

321(rhombus symbol in Fig. 5) show larger variation in the values of $\delta^{151/153}\text{Eu}_{\text{NIST3117a}}$ compared

322to any other sample in this study. In Table 4, we showed that recovery rate of JG2 is lower

323than any other samples. Eu concentration of JG2 is very low (less than 0.1 ppm). Even

324though the recovery rate of Eu was more than 97%, complete purification between Eu and Gd

325was very difficult due to large difference of concentration and similar distribution coefficient

326between two elements (Table 4). Such low concentration of Eu and relatively high Gd

327impurity seems to make dispersion of Eu isotope ratio determined by MC-ICP-MS.

328Particularly, the variance of Eu isotope ratio showed a tendency to increase in the samples

329subjected to the ^{154}Gd effect of more than 0.1% for ^{154}Sm when we used Sm isotope

330normalization to determine for Eu isotope ratio by MC-ICP-MS.

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332*3.5. Optimal standardization for Eu isotope ratios during MC-ICP-MS analysis*

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334   Previous report [10], we used ^{150}Sm-^{154}Sm isotope pair for normalization under 7 Faraday

335collecters for Eu isotope ratio determination by MC-ICP-MS. And, we could confine that the

336Eu isotope ratio of pure Eu standard reagent (NIST3117a) measured by MC-ICP-MS show

337almost the same regardless of the type of Sm isotope pair for normalization. However, in

338Figs. 4-6, we can observe that, if the effect of ^{154}Gd on the spike isotope ^{154}Sm is less than

3390.1%, the values of $\delta^{151/153}\text{Eu}_{\text{NIST3117a}}$ from each rock reference material determined by Sm

340normalization are almost same regardless of the kind of Sm isotope pair. Particularly, Figs. 4-

3416 suggest that, when we consider Gd matrix effect during Sm normalization, ^{147}Sm-^{154}Sm or

342^{147}Sm-^{149}Sm isotope pairs is more profitable in determining precise and accurate Eu isotope

343ratio determination rather than ^{150}Sm-^{154}Sm and the others.

344

345**4.   Conclusions**

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347   We compared Sm and Gd isotopic pairs used as internal standards for measuring Eu

348isotope ratios by MC-ICP-MS in order to find an optimal method for determining precise and

349accurate Eu isotope ratio from various kinds of the geological rocks. The isotope pair ^{147}Sm-

350^{149}Sm, ^{147}Sm-^{154}Sm, ^{149}Sm-^{154}Sm, ^{150}Sm-^{154}Sm and ^{155}Gd-^{157}Gd were used to perform bracketed

351mass bias correction (C-SSBIN). Our results demonstrated that the ^{147}Sm-^{149}Sm or ^{147}Sm-

352^{154}Sm isotope pair provides the most accurate and precise results (least instrumental mass

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353 fractionation) for Eu isotope ratios measured from geological samples whereas ultrapure
354 chemical reagent such as NIST3117a Eu standard material do not make any kind of Eu
355 isotope ratio variation during operating of MC-ICP-MS using Sm or Gd isotope pairs
356 normalization mentioned above. Particularly, high silica geological rocks such highly
357 fractionated granite and rhyolite require higher purity of Eu separation with little of Gd
358 impurity with very high degree of Eu recovery because incomplete separation of Eu from Gd
359 during sample preparation can bias severe Eu isotope ratio estimates due to interference.
360

361 **Declaration of interests**

362   The authors declare that they have no known competing financial interests or personal
363 relationships that could have influenced or appeared to influence the research reported in this
364 paper.

365

366 **CRediT author statement**

367 Seung-Gu Lee: Conceptualization, Methodology, Validation, Formal measurement,
368   Writing-Original Draft, Writing- Reviewing and Editing.
369 Tsuyoshi Tanaka: Writing- Reviewing and Editing, Conceptualization.

370

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468

469 Figure Captions

470

471 Fig. 1. Eu purification result from Sm and Gd. Eu and Gd can be separated almost completely
472 by 0.12 M and 0.09 M 2-hydroxybutric acid (HIBA). The intensity of Eu, Sm and Gd were
473 measured by Neptune Plus MC-ICP-MS.

474

475 Fig. 2. Eu isotopic ratios of the NIST3117a measured by MC-ICP-MS using different Sm and
476 Gd internal isotope pairs without Gd or Sm matrix, respectively. (^{150}Sm/^{154}Sm = 0.3244 [10
477 and 0.325387 [23], ^{147}Sm/^{154}Sm = 0.6626506, ^{147}Sm/^{149}Sm = 1.0868, ^{149}Sm/^{154}Sm =
478 0.609726, ^{147}Sm/^{152}Sm = 0.562992 and ^{155}Gd/^{157}Gd = 0.947645 [23]). For comparison, we
479 calculated the Eu isotope ratio normalized by different value of ^{150}Sm/^{154}Sm. Eu isotope
480 ratio normalized by ^{150}Sm/^{154}Sm is the same regardless of the value of ^{150}Sm/^{154}Sm.

481

482 Fig. 3. Eu isotope ratio variation (y-axes) of the NIST3117a influenced by ^{152}Gd or ^{154}Gd
483 interference or matrix effects (x-axes) for different Sm isotope pairs used to correct for
484 mass bias during MC-ICP-MS analysis. C-SSBIN: (a) ^{150}Sm/^{154}Sm, (b) ^{147}Sm/^{154}Sm, (c)
485 ^{149}Sm/^{154}Sm, (d) ^{149}Sm/^{154}Sm, (e) ^{147}Sm/^{152}Sm, (f) SSB without Sm normalization.

486

487 Fig. 4. . Eu isotope ratio variation (y-axes) of three basalts (BCR2 and BIR2 from USGS; JB3
488 from GSJ) influenced by ^{152}Gd or ^{154}Gd interference or matrix effects (x-axes) for different
489 Sm isotope pairs used to correct for mass bias during MC-ICP-MS analysis. The Eu
490 isotope ratio was determined using (a) ^{150}Sm/^{154}Sm = 0.325396, (b) ^{147}Sm/^{154}Sm =
491 0.6626506, (c) ^{147}Sm/^{149}Sm = 1.0868, (d) ^{149}Sm/^{154}Sm = 0.609726, (e) ^{147}Sm/^{152}Sm =
492 0.562992 [23] (f) standard-sample-bracketing method without normalization.

493

494 Fig. 5. Eu isotope ratio variation (y-axes) of three granites (GSP2 from USGS; JG1a and JG2
495 from GSJ) influenced by ^{152}Gd or ^{154}Gd interference or matrix effects (x-axes) for different
496 Sm isotope pairs used to correct for mass bias during MC-ICP-MS analysis. The Eu
497 isotope ratio was determined using (a) ^{150}Sm/^{154}Sm = 0.325396, (b) ^{147}Sm/^{154}Sm =
498 0.6626506, (c) ^{147}Sm/^{149}Sm = 1.0868, (d) ^{149}Sm/^{154}Sm = 0.609726, (e) ^{147}Sm/^{152}Sm =
499 0.562992 [23] (f) standard-sample-bracketing method without normalization.

500 Fig. 6. Eu isotope ratio variation (y-axes) of gabbro (JGb2, GSJ) and rhyolite (RGM2, USGS)
501 influenced by ^{152}Gd or ^{154}Gd interference or matrix effects (x-axes) for different Sm isotope

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502 pairs used to correct for mass bias during MC-ICP-MS analysis. The Eu isotope ratio was

503 determined using (a) $^{150}Sm/^{154}Sm = 0.325396$, (b) $^{147}Sm/^{154}Sm = 0.6626506$, (c) $^{147}Sm/^{149}Sm$

504 $= 1.0868$, (d) $^{149}Sm/^{154}Sm = 0.609726$, (e) $^{147}Sm/^{152}Sm = 0.562992$ [23] (f) standard-

505 sample-bracketing method without normalization.

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