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Determination of REE abundances and Eu isotope ratio in GSJ and NIST feldspar reference standards (JF-1, JF-2, SRM 70a, 70b and SRM 99a) using ICP-QMS and MC-ICP-MS

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Determination of REE abundances and Eu isotope ratio in GSJ and NIST feldspar reference standards (JF-1, JF-2, SRM 70a, 70b and SRM 99a) using ICP-QMS and MC-ICP-MS

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ABSTRACT

Rare earth element concentrations in feldspars provide valuable information for understanding geochemical implications during the evolution of igneous rocks due to magma differentiation. Europium exists in Eu^{2+} and Eu^{3+} states, which becomes a cause of Eu anomaly due to feldspar crystallization, and has two stable isotopes (^{151}Eu and ^{153}Eu). Recent reports for Eu isotope ratio in igneous rocks suggest that magma differentiation might bring out Eu isotope fractionation due to feldspar crystallization. Here, we first report Eu isotope ratio and REE concentration for five feldspar standard reference materials from NIST and GSJ. Most feldspar SRMs have large Eu positive anomalies except for NIST SRM70b. The potassium feldspar SRMs are enriched in the lighter Eu isotope (^{151}Eu), whereas the sodium feldspar SRM is enriched in the heavier Eu isotope (^{153}Eu). Our results indicate that

crystallization of sodic and potassic feldspars may produce Eu isotope fractionation in the geological materials.

Keywords: Feldspars, , REEs, Eu isotope fractionation

1. Introduction

The REE geochemistry have provide abundant information for understanding the geochemical evolution of Earth and extraterrestrial materials as a result of their similar chemical behavior and continuously varying atomic masses of REEs. Particularly, Eu behavior in igneous rocks provides valuable information to understand magmatic differentiation in crust-mantle system (Burnham et al., 2015). For example, Eu anomalies in the chondrite-normalized REE patterns in igneous rocks were derived from feldspar fractional crystallization during magma evolution (Shearer and Papike, 1989).

Recently, Lee's groups (2019, 2021a, 2023, 2024) developed a method for determining highly precise and accurate Eu isotope ratios from geological materials using MC-ICP-MS, and reported that Eu anomaly by feldspar crystallization and Eu isotope fractionation has a good relationship. Schauble (2023) suggested that Eu isotope fractionation might be produced by feldspar crystallization whereas Hu et al. (2023) proposed that Eu isotope fractionation might be produced by hydrothermal reaction. It means that REE concentrations and Eu isotope ratios in feldspars are important factor in understanding the geochemical significance of Eu isotope fractionation. However, there is little precise data on the REEs concentration in feldspar in the standard reference materials (SRMs). Analytical data on the Eu isotope ratio in feldspars also have not been reported yet. Therefore, we determined REE concentration and Eu isotope ratio of the feldspar SRMs produced by Geological Survey of Japan (GSJ) and National Institute of standards and Technology (NIST). We also performed cross-checking experiments using different kinds of ICP-MS at Korea Institute of Geoscience and Mineral Resources (KIGAM) and at Nagoya University, Japan to improve the reliability of the REE concentration data for JF-1, JF-2 and SRM 70b.

2. Materials and analytical methods

2.1. Materials

The SRMs used in this study are SRM 70a, SRM 70b, SRM 99a, JF-1 and JF-2. SRM 70a and SRM 70b of NIST and JF-1 and JF-2 of GSJ are potassium feldspars, and SRM 99a is sodium feldspar.

2.2. Sample digestion (Fig. S1)

Sample digestion procedures at KIGAM followed those described in Lee (2024). Commercially available ultrapure HF, HNO_3 and HCl purchased from Merck company were used to dissolve samples along with sub-boiled, high-purity perchloric acid ($HClO_4$, Merck). Approximately 100 ~ 200 mg of each SRM was decomposed by a 2:1 mixture of 2 mL of concentrated HF and 1 mL of concentrated HNO_3 at ca. 160 ºC for more than 72 hours in 30 mL Savillex vial. After the addition of 0.1~0.2 mL of concentrated $HClO_4$, the decomposed sample solution was heated to dryness at ca. 180 ºC for more than 1 day. The dried cakes were redissolved in a 2:1 mixture of 1 mL of concentrated HCl and 0.5 mL of concentrated HNO_3 at ca. 160 ºC for 1 day. The re-dried samples were diluted in 10 mL of 6 M HCl as a stock solution to determine REEs concentration and Eu isotope ratio.

In a cross-checking experiment for REE analysis, approximately 40 mg of three SRMs (JF-1, JF-2, SRM 70b) was decomposed by a 2:1 mixture of 2 mL of concentrated HF and 1 mL of concentrated HNO_3 at ca. 140 ºC for more than 24 hours in 15 mL Savillex vial at KIGAM and Nagoya University. As for the sample digestion procedure at Nagoya University, commercially available ultrapure HF (TAMAPURE AA-100), HNO_3 (TAMAPURE AA-100) and $HClO_4$ (Kanto Chemical, Ultrapur™) were used to dissolve the samples. After the addition of 0.1 mL of concentrated $HClO_4$, the decomposed sample solution was heated to dryness at ca. 140 ºC for more than 1 day. The dried cakes were redissolved in a 2:1 mixture of 1 mL of concentrated HCl and 0.5 mL of concentrated HNO_3 at ca. 160 ºC for 1 day. The re-dried samples were diluted in 10 ml of 2% HNO_3 as a stock solution to determine REEs concentration for cross-checking experiment of REE abundance determination at Nagoya University and KIGAM.

2.3. Instrumentation and analytical procedures (Supplementary Table S1)

REE analysis was performed using inductively coupled plasma mass spectrometer (ICP-MS) , NexION350, Perkin Elmer at KIGAM and Agilent7700x at Nagoya University) (Supplementary Table S1). REE analysis using NexION350 ICP-MS at KIGAM was applied the method by Lee et al. (2014, 2016) using one-point standard solution for each element based on the concentration values for a chosen standard solution, which is similar to the method by Schudel et al. (2015). REE analysis using Agilent7700 at Nagoya University was performed using six standard solutions: the concentrations of individual elements in the six REE standard solutions cover the concentration range estimated for dilute solutions of natural terrestrial samples. Before the sample measurement, production rates of LREE oxides which make interferences on HREE were determined by using several LREE solutions. The concentrations of the elements were measured using an internal standard (In), and two different cell modes were used: helium (He) collision and No Gas modes. Normally, there was no difference between the REE concentration data in He collision mode and No Gas mode because the rates of isobaric interference due to oxide production were small and stable.

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 isotopes ^{147}Sm(L4), ^{149}Sm(L3), ^{150}Sm(L2), ^{151}Eu(L1), ^{152}Sm(C), ^{153}Eu(H1), ^{154}Sm(H2), ^{155}Gd(H3), and ^{157}Gd(H4) were monitored simultaneously using nine Faraday cups for Sm normalization and Gd interference correction (Lee, 2024, and reference in).

The procedures for Eu separation from other REEs were described well by Lee (2024). The REE fraction for Eu purification was separated by precleaned cation exchange chromatography (BioRad AG50W-X8 resin) using 6 M HCl. Eu was separated from the obtained REE fraction using 0.12 M 2-hydroxyisobutyric acid (HIBA, pH 4.5 ~ 4.6) and on a quartz column (0.3 cm × 9.8 cm column) filled with 0.8 mL of cation-exchange resin (BioRad AG50W-X8 resin, 200-400 mesh). Because incomplete Eu purification due to the very low abundance of Eu becomes a cause of isobaric interference during Eu isotope ratio measurement by MC-ICP-MS using Sm internal standardization (Lee, 2024), we always checked for tailing of neighboring elements such as Sm and Gd to minimize isobaric interference.

3. Results and Discussion

REE concentrations and Eu isotope ratios for the feldspar SRMs in this work were described in Tables S2 and S3, respectively. Figure 1 indicates chondrite-normalized REE patterns for 5 feldspar SRMs. REE data for JF-1, JF-2 and SRM 70b for a cross-checking experiment show that REE concentrations measured at KIGAM are consistent with those measured at Nagoya University (Table S2).

The REE data in this study are not consistent with some of the GSJ recommended values, but they show relatively smooth HREE patterns (Figure 1), strongly suggesting that our new data are more reliable. Except for SRM 70b, 4 SRMs have extremely large Eu positive anomaly. In addition, four SRMs are enriched in LREEs (La-Sm) and relatively flattened HREEs (Gd-Lu). However, SRM 70b has a LREE enriched and relatively flattened HREE pattern with almost no Eu anomaly. Another geochemical feature of the REE patterns from the SRMs seems to be Ce negative anomalies from JF-2 and SRM 70a. Ce anomalies in igneous rocks were interpreted as a tracer of previously supracrustal material in source regions of igneous rocks (Shimizu et al., 1992; Class and Le Roex, 2008), and may provide evidence for the elevated redox state of magmas (Zhong et al., 2019).

Figure 2 shows Eu isotope ratios for five SRMs. Except for SRM 99a, four SRMs show ^{151}Eu enrichment compared to NIST3117a. However, SRM 99a clearly shows ^{153}Eu enrichment compared to NIST3117a. Except for SRM 99a, the others are potassium feldspars. Figure 2 seems to suggest that Eu isotope fractionation is a product of feldspar crystallization during magmatic differentiation. Therefore, Fig. 2 is different from the result that Eu isotope fractionation may not be produced by simple feldspar crystallization (Lee et al., 2023; Schauble, 2023).

Ismail et al. (1998) also found isotope effects in which the heavier isotope ^{153}Eu is enriched in Eu^{2+} in the Eu^{2+}/Eu^{3+} electron exchange system. It means that substitution of Eu^{2+} for Ca^{2+} in plagioclase during differentiation of the source magma brought about an isotope effect that enriched the heavier or lighter Eu isotope (^{153}Eu) in Eu^{2+}. The study of Eu isotope fractionation is still in its early stages. However, rare earth elements in igneous rocks are distributed with the strongest regularity compared to other elements in the periodic table.

Therefore, our data for REE concentration and Eu isotope ratio for feldspar can be a strong indicator in the field of REE geochemistry and Eu isotope fractionation.

4. Conclusion

In this study, we measured REE concentration and Eu isotope ratios for 5 feldspar SRMs (JF-1, JF-2, SRM 70a, SRM 70b and SRM 99a). In chondrite-normalized REE patterns, except for SRM 70b, the others have extremely large Eu positive anomalies. In Eu isotope ratios, SRM 99a shows heavier Eu isotope (^{153}Eu) enrichment whereas the others show lighter Eu isotope (^{151}Eu) enrichment. Our results support that feldspar crystallization is one of the main causes of Eu isotope fractionation during magma differentiation.

CRediT authorship contribution statement

S-G. Lee performed ICP-MS and MC-ICP-MS experiments and wrote the manuscript. **Y. Asahara** performed ICP-MS experiments and wrote the manuscript. G. Kim prepared SRM 70a and SRM 99a samples.

Declaration of competing interest

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

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Figure captions

Fig. 1. Chondrite (McDonough and Sun, 1995)-normalized REE patterns for 5 feldspar SRMs. NIST SRM 70b has almost no Eu anomaly.

Fig. 2. Eu isotope ratios of feldspar standard reference materials. Average value means the average of the five values calculated by each Sm isotope pair. The numbers of x-axis indicate that there are no Gd isobar and Ba oxide interference during Eu isotope ratio measurement via Neptune MC-ICP-MS.

$$\delta^{153}Eu = \left[\frac{(\frac{153}{151}Eu)_{sam}}{(\frac{153}{151}Eu)_{NIST3117a}} - 1\right] \times 1{,}000$$

Figure1

Click here to access/download;Figure;LSG-Figure-1.tif

Figure 1

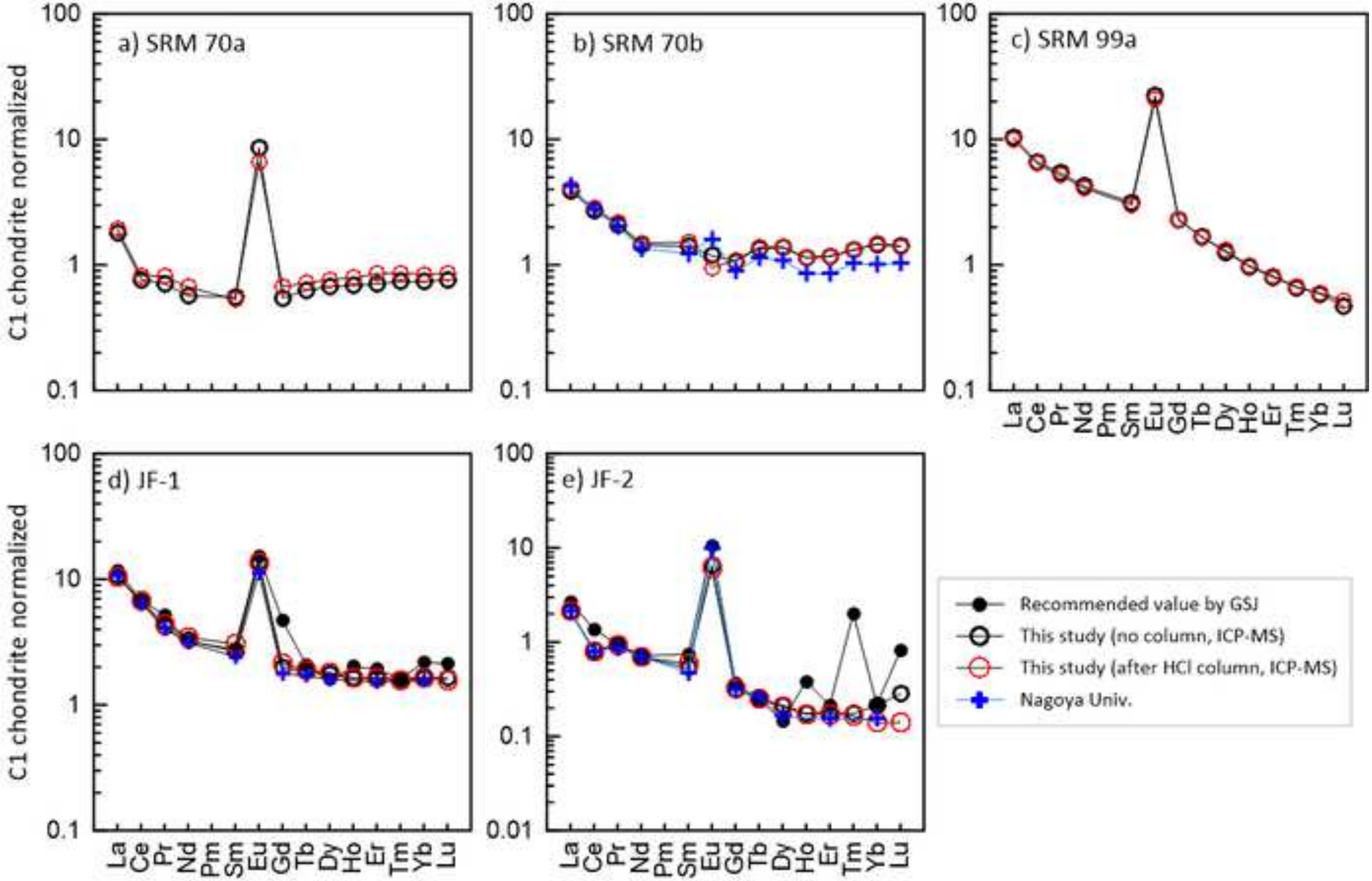


Figure2

Figure 2

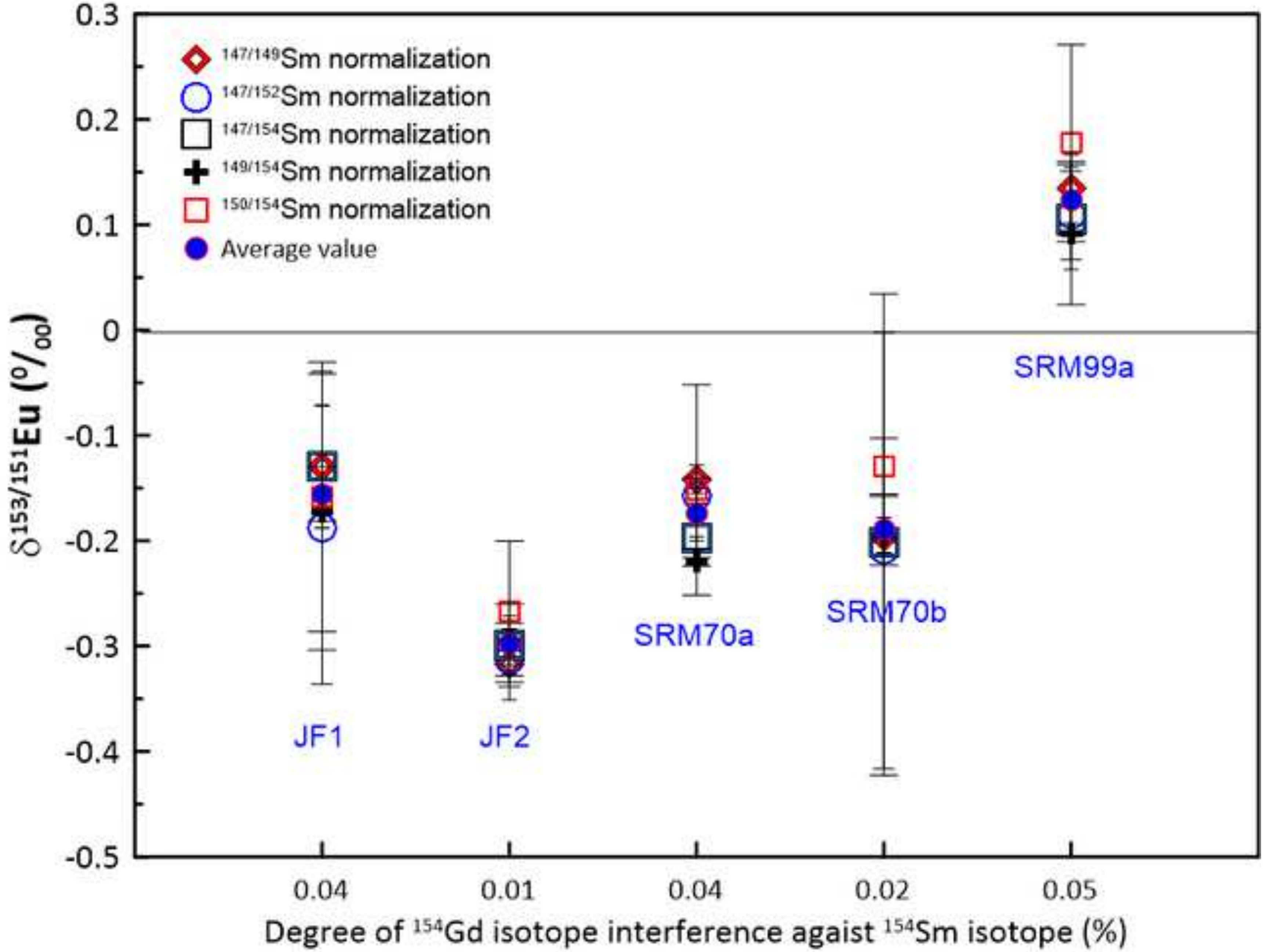
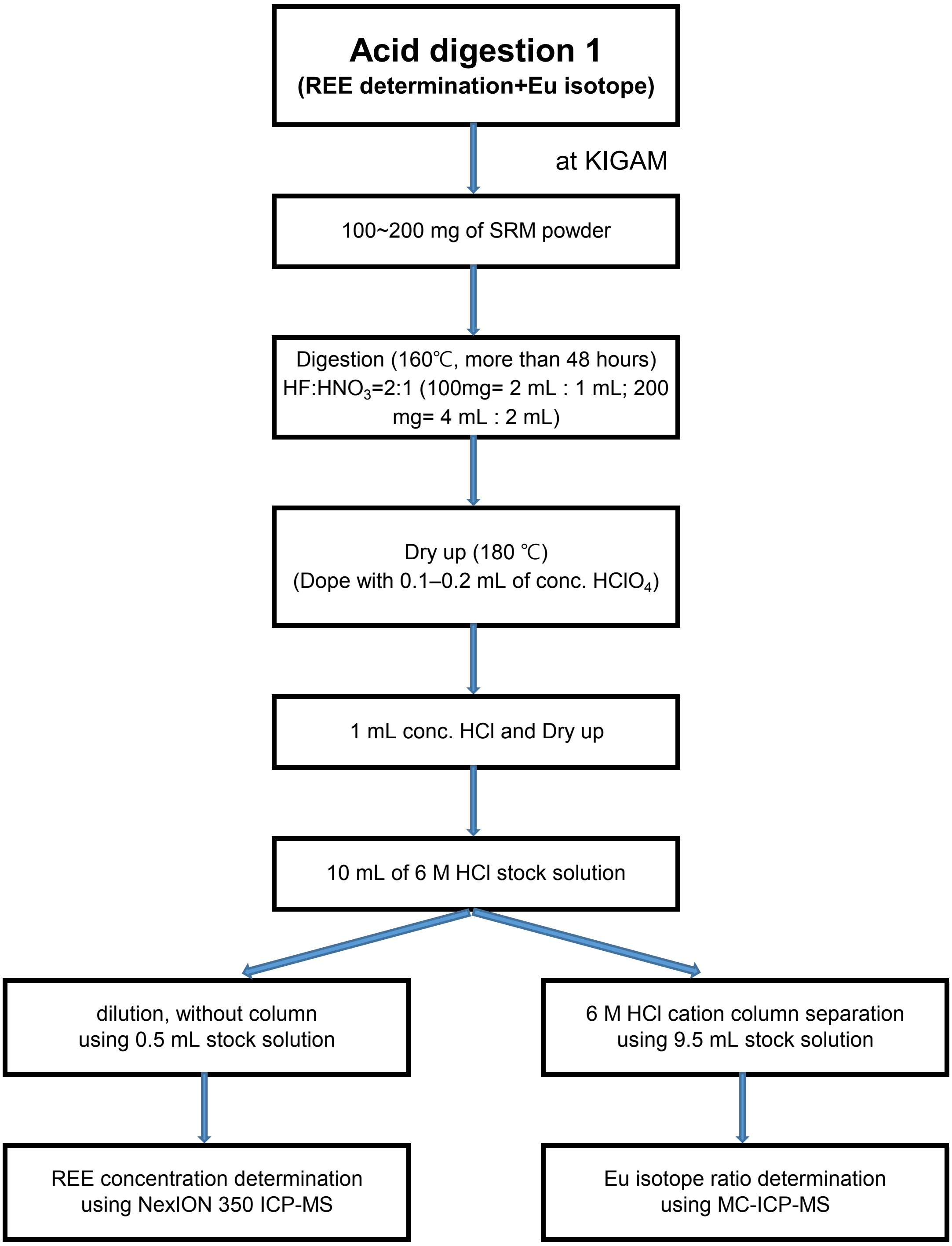


Figure S1


Acid digestion 1
(REE determination+Eu isotope)
at KIGAM
100~200 mg of SRM powder
Digestion (160℃, more than 48 hours)
HF:HNO3=2:1 (100mg= 2 mL : 1 mL; 200 mg= 4 mL : 2 mL)
Dry up (180 ℃)
(Dope with 0.1–0.2 mL of conc. HClO4)
1 mL conc. HCl and Dry up
10 mL of 6 M HCl stock solution
dilution, without column
using 0.5 mL stock solution
6 M HCl cation column separation
using 9.5 mL stock solution
REE concentration determination
using NexION 350 ICP-MS
Eu isotope ratio determination
using MC-ICP-MS

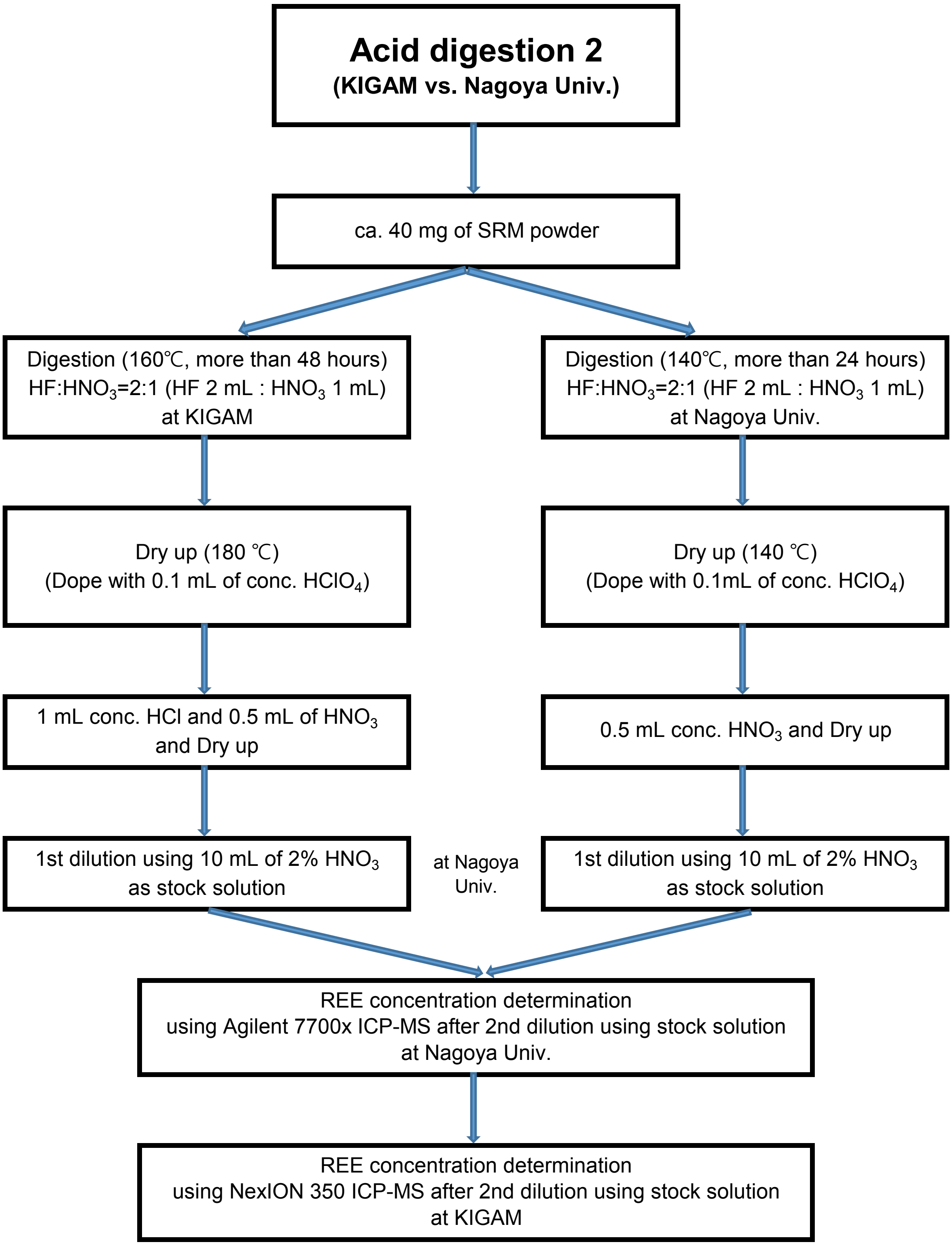

Acid digestion 2
(KIGAM vs. Nagoya Univ.)
ca. 40 mg of SRM powder
Digestion (160℃, more than 48 hours)
$HF:HNO_3$=2:1 (HF 2 mL : HNO_3 1 mL)
at KIGAM
Digestion (140℃, more than 24 hours)
$HF:HNO_3$=2:1 (HF 2 mL : HNO_3 1 mL)
at Nagoya Univ.
Dry up (180 ℃)
(Dope with 0.1 mL of conc. $HClO_4$)
Dry up (140 ℃)
(Dope with 0.1mL of conc. $HClO_4$)
1 mL conc. HCl and 0.5 mL of HNO_3
and Dry up
0.5 mL conc. HNO_3 and Dry up
1st dilution using 10 mL of 2% HNO_3
as stock solution
at Nagoya
Univ.
1st dilution using 10 mL of 2% HNO_3
as stock solution
REE concentration determination
using Agilent 7700x ICP-MS after 2nd dilution using stock solution
at Nagoya Univ.
REE concentration determination
using NexION 350 ICP-MS after 2nd dilution using stock solution
at KIGAM

Table S1

Table S1 Typical analytical condition of ICP-MS for determining REE concentrations in feldspar SRMs

Model	Perkin Elemer NexION 350X	Agilent 7700x
ICP-MS		
ICP RF power	1400 W	1550 W
Gas flow rate Plasma	Ar gas 18 L/min	Ar gas 15 L/mi
Auxiliary gas	1.2 L/min	0.9 L/min
Nebulizer gas	0.96 L/min	1.01~1.11 L/mi
Chamber type	Glass cyclonic spray chamber	Spray chamber (qu
Nebulizer type	Quartz type A nebulizer (0.5 mL/min.)	MicroMist nebulizer (s
Deflector voltage	-9.55 V	–
Collision Reaction Cell	CH_4, Universal Reaction Cell^{TM}	No Gas / He collis
Vaccum pressure	3.30e-7 Torr	1.1e-6 Torr (Analysis
Analog stage voltage	-1820 V	2100 V
Pulse stage voltage	-1250 V	1130 V
Data acquisition		
Sweeps	20	100
Reading	1 sec.	0.25 sec
Replicates	3	3

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Table S2

Table S2 Rare earth element concentrations (ppm) of five feldspar SRMs in this study

Element	JF-1							JF-2				
	This study					Watkins & Le Roex (1992)	Rec.[*2]	This study				
	NexION 350 (KIGAM)		Agilent 7700 (Nagoya U.)	**Ave.**	1SD			NexION 350 (KIGAM)		Agilent 7700 (Nagoya U.)	**Ave.**	1SD
	no Colu.[*1]	Colu.*1	no Colu.					no Colu.	Colu.	no Colu..		
La	2.514	2.492	2.533	**2.513**	0.020	2.730	2.800	0.505	0.502	0.513	**0.507**	0.006
Ce	4.023	4.175	3.980	**4.060**	0.102	4.060	4.190	0.504	0.484	0.480	**0.489**	0.013
Pr	0.387	0.408	0.377	**0.391**	0.016	0.420	0.480	0.088	0.087	0.082	**0.085**	0.003
Nd	1.461	1.573	1.430	**1.488**	0.075	1.510	1.460	0.315	0.318	0.320	**0.318**	0.002
Sm	0.371	0.453	0.359	**0.394**	0.051	0.410	0.410	0.079	0.087	0.071	**0.079**	0.008
Eu	0.916	0.760	0.635	**0.770**	0.141	0.740	0.870	0.367	0.345	0.549	**0.420**	0.112
Gd	0.405	0.422	0.355	**0.394**	0.035	0.400	0.930	0.063	0.065	0.063	**0.064**	0.001
Tb	0.068	0.069	0.062	**0.066**	0.004	0.069	0.076	0.009	0.009	0.009	**0.009**	0.000
Dy	0.450	0.444	0.395	**0.430**	0.030	0.450	0.390	0.053	0.051	0.040	**0.048**	0.007
Ho	0.093	0.090	0.084	**0.089**	0.005	-	0.110	0.010	0.009	0.009	**0.009**	0.000
Er	0.284	0.260	0.246	**0.263**	0.019	0.290	0.310	0.029	0.028	0.025	**0.027**	0.002
Tm	0.044	0.039	0.036	**0.040**	0.004	-	0.040	0.004	0.004	0.004	**0.004**	0.000
Yb	0.289	0.262	0.250	**0.267**	0.020	0.310	0.350	0.034	0.022	0.025	**0.027**	0.006
Lu	0.046	0.039	0.037	**0.040**	0.005	-	0.053	0.007	0.003	0.004	**0.005**	0.002

[*1] colu: column chromatography

[*2] Rec.: recommend

[*3] SRMs of NIST do not have recommended values of REE.

		SRM 70b[*3]					SRM 70a[*3]				SRM	
		This study										
Watkins & Le Roex (1992)	Rec.	NexION 350 (KIGAM)		Agilent 7700 (Nagoya U.)	**Ave.**	1SD	NexION 350 (KIGAM)		**Ave.**	1SD	NexION 350 (KIGAM)	
		no Colu.	Colu.	no Colu.			no Colu.	Colu.			no Colu.	Colu.
0.640	0.630	0.925	0.959	1.003	**0.962**	0.039	0.426	0.460	**0.443**	0.024	2.458	2.336
0.530	0.840	1.661	1.729	1.691	**1.694**	0.034	0.471	0.506	**0.488**	0.025	4.065	3.914
0.088	0.088	0.192	0.201	0.189	**0.194**	0.006	0.066	0.076	**0.071**	0.007	0.501	0.477
0.330	0.330	0.658	0.682	0.619	**0.653**	0.032	0.259	0.305	**0.282**	0.033	1.935	1.858
0.084	0.110	0.209	0.225	0.183	**0.206**	0.021	0.083	0.078	**0.081**	0.003	0.468	0.446
0.520	0.590	0.067	0.053	0.091	**0.070**	0.019	0.481	0.373	**0.427**	0.076	1.256	1.174
0.072	0.072	0.214	0.218	0.177	**0.203**	0.023	0.109	0.134	**0.121**	0.018	0.458	0.453
0.009	0.009	0.049	0.050	0.041	**0.047**	0.005	0.023	0.026	**0.024**	0.002	0.060	0.060
0.056	0.036	0.338	0.343	0.266	**0.316**	0.043	0.165	0.188	**0.176**	0.016	0.312	0.321
-	0.021	0.062	0.063	0.047	**0.057**	0.009	0.037	0.043	**0.040**	0.004	0.053	0.054
0.034	0.034	0.187	0.189	0.137	**0.171**	0.030	0.113	0.137	**0.125**	0.017	0.129	0.131
-	0.050	0.033	0.032	0.025	**0.030**	0.004	0.018	0.021	**0.020**	0.002	0.016	0.017
0.037	0.035	0.235	0.238	0.162	**0.212**	0.043	0.119	0.136	**0.127**	0.012	0.095	0.096
-	0.020	0.035	0.034	0.026	**0.032**	0.005	0.019	0.021	**0.020**	0.001	0.012	0.013

99a[*3]	
Ave.	1SD
2.397	0.086
3.990	0.107
0.489	0.017
1.896	0.054
0.457	0.016
1.215	0.058
0.455	0.003
0.060	0.000
0.316	0.007
0.053	0.000
0.130	0.002
0.016	0.000
0.095	0.001
0.012	0.001

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Table S3

Table S3 Eu isotope ratio of feldspar standard reference materials used in this study

	Intensity (V)			**^{154}Gd/^{154}Sm intensity ratio[a)] (%)**		
	^{153}Eu	^{154}Sm	^{155}Gd		$^{147/149}$Sm	$^{147/152}$Sm
JF1-Aridus II	20.528	16.605	0.106	**0.094**	-0.210	-0.420
	18.631	16.488	0.102	**0.091**	-0.183	-0.423
JF1-1_Spray chamber	2.267	2.400	0.006	**0.038**	-0.118	-0.121
	2.724	2.427	0.010	**0.062**	-0.108	-0.104
	4.090	5.849	0.001	**0.004**	*-0.163*	-0.160
	4.565	5.455	0.006	**0.016**	*-0.028*	-0.049
	3.179	4.353	0.003	**0.011**	*-0.145*	-0.140
	4.172	4.903	0.008	**0.023**	*-0.082*	-0.084
Average					**-0.130**	**-0.188**
1 SD					**0.058**	**0.148**
JF2-1	3.367	4.869	0.002	**0.005**	*-0.314*	-0.307
	3.095	4.515	0.001	**0.003**	*-0.272*	-0.281
	3.957	6.836	0.002	**0.005**	*-0.349*	-0.331
	2.564	4.476	0.009	**0.031**	*-0.334*	-0.334
Average					**-0.317**	**-0.313**
1 SD					**0.034**	**0.025**
SRM70a	2.395	4.121	0.001	**0.004**	*-0.132*	-0.152
	0.948	0.554	0.003	**0.070**	*-0.151*	-0.162
Average					**-0.142**	**-0.157**
1 SD					**0.013**	**0.007**
SRM70b	0.980	1.368	0.002	**0.023**	*-0.210*	-0.209
	0.816	1.346	0.001	**0.014**	*-0.183*	-0.207
Average					**-0.197**	**-0.208**
1 SD					**0.019**	**0.001**
SRM99a	1.215	4.277	0.003	**0.009**	*0.172*	0.170
	2.771	1.559	0.009	**0.082**	*0.170*	0.098
	1.786	6.553	0.005	**0.010**	*0.146*	0.152
	2.423	2.080	0.009	**0.066**	*0.106*	0.074
	2.180	1.955	0.009	**0.064**	*0.107*	0.082
	1.271	1.138	0.003	**0.042**	*0.104*	0.077
Average					**0.134**	**0.109**
1 SD					**0.032**	**0.042**

a) ^{154}Gd/^{154}Sm = Calculated intensity of ^{154}Gd/measured intensity of ^{154}Sm × 100 (%)

$\delta^{153/151}$Eu (‰)			
$^{147/154}$Sm	$^{149/154}$Sm	$^{150/154}$Sm	no normalization
-0.195	-0.364	-0.331	-0.683
-0.208	-0.386	-0.378	-0.552
-0.117	-0.125	-0.092	-0.198
-0.083	-0.071	-0.071	-0.157
-0.161	-0.162	-0.170	-0.202
-0.052	-0.064	-0.058	0.194
-0.151	-0.152	-0.127	-0.301
-0.073	-0.056	-0.042	-0.109
-0.130	**-0.173**	**-0.158**	**-0.251**
0.058	**0.131**	**0.128**	**0.270**
-0.302	-0.298	-0.233	-0.148
-0.293	-0.304	-0.308	-0.198
-0.334	-0.328	-0.337	-0.266
-0.268	-0.248	-0.191	-0.545
-0.299	**-0.294**	**-0.267**	**-0.289**
0.028	**0.034**	**0.067**	**0.177**
-0.199	-0.223	-0.222	-0.233
-0.197	-0.217	-0.081	-0.127
-0.198	**-0.220**	**-0.152**	**-0.180**
0.002	**0.004**	**0.100**	**0.075**
-0.195	-0.194	-0.111	-0.109
-0.208	-0.228	-0.150	-0.177
-0.202	**-0.211**	**-0.130**	**-0.143**
0.010	**0.024**	**0.028**	**0.048**
0.172	0.174	0.187	0.019
0.056	0.009	0.306	0.157
0.159	0.169	0.266	0.135
0.098	0.094	0.134	0.073
0.067	0.039	0.081	0.187
0.084	0.067	0.090	0.053
0.106	**0.092**	**0.177**	**0.104**
0.048	**0.068**	**0.093**	**0.065**