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Note

A Simple Method for Precise Determination of 23 Trace Elements in Granitic Rocks by ICP-MS after Lithium Tetraborate Fusion

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Abstract: An improved alkali fusion method followed by HF-HNO_3-$HClO_4$ treatment is performed for simultaneous determination of 23 trace elements (Sr, Y, Zr, Nb, Ba, Hf, Ta, Th, U, and REE) by ICP-MS in rock reference materials: basaltic rocks (JB-2, JB-3) and granitic rocks (JG-1a, JG-2, JG-3). Our improved method offers several advantages including: (1) suppression of whitish precipitates probably composed of insoluble fluorides by addition of $HClO_4$, (2) simple and reliable preparation procedure, (3) instrument calibration which enables straightforward simultaneous multi-elemental analysis, and (4) the very low background levels by using pure lithium tetraborate flux. We obtained the analytical results with a reproducibility of mostly <2 % (1σ) for the basaltic rocks and <7 % for the granitic rocks. The higher relative standard deviation (RSD) values for granitic rocks may be attributed to sample heterogeneity of coarse-grained granitic rocks. The analytical results of the granitic rocks demonstrate that Zr and Hf abundances are consistent with the compiled values and that REE concentrations agree well with recently published data, suggesting that the $Li_2B_4O_7$ fusion method applied in the present study is suitable for the analysis of the granitic rocks.

Keywords: ICP-MS, alkali fusion method, HF-HNO_3-$HClO_4$ treatment, granitic rock, acid-resistant mineral, lithium tetraborate

1. Introduction

Accumulating knowledge of trace element systematics in variety of geological samples allows us to understand their origin, source material, and complex history of magmatic, metamorphic, and/or sedimentary processes. In particular, obtaining precise and accurate analytical data for various elements in granitic rocks is very useful for exploring mineral resources, because several types of important terrestrial ore deposits including porphyry copper, skarn, and vein-type deposits are known to be genetically related to granitic rocks.

Inductively coupled plasma mass spectrometry (ICP-MS) has been widely used for determination of trace element concentrations in geological materials (e.g., Hirata et al., 1988; Imai, 1990; Kato et al., 1998, 2005a; Kimura et al., 2002) because of its great sensitivity and high sample throughput. Although a laser ablation technique is being developed (Eggins, 2003; Orihashi and Hirata, 2003), acid digestion of solid samples including basaltic rocks (e.g., Nakamura and Kato, 2004; Nozaki et al., 2005) and sedimentary rocks (e.g., Kato et al., 2002, 2005b; Kato and Nakamura, 2003) is still very popular and useful technique for ICP-MS analysis. However, the acid digestion technique is not always valid for granitic rocks because these rocks often contain acid-resistant minerals such as zircon, magnetite and rutile that concentrate rare earth elements (REE) and high field strength elements (HFSE).

A fusion method with an alkali flux (lithium borate: $LiBO_2$ and $Li_2B_4O_7$, sodium peroxide: Na_2O_2, sodium carbonate: Na_2CO_3, and boric acid: H_3BO_3) is well known to be effective for decomposition of the refractory minerals in granitic rocks (Jarvis and Jarvis, 1992). The major disadvantage of fusion method, however, is that it introduces large amounts of total dissolved solids which necessitate greater dilution of samples for analysis. These dilution factors decrease some trace element concentrations in solutions below the detection limits. In addition, large quantities of flux into samples may cause serious contamination of some analyzed elements.

In this study, we present an improved $Li_2B_4O_7$ fusion method followed by HF-HNO_3-$HClO_4$ treatment for simultaneous determination of 23 trace elements (Sr, Y, Zr, Nb, Ba, Hf, Ta, Th, U, and REE) in granitic rocks. We employed HF-HNO_3-$HClO_4$ treatment here to remove Si and B as volatile fluorides (Panteeva et al., 2003) without formation of precipitates such as insoluble Ca-, Al-, and Mg-fluorides (Yokoyama et al., 1999).

2. Experimental

2.1. Reagents, rock reference materials, and instrumentation

Nitric acid (HNO_3) and hydrofluoric acid (HF) were of the grade for atomic absorption spectrometry (Cica-Reagent, Kanto Chemical). Perchloric acid ($HClO_4$) was TAMAPURE-AA-100 grade (Tama Chemicals). Lithium

Table 1 Instrumental operating conditions.

Element	Mass	Integration time (s)	
		Acid digestion	Alkali fusion
Sr	88	0.3	0.3
Y	89	0.3	0.3
Zr	90	0.3	0.3
Nb	93	2.1	2.1
Ba	137	0.3	0.3
La	139	0.3	0.9
Ce	140	0.3	0.9
Pr	141	0.9	2.1
Nd	146	0.9	2.1
Sm	147	1.5	3
Eu	153	1.5	3
Gd	157	1.5	3
Tb	159	1.5	3
Dy	163	1.5	3
Ho	165	1.5	3
Er	166	1.5	3
Tm	169	2.1	9
Yb	172	2.1	3
Lu	175	3	9
Hf	178	3	3
Ta	181	9	9
Th	232	6	6
U	238	6	6

ICP-MS instrument		Agilent 7500c
RF power		1.6 kW
Argon gas flow		
Nebulizer		1.2 L/min
Auxiliary		0-1.0 L/min
Plasma		15 L/min
Nebulizer		Babington nebulizer
Sample Uptake Time		80 s
Acquisition Time	Acid digestion 53 × 3 s	Alkali fusion 80 × 3 s
Rinse Time		120 s
Sensitivity		
Co (59)		> 10 Mcps/ppm
Y (89)		> 10 Mcps/ppm
Tl (205)		> 8 Mcps/ppm
Background		
5 amu		< 2 cps
220 amu		< 1 cps
Average oxides (CeO^+/Ce^+)		1.4 %
Average doubly charged (Ce^{2+}/Ce^+)		1.9 %

tetraborate ($Li_2B_4O_7$) for alkali flux was Spectromelt® A 10 (Merck). The experimental water was purified by the MILLI-Q SP ICP-MS system (Millipore Japan). Five rock reference materials of two basaltic rocks (JB-2, JB-3) and three granitic rocks (JG-1a, JG-2, JG-3) issued by the Geological Survey of Japan (GSJ) were chosen to validate the proposed method. The ICP-MS instrument used here was Agilent 7500c (Agilent Technologies) at the Department of Geosystem Engineering, University of Tokyo. Details of operating conditions are shown in Table 1.

2.2. Instrument calibration

Instrument calibration is performed using the GSJ standard JB-1 following digestion procedures identical to those employed for the unknown samples. The use of JB-1 enables a simple simultaneous multi-elemental analysis, because it contains most elements in high concentration. In addition, matrix effect can be corrected by using reference materials which has similar matrix to that of the samples (Imai, 1990). This is particularly important for a fusion method for which significantly high matrix level is expected. In the present study, we use recently published concentration data for JB-1 by Makishima and Nakamura (1997) and Makishima et al. (1999) as reference values. For a calibration standard, the use of rock reference materials with abundance of high-precision data such as United States Geological Survey (USGS) reference materials is desirable. JB-1 is one of the most suitable reference materials in the GSJ standard rock samples. Instead of JB-1, JB-2 and JB-3 with our preferred concentration values (Makishima and Nakamura, 1997; Makishima et al., 1999) are also recommended as calibration standard materials.

Although several researchers pointed out the drawbacks of calibrating against natural reference materials (e.g., Ujiie and Imai, 1995; Robinson et al., 1999), we believe that using a reference material as a calibration standard with appropriate reference values is worthwhile for simple and simultaneous determination by our fusion method. Moreover, in the case of future change of reference values, existing data can be corrected readily by the ratio of the revised and previous values (Eggins et al., 1997).

2.3. Sample preparation

Two digestion techniques of (1) acid digestion and (2) alkali fusion followed by acid treatment were applied to the decomposition of rock reference materials (Fig. 1).

2.3.1. Acid digestion: 50 mg of powdered rock sample was dissolved by 2 ml of 50% m/m HF, 2 ml of 60 % m/m HNO_3, and 1 ml of 70 % m/m $HClO_4$ in a tightly sealed 15 ml Teflon PFA screw-cap beaker, heated for 15 hours on a hot plate at 160°C. The sample was evaporated in a stepwise manner at 120°C for 12 hours, 160°C for 3 hours, and 190°C until dryness. The residue was dissolved with 5 ml of 30 % m/m HNO_3, heated for 3 hours at 120°C and the solution was diluted to 100 ml total volume.

2.3.2. Alkali fusion: A 4:1 ratio of flux (400 mg) to powdered rock sample (100 mg) was weighed into a 95 % Pt-5 % Au crucible (~3 cm in diameter: CS-2, Tokyo Kagaku), then stirred, a few drops of LiBr solution added, and the mixture was fused at 1190°C for 10-20 min in a Bead & Fuse-Sampler (TK-4100, Tokyo Kagaku). By applying the well established method for XRF, complete fusion digestion can be achieved readily. Moreover, a fused glass bead can be easily ripped up from the 95 % Pt-5 % Au crucible after fusion by adding a few drops of

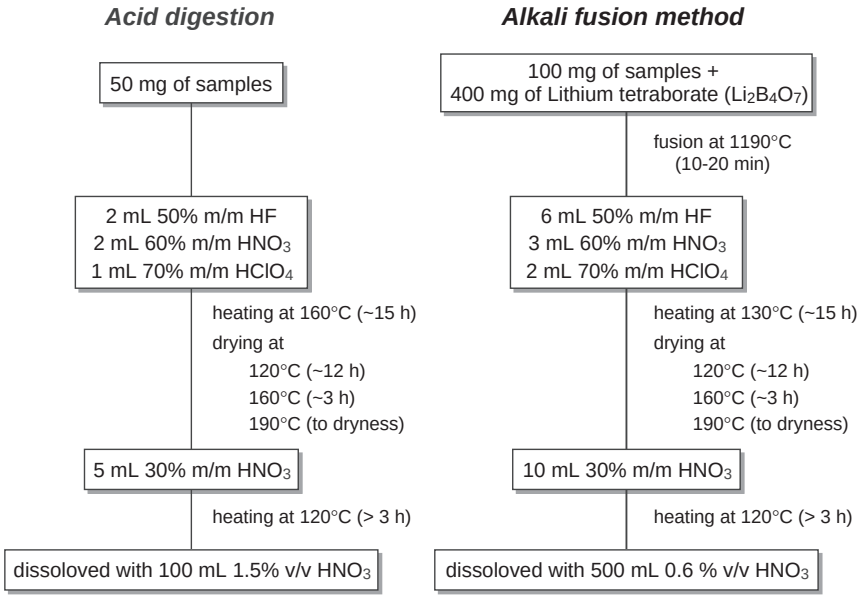

Fig. 1 Flow chart of analytical procedure of acid digestion and alkali fusion method.

Table 2 Background counts and detection limits for acid digestion and fusion method.

	Acid digestion		Alkali fusion	
	Background count for sample blank (cps)	Detection limit (ppm)	Background count for sample blank (cps)	Detection limit (ppm)
Sr	43.1	0.011	196	0.027
Y	20.0	0.016	16.4	0.023
Zr	67.7	0.037	106	0.057
Nb	17.7	0.0081	13.8	0.016
Ba	23.6	0.099	28.2	0.19
La	5.92	0.0026	7.70	0.012
Ce	12.3	0.0067	13.7	0.011
Pr	3.44	0.0020	4.19	0.0027
Nd	2.07	0.0054	2.33	0.011
Sm	0.67	0.0032	1.13	0.0039
Eu	0.93	0.0002	1.38	0.0023
Gd	1.02	0.0026	1.07	0.0074
Tb	1.62	0.0007	1.27	0.0011
Dy	1.24	0.0007	1.16	0.0027
Ho	1.11	0.0005	0.98	0.0008
Er	1.64	0.0022	0.84	0.0013
Tm	1.08	0.0002	1.08	0.0009
Yb	0.79	0.0008	1.15	0.0055
Lu	1.14	0.0004	1.50	0.0013
Hf	2.07	0.0028	2.62	0.0076
Ta	2.60	0.0007	3.97	0.0034
Th	5.41	0.0020	3.80	0.0022
U	1.97	0.0008	1.51	0.0012

LiBr solution. A glass bead droplet (~1 cm in diameter) was transferred to a 15 ml Teflon PFA screw-cap beaker and dissolved by 6 ml of 50 % HF, 3 ml of 60 % HNO_3, and 2 ml of 70 % $HClO_4$ in the tightly sealed beaker, heated for 15 hours on a hot plate at 130°C. The sample was evaporated in a stepwise manner at 120°C for 12 hours, 160°C for 3 hours, and 190°C until dryness. HF treatment following $Li_2B_4O_7$ fusion is known to remove Si and B as volatile SiF_4 and BF_4 (Yu et al., 2001; Panteeva et al., 2003), which reduces total dissolved solids in final solution. As mentioned above, we employed HF-HNO_3-$HClO_4$ treatment instead of simple HF or HF-HNO_3 ones, because we found that whitish precipitates probably composed of fluorides often formed in the absence of $HClO_4$. It is known that the presence of insoluble fluorides in the sample solution can cause erroneous results of trace element concentrations (Yokoyama et al., 1999). Finally, the residue was dissolved with 10 ml of 30 % HNO_3, heated for 3 hours at 120°C and the solution was diluted to 500 ml total volume.

2.4. Interference corrections

Although the ICP parameters are optimized, spectral overlap from oxides (MO^+) and hydroxides (MOH^+) of Ba and light REE on the heavier REE ($^{137}Ba^{16}O^+$ on $^{153}Eu^+$, $^{140}Ce^{16}O^1H^+$ and $^{141}Pr^{16}O^+$ on $^{157}Gd^+$, and $^{143}Nd^{16}O^+$ on $^{159}Tb^+$) should be taken into consideration. The interference of $^{165}Ho^{16}O^+$ on $^{181}Ta^+$ is also significant especially for Ta-depleted samples such as island arc tholeiites like JB-2 (Shibata and Nakamura, 1997). The interference corrections were made by measuring 500 µg/l Ba, 100 µg/l Ce, Pr, Nd, and 10 µg/l Ho solutions and calculating MO^+/M^+ and MOH^+/M^+ ratios. For applying the correction equations based on these data, MO^+/M^+ and MOH^+/M^+ ratios were assumed to be matrix- and time-independent.

3. Results and Discussion

3.1. Detection limits

Average background counts and detection limit data for elements determined by acid digestion and fusion method are shown in Table 2. Detection limits were calculated as the concentration equivalent of three times the standard deviation of replicate measurements of the analyte in blank solution, considering the dilution factor. The averages and standard deviations are obtained from individual five blank solutions.

One of the major disadvantages of fusion method is contamination from impure lithium borate fluxes (e.g. Yu et al., 2001). Eggins (2003) pointed out the significant contamination of La from some lithium borate fluxes. However, we found that $Li_2B_4O_7$ flux used in the present investigation is enough pure for the trace element determination, and thus the low background levels for

La as well as other elements were achieved (Table 2).

3.2. Reproducibility in the analysis of rock reference materials

The analytical results of five rock reference materials obtained by alkali fusion are given in Table 3 together with those by acid digestion. Reference values for JB-2 and JB-3 (Makishima and Nakamura, 1997; Makishima et al., 1999) and compiled values for JG-1a, JG-2, and JG-3 (Imai et al., 1995) are also presented. The averages and relative standard deviations (RSD) are obtained from five sample solutions prepared separately from the decomposition. The replicate data show that the analytical reproducibility (1σ) is mostly <2 % for basaltic rocks except for some elements with low concentrations (Nb, Yb, Ta, Th, U for JB-2 and Ta for JB-3) and <7 % for granitic rocks. The higher RSD values for granitic rocks may be attributed to sample heterogeneity of coarse-grained granitic rocks.

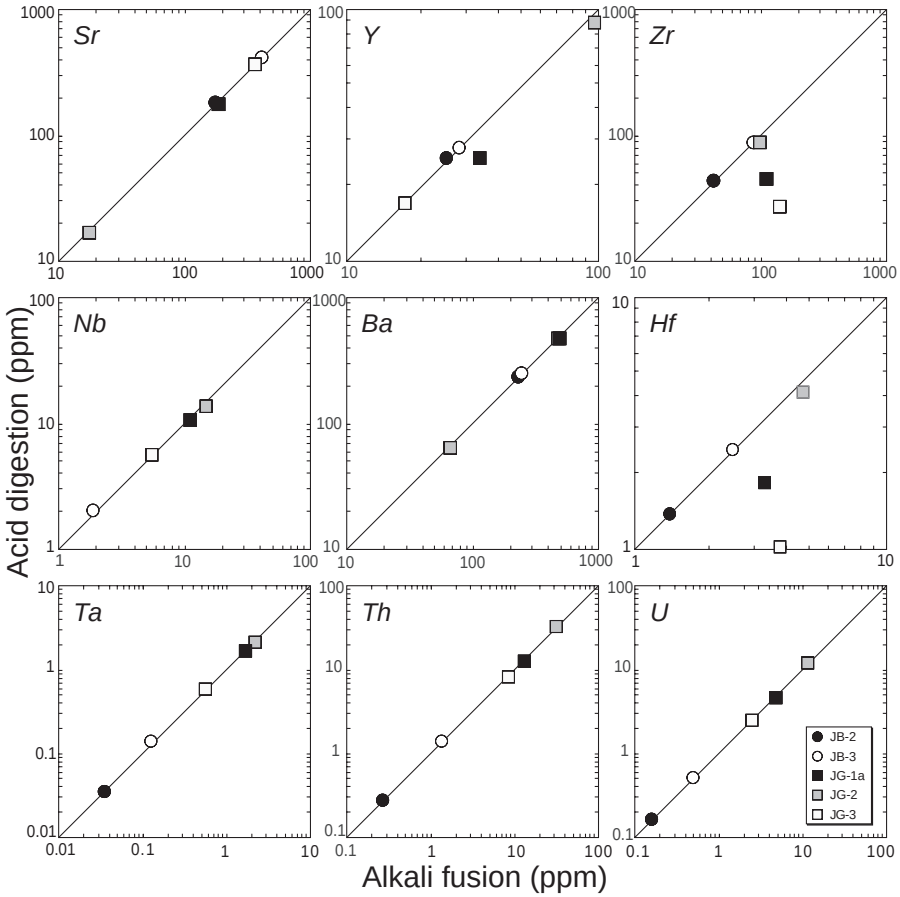

Fig. 2 Comparison of the analytical values by acid digestion with those by alkali fusion method.

3.3. Comparison of the present results with reference values

For the basaltic rocks, analytical results obtained by the two different digestion methods agree well with each other and also with reference values (Fig. 2, Table 3). Acid digestion and alkali fusion procedures yield similar precision and accuracy for basaltic rocks in spite of the increased dilution of samples for the fusion method. It is also suggested that HNO_3-HF-$HClO_4$ digestion used here was valid for basaltic rocks. In contrast, analytical results of granitic rocks show large discrepancies in Zr, Hf, Y, and heavy REE (HREE) between the two methods (Fig. 2, Table 3). The lower values of these elements obtained by the acid digestion are very likely caused by incomplete decomposition of zircon (Imai, 1990). On the other hand, Zr and Hf abundances by the alkali fusion method are consistent with the compiled values by Imai et al. (1995). This suggests that acid-resistant minerals such as zircon are completely decomposed by the fusion method applied here, although REE contents still have some differences between our data and the compiled values.

Figure 3 shows chondrite-normalized REE patterns by the two digestion methods for the basaltic rocks. Also shown for comparison are published data for JB-2 and JB-3 (Makishima and Nakamura, 1997; Orihashi and Hirata, 2003). Our REE patterns by the two different methods exhibit quite smooth patterns with REE abundances comparable with those of Makishima and Nakamura (1997). Chondrite-normalized REE patterns by the two digestion methods for the granitic rocks are shown in Figure 4, and the compiled values for JG-1a, JG-2, and JG-3 (Imai et al., 1995) are shown for comparison. The HREE concentrations obtained for the granitic rocks by the acid digestion are 6-30 % lower than those by the fusion method (Table 3), reflecting incomplete decomposition of refractory minerals. In contrast, our data obtained by the fusion method agree well with recently published ICP-MS data for the reference materials (Fig. 5), although the compiled values (Imai et al., 1995) are slightly different from our results (Fig. 4). The analytical results demonstrated herein suggest that the proposed method is suitable for the analysis of the granitic rocks.

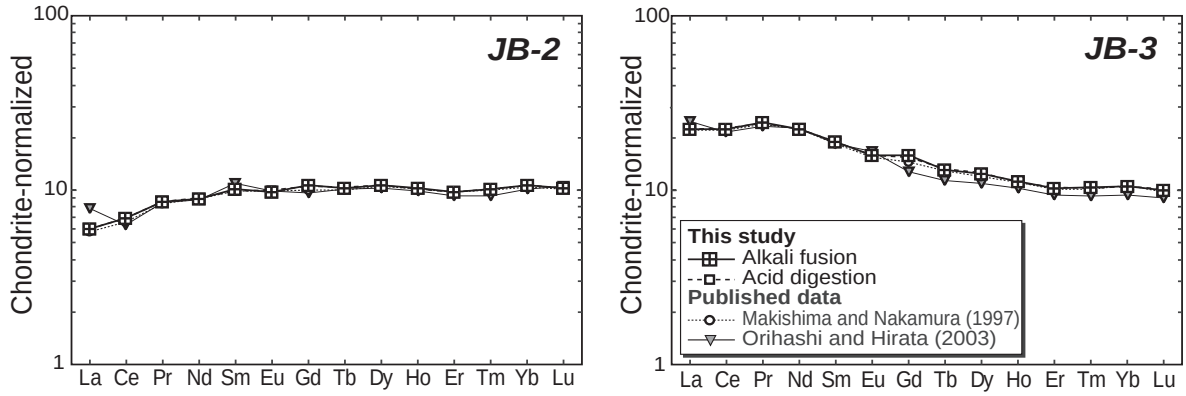

Fig. 3 Chondrite-normalized REE patterns by acid digestion and alkali fusion method for JB-2 and JB-3. Also shown for comparison are published data (Makishima and Nakamura, 1997; Orihashi and Hirata, 2003). Normalizing chondrite values are after Masuda et al. (1973) and Masuda (1975).

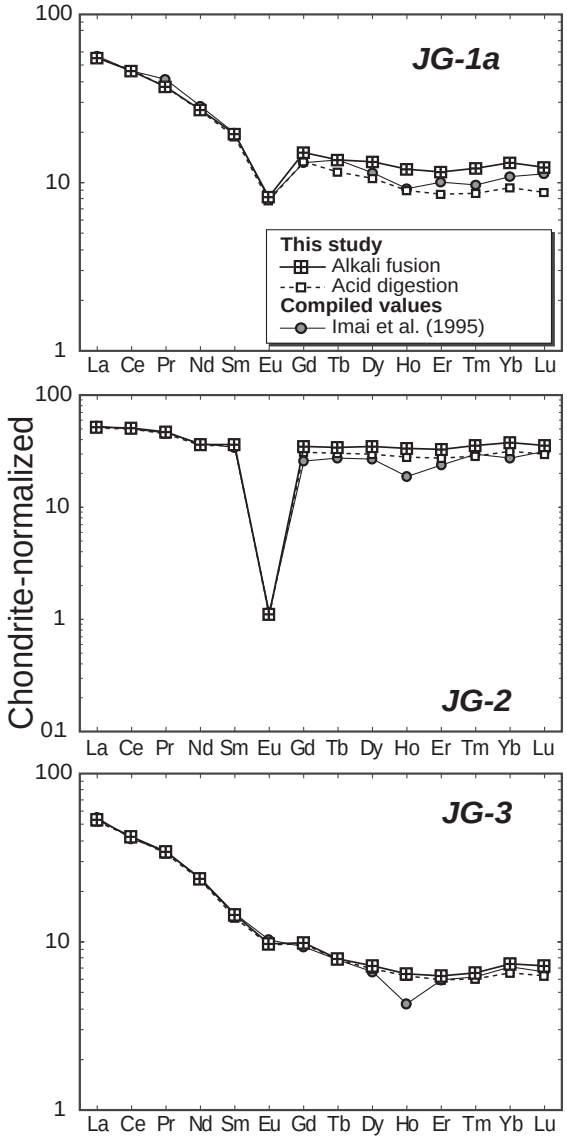

Fig. 4 Chondrite-normalized REE patterns by acid digestion and alkali fusion method for JG-1a, JG-2, and JG-3. Compiled values (Imai et al., 1995) are shown for comparison.

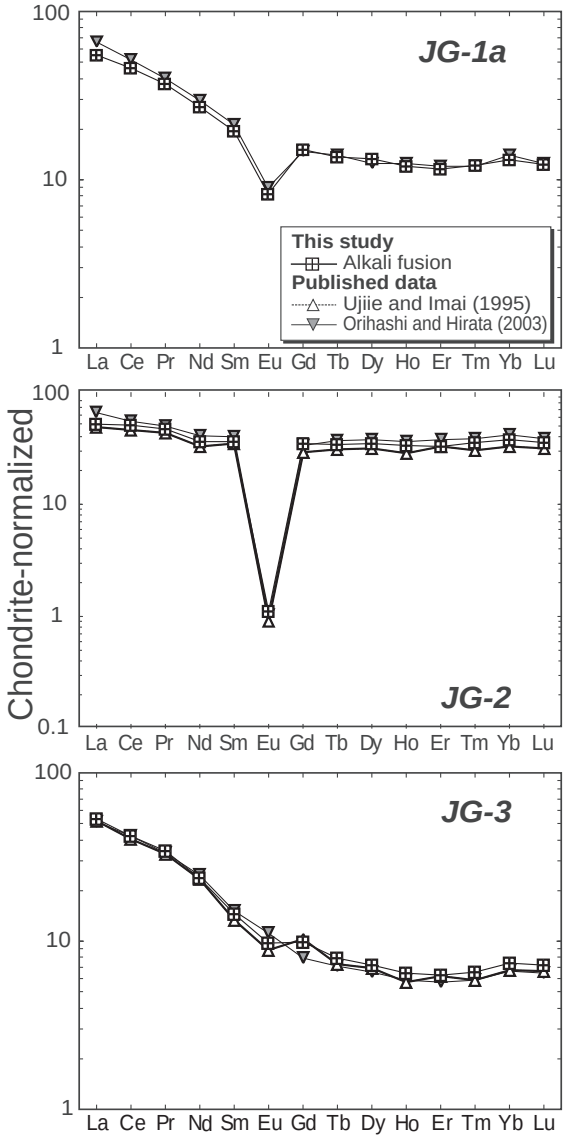

Fig. 5 Chondrite-normalized REE patterns by alkali fusion method for JG-1a, JG-2, and JG-3, and those of published data (Ujiie and Imai, 1995; Orihashi and Hirata, 2003).

Table 3 Trace element concentrations in rock reference materials compared to reference and compiled values.

	JB-2					JB-3				
	Ref (A)	Alkali fusion			Acid	Ref (A)	Alkali fusion			Acid
	(ppm)	Average (ppm)	RSD (%, 1sd)	Difference (%)	digestion (ppm)	(ppm)	Average (ppm)	RSD (%, 1sd)	Difference (%)	digestion (ppm)
Sr	177	179	0.4	1.3	179	423	413	0.2	-2.3	414
Y	25.9	25.1	0.8	-3.1	25.7	28.6	28.0	0.8	-2.2	27.9
Zr	46	43.0	0.4	-6.5	43.6	89.4	87.8	0.4	-1.8	87.2
Nb	0.43	0.43	3.5	1.0	0.48	1.79	1.88	1.7	4.8	2.03
Ba	229	230	0.4	0.5	230	240	247	0.4	2.8	249
La	2.19	2.25	1.0	2.8	2.28	8.36	8.50	0.6	1.6	8.44
Ce	6.43	6.71	0.3	4.3	6.77	21.6	21.9	0.6	1.3	22.2
Pr	1.13	1.17	0.7	3.4	1.17	3.23	3.32	0.9	2.9	3.30
Nd	6.39	6.42	1.2	0.4	6.43	16.1	16.1	0.8	-0.1	16.0
Sm	2.27	2.32	1.1	2.2	2.27	4.23	4.38	1.2	3.6	4.35
Eu	0.86	0.85	0.8	-1.3	0.87	1.35	1.37	0.8	1.7	1.38
Gd	3.12	3.33	1.5	6.6	3.27	4.53	4.91	1.0	8.4	4.78
Tb	0.592	0.60	1.1	1.7	0.61	0.761	0.77	1.4	1.6	0.78
Dy	4.13	4.16	0.9	0.8	4.16	4.65	4.85	0.8	4.3	4.88
Ho	0.898	0.91	0.3	1.3	0.90	0.983	1.00	1.2	1.8	0.99
Er	2.47	2.49	1.5	1.0	2.48	2.58	2.62	1.7	1.6	2.64
Tm	0.392	0.40	0.5	1.0	0.39	0.393	0.40	0.8	2.6	0.40
Yb	2.6	2.64	2.4	1.6	2.66	2.67	2.63	0.7	-1.4	2.62
Lu	0.397	0.40	0.4	1.2	0.40	0.382	0.39	0.6	2.5	0.40
Hf	1.45	1.38	1.5	-4.5	1.36	2.56	2.44	1.2	-4.6	2.47
Ta	0.0327	0.04	5.1	7.8	0.03	0.126	0.13	4.0	3.1	0.14
Th	0.277	0.27	2.8	-3.2	0.27	1.36	1.37	1.2	0.5	1.35
U	0.166	0.16	2.9	-1.6	0.16	0.517	0.50	1.9	-3.1	0.52

(A) Makishima and Nakamura (1997); Makishima et al. (1999)

Table 3 (continued)

	JG-1a					JG-2				
	Ref (B)	Alkali fusion			Acid	Ref (B)	Alkali fusion			Acid
	(ppm)	Average (ppm)	RSD (%, 1sd)	Difference (%)	digestion (ppm)	(ppm)	Average (ppm)	RSD (%, 1sd)	Difference (%)	digestion (ppm)
Sr	187	190	4.3	1.4	175	17.9	17.8	1.0	-0.4	16.8
Y	32.1	33.8	2.2	5.4	25.4	86.5	97.2	2.5	12.3	87.7
Zr	118	113	5.7	-4.0	44.1	97.6	99.8	3.5	2.3	87.4
Nb	11.4	11.1	4.4	-2.6	10.6	14.7	14.8	6.3	1.0	13.5
Ba	470	495	4.6	5.4	466	81	66.7	1.4	-17.7	62.5
La	21.3	20.7	4.2	-2.7	20.8	19.9	19.6	5.7	-1.7	19.0
Ce	45	45.0	3.5	0.0	45.5	48.3	49.3	6.2	2.2	48.3
Pr	5.63	5.08	3.2	-9.8	5.06	6.2	6.38	5.8	2.9	6.19
Nd	20.4	19.3	3.6	-5.3	19.1	26.4	26.1	5.6	-1.0	25.4
Sm	4.53	4.49	2.9	-0.9	4.33	7.78	8.37	3.8	7.6	8.21
Eu	0.7	0.71	4.1	1.9	0.68	0.1	0.10	3.8	-3.2	0.10
Gd	4.08	4.67	1.8	14.5	4.11	8.01	10.7	0.5	34.0	9.68
Tb	0.81	0.80	1.4	-1.0	0.68	1.62	2.01	1.6	24.0	1.79
Dy	4.44	5.17	2.2	16.4	4.11	10.5	13.6	2.3	30.0	11.7
Ho	0.82	1.08	1.9	31.1	0.80	1.67	2.99	2.7	78.8	2.51
Er	2.57	2.97	2.9	15.5	2.17	6.04	8.42	3.4	39.4	7.05
Tm	0.38	0.48	5.1	25.5	0.34	1.16	1.38	2.6	19.0	1.12
Yb	2.7	3.26	5.0	20.8	2.32	6.85	9.47	1.6	38.2	7.77
Lu	0.44	0.48	4.1	9.4	0.34	1.22	1.38	1.2	13.3	1.16
Hf	3.59	3.28	7.0	-8.6	1.82	4.73	4.68	4.8	-1.1	4.15
Ta	1.9	1.69	5.8	-10.9	1.67	2.76	2.27	4.4	-17.6	2.06
Th	12.8	13.4	4.3	4.4	12.1	31.6	32.5	2.3	2.8	32.3
U	4.69	4.87	7.3	3.9	4.53	11.3	11.7	2.3	3.4	11.7

(B) Imai et al. (1995)

Table 3 (continued)

	JG-3				
	Ref (B)	Alkali fusion			Acid
	(ppm)	Average (ppm)	RSD (%, 1sd)	Difference (%)	digestion (ppm)
Sr	379	367	1.2	-3.1	358
Y	17.3	17.1	2.6	-0.9	16.9
Zr	144	145	2.8	0.9	26.9
Nb	5.88	5.57	1.3	-5.4	5.59
Ba	466	479	2.5	2.8	463
La	20.6	20.0	1.6	-2.8	19.6
Ce	40.3	41.3	0.9	2.6	40.9
Pr	4.7	4.64	0.8	-1.3	4.52
Nd	17.2	16.9	0.8	-1.7	16.8
Sm	3.39	3.31	2.5	-2.3	3.21
Eu	0.9	0.85	2.7	-6.1	0.84
Gd	2.92	3.06	2.4	4.8	3.01
Tb	0.46	0.46	3.2	1.0	0.46
Dy	2.59	2.81	2.8	8.4	2.68
Ho	0.38	0.57	3.1	51.0	0.56
Er	1.52	1.61	2.1	6.0	1.51
Tm	0.24	0.25	2.4	6.2	0.23
Yb	1.77	1.83	2.1	3.6	1.62
Lu	0.26	0.28	1.5	8.7	0.24
Hf	4.29	3.78	2.0	-11.8	1.02
Ta	0.7	0.58	4.0	-16.9	0.56
Th	8.28	8.80	2.9	6.3	7.88
U	2.21	2.49	2.1	12.7	2.41

(B) Imai et al. (1995)

4. Conclusions

We presented an improved $Li_2B_4O_7$ fusion method followed by HF-HNO_3-$HClO_4$ treatment for simultaneous determination of 23 trace elements in granitic rocks. This method offers several advantages including: (1) suppression of insoluble fluorides by addition of $HClO_4$, (2) simple and reliable preparation procedure, (3) straightforward instrument calibration, and (4) the very low background levels by using pure $Li_2B_4O_7$ flux. Our results demonstrate that Zr and Hf abundances are consistent with the compiled values and that REE concentrations agree well with recently published data, suggesting that the proposed method is suitable for the analysis of the granitic rocks.

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