

**NOTE****Evaluation of a rapid, effective sample digestion method for trace element analysis of granitoid samples containing acid-resistant minerals: Alkali fusion after acid digestion**

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(Received March 21, 2013; Accepted August 22, 2013)

Alkali fusion after acid digestion method (AFAD) was used for determination by ICP-MS of twenty-five trace elements (Rb, Sr, Y, Zr, Nb, Cs, Ba, Hf, Pb, Th, U, and rare earth elements) in four silicate reference materials (JG-1a, JG-2, and JG-3 granitoids and JB-2 basalt) from the Geological Survey of Japan (GSJ). Results were compared with those obtained by acid digestion (AD) method. Our results are in excellent agreement with previously reported data obtained by fusion methods. The reproducibility of replicate analyses is better than 5% ( $1\sigma$ ) for all the elements, except Rb, Cs, and Pb in JG-2.

Keywords: silicate digestion method, trace element abundance, silicate reference material, alkali fusion

**INTRODUCTION**

Acid-resistant minerals, such as zircon, fluorides and chromite make rocks difficult to dissolve completely, leading to poor bulk rock trace element analysis. Although minor components, these minerals strongly affect bulk rock chemical composition because of the high abundance of Zr, Hf, and heavy rare earth elements (HREEs). The most widely accepted method for dissolving bulk rock powders is acid digestion (AD) with HF, HNO<sub>3</sub>, and HClO<sub>4</sub> (e.g., Yokoyama *et al.*, 1999). However, acid-resistant minerals are insoluble even with the use of Teflon bombs in microwave digestion technique (e.g., Jarvis and Jarvis, 1992; Yu *et al.*, 2001) and fusion of rock powders with alkali flux up to 900°C is often used (e.g., Jarvis and Jarvis, 1992; Yu *et al.*, 2001). Fusion methods are subject to matrix-induced instability during analyses owing to increased matrix elements from the flux (e.g., Li, B, C and Na). Pt or zirconium crucibles used for high-temperature fusion are another source of contamination. All these factors must be accounted for a correct application of fusion methods.

Roser *et al.* (2000) proposed a method, referred to as Alkali Fusion after Acid Digestion (AFAD). This method consists of AD with HF–HClO<sub>4</sub> in a Pt-crucible, followed

by fusion with an anhydrous Na<sub>2</sub>CO<sub>3</sub> flux in the same crucible to digest sedimentary rock samples prior to analysis by ICP-MS. The AD step reduces the amount of the silica fraction, by releasing SiF<sub>4</sub>, so that less Na<sub>2</sub>CO<sub>3</sub> is required for the following fusion step. Fusion of the sample residue ensures decomposition of acid-resistant minerals or minerals that precipitate during AD, such as fluorides (e.g., Yokoyama *et al.*, 1999).

We applied the AFAD method of Roser *et al.* (2000) on three granitoids (JG-1a, JG-2 and JG-3) and one basalt (JB-2) reference materials from the Geological Survey of Japan (GSJ) and measured their trace element contents by ICP-MS. These reference samples have been rigorously analyzed by AF methods (Shimizu *et al.*, 2011; Awaji *et al.*, 2006) and recommended values were reported (Imai *et al.*, 1995). AD method was also used for comparison.

**METHODS***Digestion methods*

All reagents used in this study are shown in Supplementary Table S1. For AFAD and AD methods, the analytical flow charts are shown in Fig. 1. Sample powder and alkali flux should be weighed accurately for maintaining the same sample to matrix ratio. HClO<sub>4</sub> was added prior to HF to avoid violent reactions and formation of fluorides in ADAF and AD. Sequential evaporation of HF followed by evaporation of HClO<sub>4</sub> was done by step heat-

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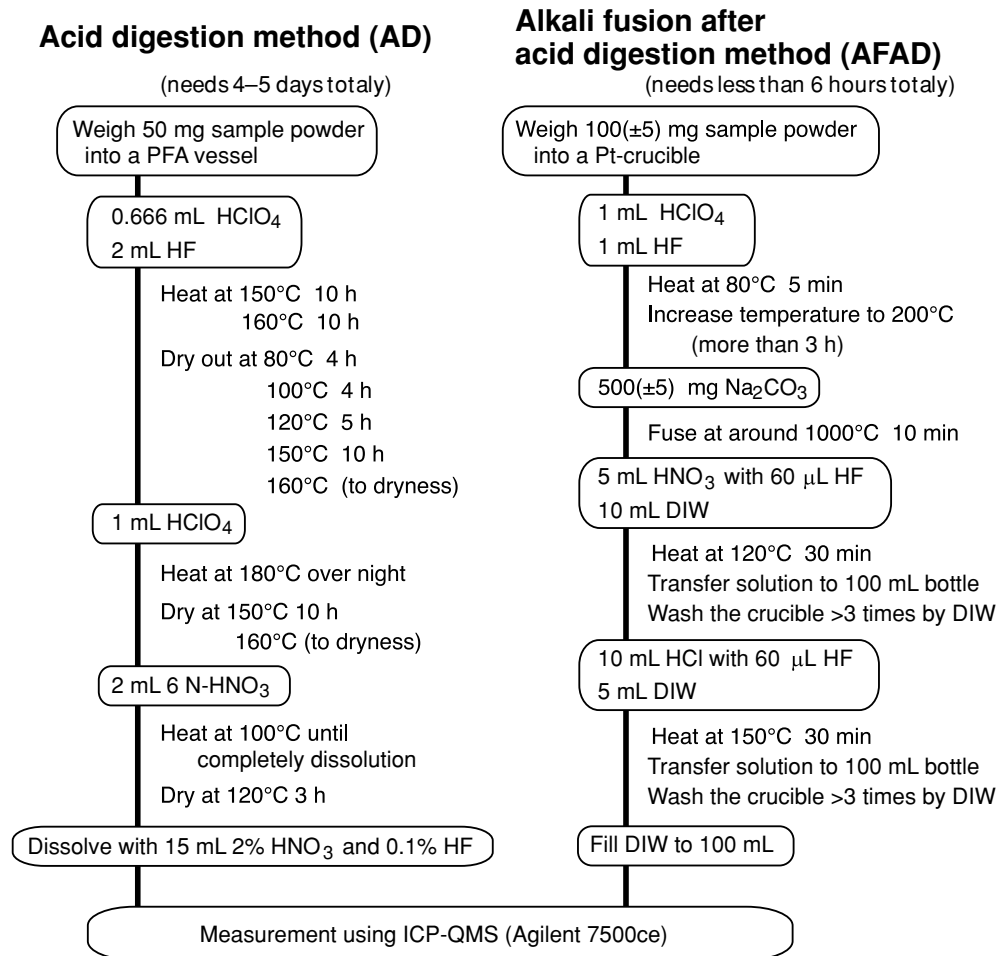


Fig. 1. Analytical protocols for the acid digestion method and the alkali fusion after acid digestion method.

ing at progressively increasing temperature up to 160°C (Fig. 1). The total time required to prepare 12 samples by AFAD was ~6 h, including preparations for ICP-QMS analyses.

#### ICP-QMS analysis

ICP-QMS analysis was performed on an Agilent 7500ce at IFREE/JAMSTEC (Supplementary Table S2) following Nakamura and Chang (2007). Calibration solutions (1, 10, 100, and 1000 pg/g) were prepared by gravimetric serial dilution (Table S1). For AD, the sample solutions were diluted 5,000–30,000 fold with a mixed solution of 2% HNO<sub>3</sub> and 0.1% HF by weight containing 1 ng/mL internal standard <sup>115</sup>In and <sup>209</sup>Bi. To reduce the effects of high C and Na concentrations in the matrix, we used >20,000 fold dilution for AFAD. Calibration solutions for AFAD were prepared by addition of standard solutions to the procedural blank solution prepared with the samples to match the matrix.

Although the instrumental conditions were adjusted

to maintain the best balance between high sensitivity and low oxide formation, we had to correct for overlaps between the spectra of oxides and hydroxides for some REEs (<sup>137</sup>Ba<sup>16</sup>O<sup>+</sup> on <sup>153</sup>Eu<sup>+</sup>, <sup>140</sup>Ce<sup>16</sup>O<sup>1</sup>H<sup>+</sup> and <sup>141</sup>Pt<sup>16</sup>O<sup>+</sup> on <sup>157</sup>Gd<sup>+</sup>) (Dulski, 2001). We measured three separate solutions prepared by 1 ng/mL REEs solutions, 5 ng/mL Ce, and 10 ng/mL Ba with 2 ng/mL Pr, and the correction factors for the oxides and hydroxides were calculated (<1.5%) and applied to all the analyses.

## RESULTS AND DISCUSSION

#### Procedural blanks and detection limits

Three-sigma detection limits for both methods were obtained by measurement of procedural blank solutions (Supplementary Table S3). The detection limits for AFAD were about 10 times those for AD because of high blank levels from the alkali flux. Effects of the blanks from the Pt crucible were limited for the elements affected by interference from Pt-argides (<sup>192</sup>Pt<sup>40</sup>Ar<sup>+</sup> on <sup>232</sup>Th<sup>+</sup> and

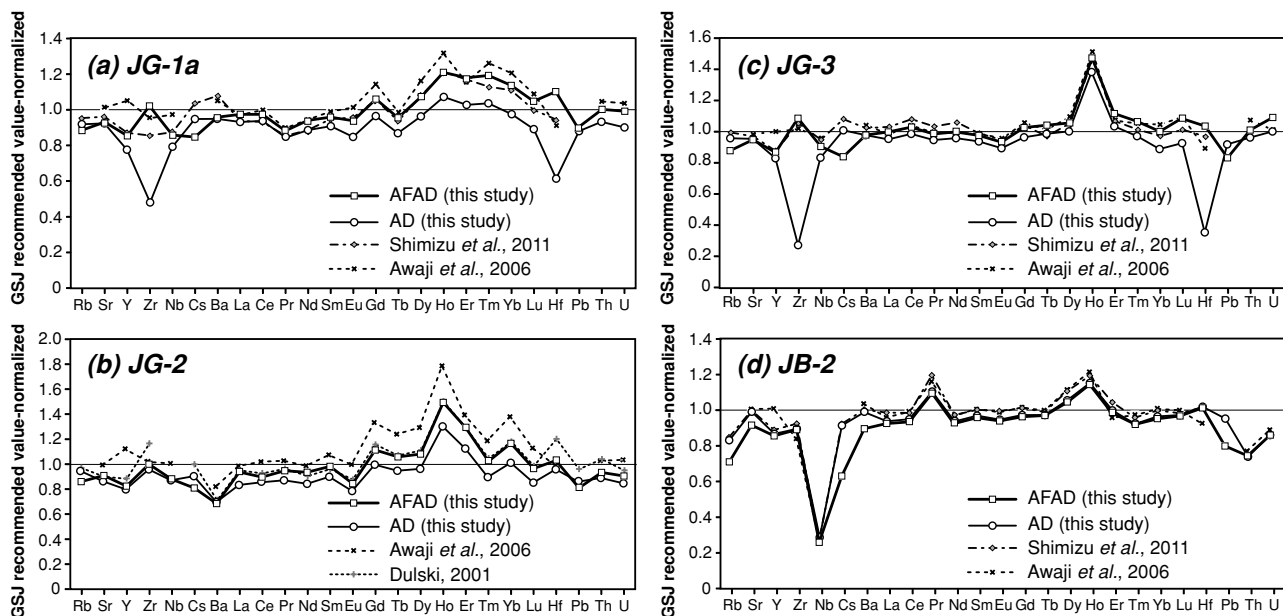


Fig. 2. Comparison of trace element abundances (normalized by GSJ recommended values; Imai *et al.*, 1995) determined in this study and in previous studies: (a) JG-1a, (b) JG-2, (c) JG-3, and (d) JB-2.

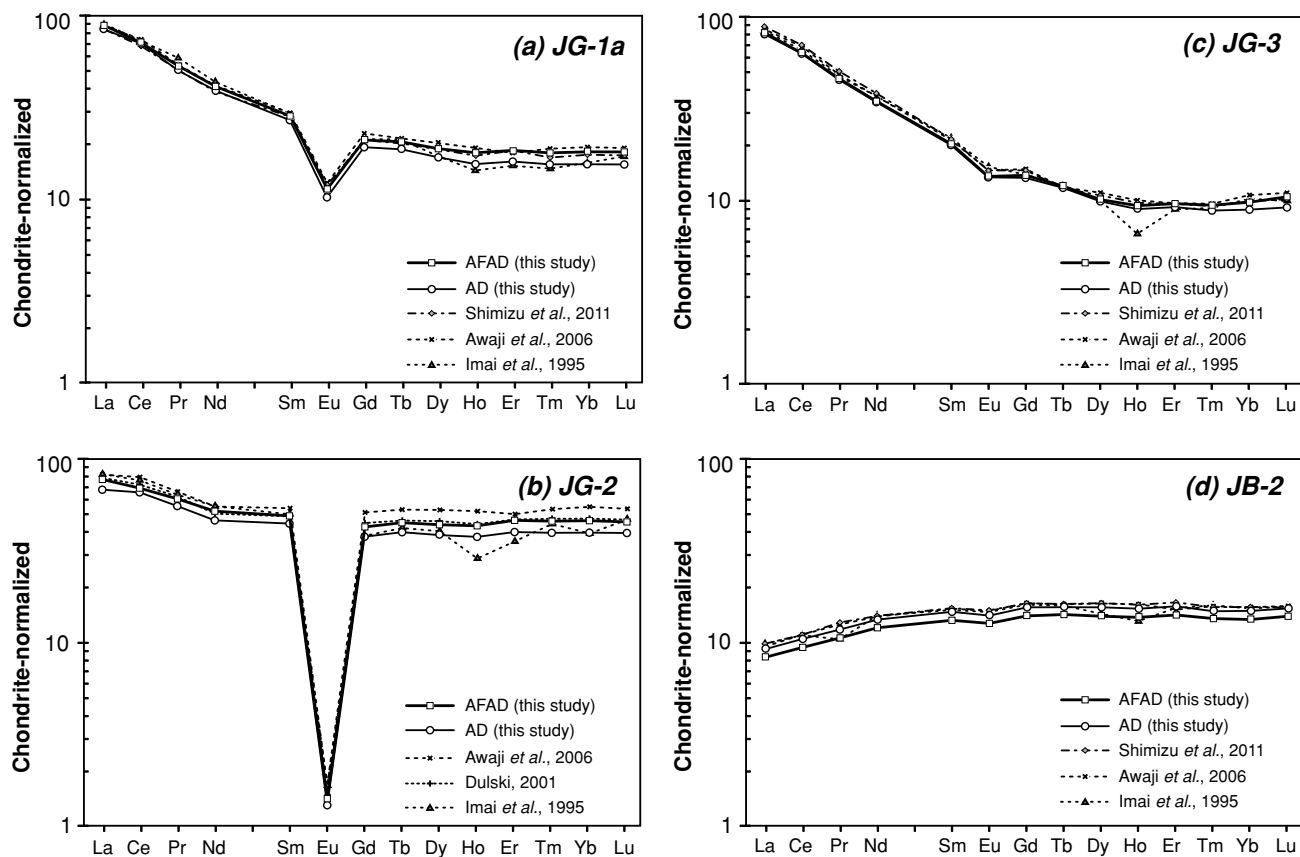


Fig. 3. Comparison of rare earth element abundances (normalized by chondrite values; McDonough and Sun, 1995) determined in this study and in previous studies: (a) JG-1a, (b) JG-2, (c) JG-3, and (d) JB-2.

$^{198}\text{Pt}^{40}\text{Ar}^+$  on  $^{238}\text{U}^+$ ) and Ta. Ta was not measured due to high levels of contamination from the Pt-crucibles. Overlap corrections for Pt-argides were negligible for the samples analyzed, although we always monitored the  $^{198}\text{Pt}^{40}\text{Ar}^+$  and  $^{198}\text{Pt}$  in blank solutions. This interference may be significant for samples with low U contents.

Impurities in procedural blanks for both methods are shown in Table S3. In the AFAD blanks, Rb, Sr, Cs, Ba, Ce and Pb originated from the alkali flux were detected at nanogram-levels or higher. The abundances of the analyzed elements in felsic rocks are usually at ppm-level, and thus low enough for AFAD.

#### *Comparison between AD and AFAD*

Granitoids and a basalt sample were analyzed by both methods and replicate analyses were performed (Supplementary Table S4, Figs. 2 and 3). One-sigma relative standard deviations (% RSD) for repeated analyses of the granitoids prepared by AFAD were <5% for all elements, except for volatiles Rb, Cs, and Pb in JG-2. These elements may have evaporated during alkali fusion, and differences in the amount of evaporation between analyses would have resulted in a large % RSD.

Abundances of high field strength elements (HFSEs) and HREEs in the granitoids by AD were always lower than those by AFAD. The % RSD values for HFSEs in samples by AD were usually higher than those by AFAD (Figs. 2 and 3). In granitoid samples, HFSEs and REEs are highly partitioned in zircon and fluorides (e.g., Bea *et al.*, 1994) and these minerals were not completely decomposed by AD. Our results show that AFAD effectively dissolved these minerals. For JB-2, the element abundances obtained by both methods were nearly identical and reproducibility was better for JB-2 than for the granitoids. These indicate that AFAD is also applicable to depleted arc basalts, like JB-2, in which trace element contents are very low (Imai *et al.*, 1995).

#### *Comparisons to previous studies*

The results obtained in this study were normalized by the recommended values (Imai *et al.*, 1995) and compared with the data previously reported by fusion methods (Fig. 2). Our AFAD data for Zr and Hf in JG-1a and JG-3 are slightly higher than previously reported data; the difference may be attributed to heterogeneity of the rock powders. Otherwise, our AFAD data for the four reference materials were in agreement with the previous results. Note that positive Ho spikes observed in all figures and negative Nb spikes in JB-2 originated from the low and high recommended (compiled) values of Imai *et al.* (1995), respectively, as has been noted by previous studies (Shimizu *et al.*, 2011; Awaji *et al.*, 2006) (see also Fig. 3).

For the volatile elements Rb and Cs, our AFAD re-

sults are always lower than those of Shimizu *et al.* (2011). They fused rock powders without any flux in a Pt-crucible heated in a tube furnace at 1600°C for 2–3 min. The short fusion may have retained the volatile elements in the flux-free fused samples.

Some middle to HREEs in JG-1a and JG-2 reported by Awaji *et al.* (2006) were higher than our AFAD results but are in good agreement for the JG-3 and JB-2 standards. Possible explanation for the difference is heterogeneity in JG-1a and JG-2 powders. Alternatively, the use of different matrix in standards may have led to fractionation of HREEs in the ICP (e.g., Tanner, 1992; Kimura and Chang, 2012) as Awaji *et al.* (2006) used solutions of various GSJ reference materials with reference values as standards, whereas we used alkali flux matrix-matched chemical standards. We have not yet determined the source of the difference.

In CI-chondrite-normalized-REE plots, smooth patterns are shown with the exception of variably negative anomalies in Eu by plagioclase fractionation (Fig. 3). The overall agreement of the analytical results with the recommended values (except for Ho) and the very good reproducibility of replicate analyses indicate that the AFAD method evaluated in this study is suitable for trace element analysis of granitoid samples. We were able to analyze 12 samples in 6 h by AFAD, and this high throughput is an additional advantage. Cs, Rb, and Pb cannot be precisely determined by AFAD; however, additional conventional AD analyses can be used to achieve precise determinations of these elements (Table S4).

**Acknowledgments**—We thank Ms. Yoko Nakamura for assistance with chemical analysis. Dr. M. G. Tejada kindly edited our English manuscript. We also thank Drs. Ken Takai and Katsuhiko Suzuki for access to the equipment. We are grateful to two anonymous reviewers for their critical comments. Dr. Daniele Pinti kindly gave his idea and useful comments for this paper.

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#### SUPPLEMENTARY MATERIALS

URL (<http://www.terrapub.co.jp/journals/GJ/archives/data/48/MS280.pdf>)  
Tables S1 to S4