



## Rapid bulk rock decomposition by ammonium fluoride (NH<sub>4</sub>F) in open vessels at an elevated digestion temperature



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### ABSTRACT

Complete dissolution is essential for achieving accurate analytical results for geological samples. Hydrofluoric acid is the most effective mineral acid for breaking up strong Si–O bonds to form SiF<sub>6</sub><sup>2-</sup> ions in acidic solution. However, HF is rather inefficient in the open-vessel acid digestion of refractory minerals such as zircon due to its low boiling point (boiling point of 38.3% HF = 112 °C). In this study, a decomposition technique using the solid compound NH<sub>4</sub>F in an open vessel (Savillex Teflon vial) has been investigated for the multi-element analysis of various rock reference materials. The higher boiling point (260 °C) of NH<sub>4</sub>F allows for an elevated digestion temperature in open vessels, which enables the decomposition of refractory phases. Using this method, Zr was completely recovered from the granodiorite GSP-2 reference material in 1–1.5 h at 250 °C, which is ~12 times faster than using conventional closed-vessel acid digestion at 190 °C (high-pressure PTFE digestion bomb). There is a positive correlation between the test sample mass and the amount of NH<sub>4</sub>F required for complete recovery of Zr, Hf, Nb, Ta, and heavy rare earth elements in GSP-2, which is due to the resistance of zircon (which is a major reservoir for heavy rare earth elements) to decomposition at lower reagent to sample ratios. The recommended proportion of NH<sub>4</sub>F, relative to the amount of sample powder required for complete element recovery, is 6:1. Unlike in NH<sub>4</sub>F-assisted high-pressure acid digestion, our results clearly indicate that adding HNO<sub>3</sub> severely inhibited the digestion capabilities of NH<sub>4</sub>F for refractory minerals such as zircon in open vessels. The most outstanding advantage of the new method is that the digestion can be performed in a conventional Savillex Teflon vial instead of a high-pressure PTFE digestion bomb. Moreover, NH<sub>4</sub>F–open-vessel acid digestion is not hampered by the formation of insoluble fluorides, which represents another important advantage of this new sample decomposition method. Similar to HF and HNO<sub>3</sub>, ultra-pure NH<sub>4</sub>F can be produced using a conventional PFA sub-boiling purification system, and it does not induce new interference species in ICP-MS analysis. Additionally, this reagent is removed by taking the sample to dryness, which is important to keep the total dissolved solid of the final solution presented to the instrument low. NH<sub>4</sub>F has many of the same safety handling requirements of HF, especially when being heated to dryness to remove the Si as SiF<sub>4</sub>, and excess reagent as HF, so safety issues are still a concern. The developed NH<sub>4</sub>F–open-vessel acid digestion method has been successfully applied to the digestion of a series of international geological reference materials. This simple, effective, and comparatively safe dissolution method shows great potential for the digestion of geological samples.

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### 1. Introduction

Despite a considerable amount of new research on solid sample introduction techniques, solution sampling remains the preferred method for most modern instrumental techniques such as quadruple inductively coupled plasma mass spectrometry (ICP-MS), multi-collector ICP-MS, magnetic sector ICP-MS and time of flight ICP-MS. Dissolution is thus required for whole rock trace element and isotope ratio analysis. In the case of geological sample analysis, dissolution is often the limiting factor for obtaining accurate results and high sample throughput due to the

presence of resistant minerals (Chao and Sanzalone, 1992; Totland et al., 1992; Qi and Grégoire, 2000; Qi et al., 2000; Yu et al., 2001; Taylor et al., 2002; Pretorius et al., 2006). Hydrofluoric acid is the most effective mineral acid for breaking up strong Si–O bonds to form SiF<sub>6</sub><sup>2-</sup> ions in acidic solution. For treatment of geological samples, HF in combination with other acids (HNO<sub>3</sub>, HCl, HClO<sub>4</sub>) is generally used in open- and closed-vessel acid digestion (Chao and Sanzalone, 1992; Eggins et al., 1997; Yu et al., 2001; Potts and Robinson, 2003). Open-vessel acid digestion is valuable for routine analysis because of its flexibility regarding the control of digestion parameters such as temperature, time and the addition or removal of reagents (Taylor et al., 2002; Potts and Robinson, 2003). However, HF is rather inefficient in open-vessel acid attack procedures due to its low boiling point (boiling point of 38.3% HF = 112 °C).

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This is especially true when applied to felsic rocks, due to the incomplete dissolution of refractory minerals such as zircon (Hall and Plant, 1992; Totland et al., 1992). In addition, this technique requires long reaction times and the use of large amount of acids, which increases the cost and potential sample contamination (Totland et al., 1992; Yu et al., 2001; Potts and Robinson, 2003).

The complete digestion of a sample is a prerequisite for achieving reproducible and accurate results in routine analysis. To improve the digestion capability of HF, most geochemists employ closed acid digestion bombs to decompose samples since 1968 (Qi et al., 2000; Pretorius et al., 2006; Hu and Gao, 2008), which was popularized by Langmyhr and Paus (1968) and Bernas (1968). Digestions performed in closed vessels can reach higher temperatures because the boiling point of the reagents is raised by the pressure generated within the vessel. These bombs produce very high pressures (7–12 MPa) when the sample and acids are subjected to high temperatures (110–250 °C) (Jarvis, 1992; Potts and Robinson, 2003). Such increased temperatures and pressures can significantly shorten sample decomposition times and allow the digestion of refractory phases (Jarvis, 1992; Potts and Robinson, 2003). In comparison with open-vessel acid digestion, the disadvantages of bomb dissolutions are the greater labor intensity, the high cost of the bomb-jacket set and increased danger due to the higher pressure produced within the vessel (Zhang et al., 2012a).

Instead of HF, an efficient attack on refractory minerals can be performed using alkali fusion (Chao and Sanzalone, 1992; Totland et al., 1992; Potts and Robinson, 2003). NaOH, KOH, Na<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, LiBO<sub>2</sub> and Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> are typically used for this type of fusion. Alkali fusion is traditionally used to analyze the major elements in geological samples. These methods are rarely used for trace element analysis in geological samples due to their relatively high blank level and the large amount of total dissolved solids in the final solution. A revised alkali fusion method based on the simple acid digestion of powdered low-dilution (flux: sample ≈2:1) glass beads has been proposed by Park et al. (2013), which somewhat overcomes the main drawback of conventional alkali fusion.

In 1931, Shead and Frederich-Smith (1931) successfully performed ammonium fluoride fusion for the determination of silica in glass sands. Bahattin Ayranci (1989) developed a rapid method for the decomposition of zirconia using a suitable combination of NH<sub>4</sub>F + (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as a fusion agent at about 350 °C. Kolikova et al. (1985) reported interactions between NH<sub>4</sub>F and silicate minerals (albite, biotite, orthoclase, labrador) by stirring solid NH<sub>4</sub>F with powdered mineral samples at ambient temperatures, resulting in the partial decomposition of the silicates. Mariet et al. (2008) reported that the digestion capacity of a mixture of HNO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> + NH<sub>4</sub>F was similar to that of HNO<sub>3</sub> + HF + HClO<sub>4</sub> in conventional open vessel acid digestion. This comparison was based on the testing of three reference materials: lichen 336, basalt BE-N, and Soil 7. Hu et al. (2010) demonstrated that a combination of NH<sub>4</sub>F and HNO<sub>3</sub> in high-pressure bomb digestion is effective for the dissolution of igneous rocks, ranging from mafic to felsic. In a recent study, an efficient and simplified digestion technique using ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>) in a screw-top Teflon vial (open-vessel digestion) was developed for the multi-element analysis of various rock samples (Zhang et al., 2012b). The high boiling point of NH<sub>4</sub>HF<sub>2</sub> (239.5 °C) allows the use of an elevated digestion temperature in Savillex screw-top Teflon vials, which enables the decomposition of refractory phases and is approximately six times faster than the use of conventional closed-vessel acid digestion at 190 °C (high-pressure PTFE digestion bomb). The elevated digestion temperature is very important. For example, a digestion time of 2–3 h for 200 mg of NH<sub>4</sub>HF<sub>2</sub> in a Savillex Teflon vial at 230 °C is sufficient to digest 50 mg of the felsic rock GSP-2, which is ~8–9 times faster than that at 200 °C (Zhang et al., 2012a, 2012b). We currently use the NH<sub>4</sub>HF<sub>2</sub> digestion method in our laboratory.

NH<sub>4</sub>F holds similar advantages as a decomposition reagent of NH<sub>4</sub>HF<sub>2</sub>. NH<sub>4</sub>F has a higher boiling point (260 °C vs 239 °C), which allows for an elevated digestion temperature in open vessels. NH<sub>4</sub>F is

also a solid reagent, making it relatively similar to NH<sub>4</sub>HF<sub>2</sub> in terms of safety. Similar to HF, HNO<sub>3</sub>, and NH<sub>4</sub>HF<sub>2</sub>, ultra-pure NH<sub>4</sub>F can be produced using a conventional PFA sub-boiling (heating and cooling) purification system, and it does not induce new interference species in ICP-MS analysis. It is also worth emphasizing that this reagent is removed by taking the sample to dryness, which is important to keep the TDS of the final solution presented to the instrument low. However, to our knowledge, NH<sub>4</sub>F has not been used routinely to dissolve geological samples for the accurate determination of trace elements in an open-vessel digestion. The clear advantages of the NH<sub>4</sub>F—open-vessel acid digestion method are the elimination of the use of high-pressure digestion bomb and very corrosive and toxic HF, combining the advantages of open- and closed-vessel digestion methods.

In this study, we report a systematic investigation of the decomposition capabilities of NH<sub>4</sub>F for felsic rock GSP-2 using open-vessel digestion (Savillex screw-top Teflon vial). The effects of the digestion temperature and time, addition of nitric acid, amount of NH<sub>4</sub>F used, presence of insoluble fluorides, and purification of NH<sub>4</sub>F are studied in detail. The developed NH<sub>4</sub>F—open-vessel acid digestion method is also used successfully to determine trace elements in a series of international rock reference materials.

## 2. Experimental

### 2.1. Instrumentation

Experimental digestion products were analyzed using an Agilent 7700× ICP-MS instrument (Agilent Technologies, Tokyo, Japan). The nebulizer gas and make-up gas flow rates were optimized to obtain good signal intensities for Li, Y, Ce and Tl, while keeping the Ce<sup>0</sup>/Ce<sup>+</sup> and Ce<sup>2+</sup>/Ce<sup>+</sup> ratios below 1.2%. Drift was minimized by flushing through a rock solution for 30 min before tuning the instrument for a run. Drift corrections were performed using In as an internal standard and by repeatedly analyzing a calibration solution as a drift monitor over the duration of a run. It has been well documented that the oxides (and, to a lesser extent, hydroxides) of Ba and the light rare earth elements can cause interference problems with the heavier REE (Dulski, 1994; Robinson et al., 1999). In this study, we corrected the oxide or hydroxide interferences on <sup>151</sup>Eu, <sup>158</sup>Gd, <sup>159</sup>Tb, <sup>163</sup>Dy, and <sup>166</sup>Er in granodiorite GSP-2 and granite G-2. Details of the operating conditions and measurement parameters can be found in Table 1.

### 2.2. Reagents

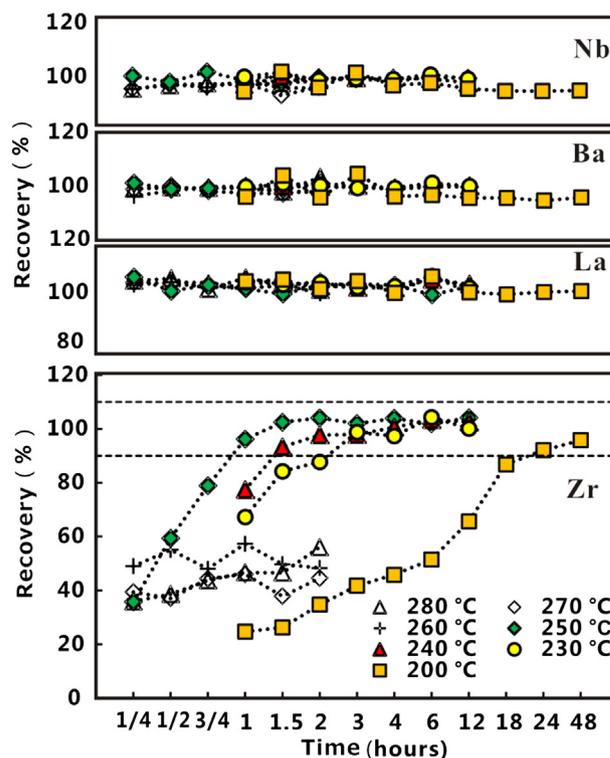
Ultra-pure water with a resistivity of 18.0 MΩ cm<sup>-1</sup> was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Commercially available nitric acid (68% v/v, GR grade) was further distilled in a sub-boiling distillation system. External calibrators (1, 10 and 50 ng ml<sup>-1</sup> for all elements) were prepared by gravimetric serial dilution from 10 μg ml<sup>-1</sup> multi-element standard solutions (SPEX CertiPrep, NJ, USA). The internal standard concentration of indium was constant at 10 ng ml<sup>-1</sup> in all final sample solutions, calibrators and blanks. Ammonium fluoride (NH<sub>4</sub>F) (98% metal basis) was purchased from Sinopharm Chemical Reagent Co. Ltd.

### 2.3. Purification of NH<sub>4</sub>F

The sub-boiling still (Savillex, Eden Prairie, MN, USA) consists of two 120 ml PFA bottles connected at right angles by a threaded PFA block, which is routinely used to purify HF. NH<sub>4</sub>F was placed into the feed bottle and heated by an infrared heat lamp to maintain a temperature of ~180 °C (Fig. 1a). At this temperature, NH<sub>4</sub>F changed from a solid to a liquid (melting point = ~170 °C) and evaporated slowly, with the vapor condensing and recrystallizing in the threaded PFA block and the collecting bottle. The purified NH<sub>4</sub>F crystallizes as small colorless prisms (Fig. 1b), and is exceedingly soluble in water. Approximately

**Table 1**  
Instrumental operating conditions for ICP-MS.

Instrumental parameters (Agilent 7500a)	
RF power	1350 W
Argon gas-flow	
Plasma gas	15 L min <sup>-1</sup>
Auxiliary gas	1.0 L min <sup>-1</sup>
Nebulizer gas	0.78 L min <sup>-1</sup>
Make up gas	0.24 L min <sup>-1</sup>
Sampling depth	7 mm
Sample uptake rate	0.1 ml min <sup>-1</sup>
Torch	Normal torch (quartz glass)
Spray chamber	Scott double-pass type (2 °C)
Sampler aperture diameter	1.0 mm (Ni)
Skimmer aperture diameter	0.4 mm (Ni)
Data acquisition parameters	
Detector mode	Dual (pulse and analog counting)
Scan mode	Peak hopping
Points per peak	1
Sweeps per reading	3
Readings per replicate	3
Replicates	3
Dwell time	100 ms per mass
Isotopes	<sup>7</sup> Li, <sup>9</sup> Be, <sup>45</sup> Sc, <sup>51</sup> V, <sup>53</sup> Cr, <sup>59</sup> Co, <sup>60</sup> Ni, <sup>63</sup> Cu, <sup>66</sup> Zn, <sup>71</sup> Ga, <sup>85</sup> Rb, <sup>88</sup> Sr, <sup>89</sup> Y, <sup>90</sup> Zr, <sup>93</sup> Nb, <sup>133</sup> Cs, <sup>137</sup> Ba, <sup>139</sup> La, <sup>140</sup> Ce, <sup>141</sup> Pr, <sup>146</sup> Nd, <sup>147</sup> Sm, <sup>151</sup> Eu, <sup>158</sup> Gd, <sup>159</sup> Tb, <sup>163</sup> Dy, <sup>165</sup> Ho, <sup>166</sup> Er, <sup>169</sup> Tm, <sup>172</sup> Yb, <sup>175</sup> Lu, <sup>178</sup> Hf, <sup>181</sup> Ta, <sup>205</sup> Tl, <sup>208</sup> Pb, <sup>232</sup> Th, <sup>238</sup> U



**Fig. 2.** Recoveries of Nb, Ba, La and Zr for 50 mg of GSP-2 as a function of the digestion time at 280 °C, 270 °C, 260 °C, 250 °C, 240 °C, 230 °C, and 200 °C. Dotted lines delimit recoveries between 90 and 110%. Note that the x-axis scale differs for each experiment.

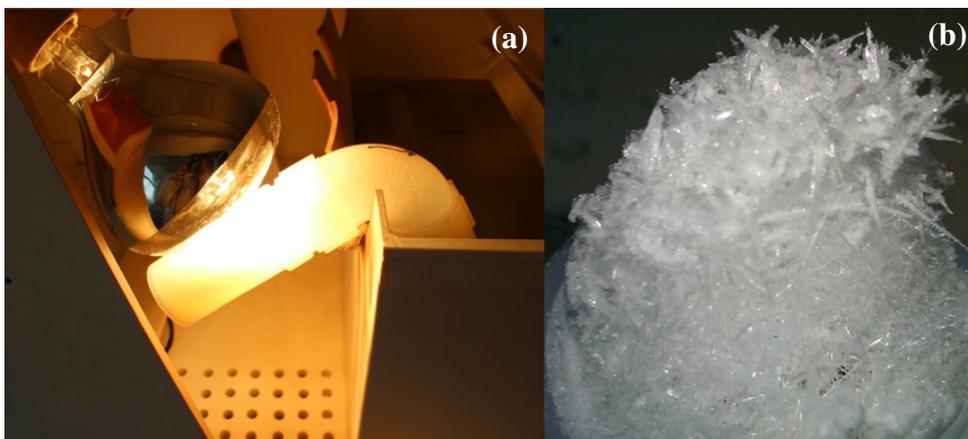
50 g of NH<sub>4</sub>F (filled in the bottle) was purified to 25 g in approximately one day. The efficiency of the sub-boiling distillation system is controlled by the distillation temperature. The higher the temperature is, the higher the efficiency.

#### 2.4. Geological materials

Zircon is known to be very difficult to dissolve. Therefore, we chose USGS GSP-2, a well characterized granodiorite reference material with especially high Zr content (580 μg g<sup>-1</sup>) to evaluate the decomposition capacity of NH<sub>4</sub>F. To further investigate the accuracy and precision of the proposed method, a series of international geological reference materials were analyzed. These rocks cover the whole compositional spectrum of igneous rock, ranging from mafic (basalts BHVO-2, BCR-2; diabase W-2) to intermediate (andesite AGV-2; granodiorite GSP-2) and finally to acidic (granites GSR-1, G-2; rhyolite RGM-1). They also include the most common sedimentary rocks of shale (GSR-5; SCo-1) and soil (GSS-4; GSS-25).

#### 2.5. Decomposition procedure

The optimized sample digestion method was ultimately used for the analyses of the twelve international RMs described above. The recommended NH<sub>4</sub>F digestion method is as follows. (1) First, 300 mg of NH<sub>4</sub>F powder and 50 mg of rock powder (grain size of <74 μm) are successively weighed into a 7-mL screw-top PFA vial and wetted with a few drops of water. (2) Next, the vials are capped and heated at 250 °C in an electric oven for 2 h. (3) After cooling, 1.5 mL of HNO<sub>3</sub> is added and evaporated to near dryness at 160 °C on a hot plate. (4) Step 3 is repeated once. (5) The final residue is then taken up in 1 mL of HNO<sub>3</sub>, 1 mL of MQ water, and 1 mL of 1 μg g<sup>-1</sup> In internal standard solution. The vials are recapped and heated for 6 h at 120 °C to obtain a clear solution. (6) The final solution is transferred to a polyethylene bottle and gravimetrically diluted with 2% (v/v) HNO<sub>3</sub> to a total of 100 g. A reagent blank solution is simultaneously prepared for each group in the same way.



**Fig. 1.** Photo of the sub-boiling still system (a) and the purified NH<sub>4</sub>F (b).

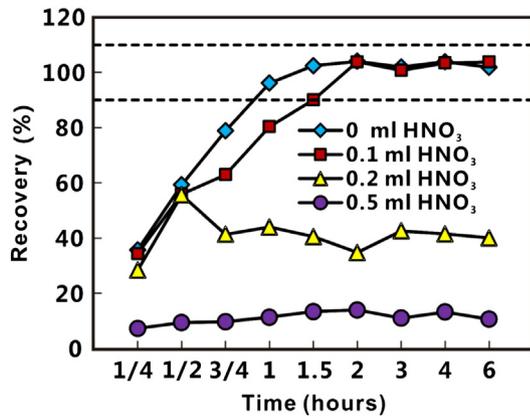


Fig. 3. Recovery of Zr as a function of the digestion time at 250 °C with the addition of 0 ml, 0.1 ml, 0.2 ml, and 0.5 ml HNO<sub>3</sub>.

3. Results and discussion

3.1. Effect of sample digestion temperature and time

The digestion temperature and time are the fundamental parameters of sample digestion. The recoveries of Nb, Ba, La, and Zr in GSP-2 as a function of time at different temperatures (200–280 °C) are shown in Fig. 2. In this experiment, we used 300 mg of NH<sub>4</sub>F to digest 50 mg of GSP-2 at different digestion temperatures and for different lengths of time. The results showed that Nb, Ba, and La were completely recovered under all given digestion conditions (200–280 °C, 0.25–48 h). In contrast, the temperature has a dramatic effect on the recovery of Zr, which is controlled by the degree to which the refractory mineral zircon is dissolved. It took 1–1.5 h, 1.5–2 h, and 3 h for Zr to be completely recovered from GSP-2 at 250 °C, 240 °C, and 230 °C, respectively, whereas 24 h were needed at 200 °C. Based on these observations, it is clear that

the complete decomposition of refractory minerals is controlled by the synergic effect of temperature and time, and the digestion temperature was the more critical factor for NH<sub>4</sub>F attack. Further increasing the digestion temperature to 260–280 °C, the recoveries of Zr were only 35–60% after 0.25–2 h digestions. The boiling point of NH<sub>4</sub>F is ~260 °C. When the digestion temperature is at or above its boiling point, the NH<sub>4</sub>F evaporates rapidly from the screw-top Teflon vial, which subsequently reduces its digestion capacity. In addition, the Teflon vials can operate stably and persistently at 250 °C. Thus, the optimum digestion temperature and time are 250 °C and 1.5 h, which is ~12 times faster than a conventional high-pressure PTFE digestion bomb (1 ml HF + 1 ml HNO<sub>3</sub>) at 190 °C. Compared to the conventional high-pressure PTFE digestion bomb, the most outstanding advantage of the new method is that the digestion can be performed in a conventional Savillex Teflon beaker instead of a high-pressure PTFE digestion bomb. The digestion mechanism of rock samples in the presence of NH<sub>4</sub>F is likely to be related to the conversion of NH<sub>4</sub>F into (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> by reaction with SiO<sub>2</sub> (SiO<sub>2</sub> + 6NH<sub>4</sub>F → (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> + 2H<sub>2</sub>O + 4NH<sub>3</sub>↑).

3.2. Effect of nitric acid

It has been reported that the ratio of NH<sub>4</sub>F(w)/HNO<sub>3</sub>(v) within the range of 0.33–0.83 provides optimal digestion capabilities in high-pressure PTFE digestion bombs (Hu et al., 2010). Fig. 3 illustrates the recoveries of Zr (relative to the reference value) as a function of the digestion time at temperature 250 °C with the addition of 0 ml, 0.1 ml, 0.2 ml and 0.5 ml of HNO<sub>3</sub>. The sample weight was fixed at 50 mg, and the added NH<sub>4</sub>F is all constant at 300 mg. The recovery of Zr was slightly decreased by the addition of 0.1 ml of HNO<sub>3</sub> when the digestion time was less than 2 h and was similar to that without the addition of HNO<sub>3</sub> for longer digestion times. In contrast, the recovery of Zr was significantly decreased with the addition of 0.2 ml or 0.5 ml of HNO<sub>3</sub> for all digestion times, being relatively constant at 40% and 10% (0.25–6 h), respectively. Contrary to our observations for high-pressure PTFE

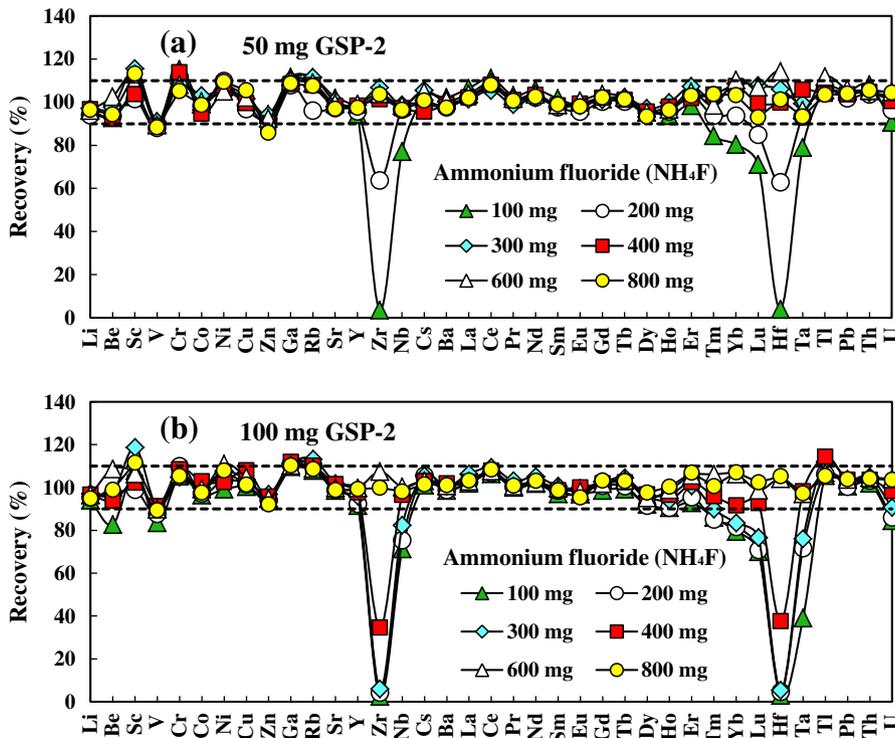


Fig. 4. Recoveries of elements for the digestion of 50–100 mg of GSP-2 as a function of the amount of NH<sub>4</sub>F added from 100 mg to 800 mg at 250 °C for two hours. The dotted lines delimit recoveries between 90 and 110%.

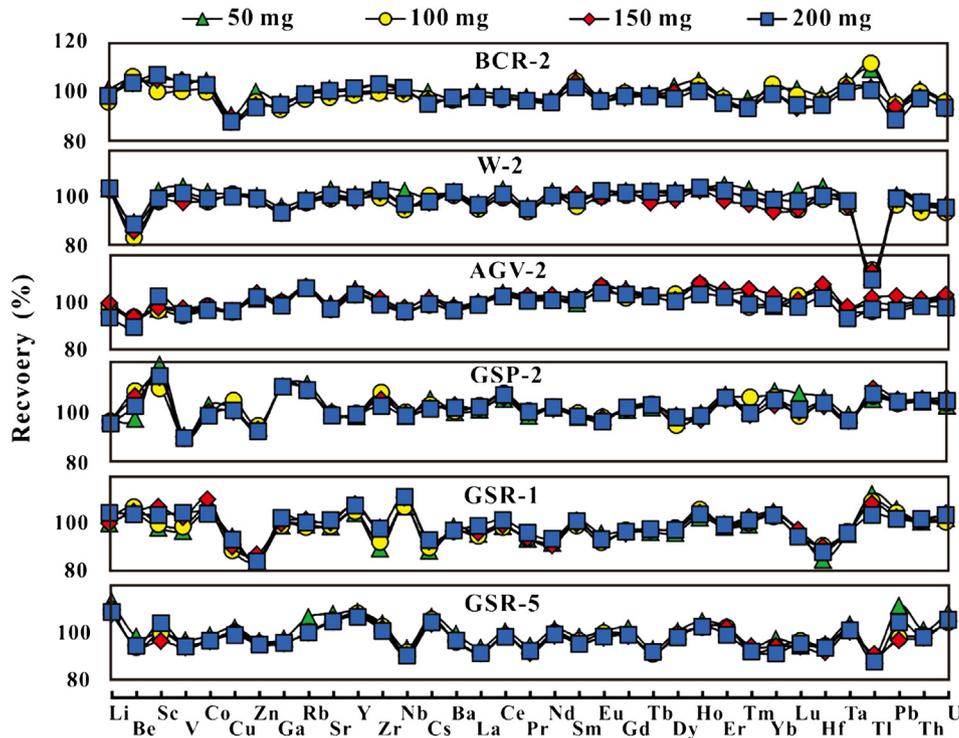


Fig. 5. Recoveries of elements for the digestion of 50 mg, 100 mg, 150 mg, and 200 mg of BCR-2 (basalt), W-2 (diabase), AGV-2 (andesite), GSP-2 (granodiorite), GSR-1 (granite), and GSR-5 (shale) at 250 °C for two hours. The proportion of  $\text{NH}_4\text{F}$  to sample mass is 6:1 for each sample.

digestion bombs, the addition of  $\text{HNO}_3$  significantly reduced the digestion capacity of  $\text{NH}_4\text{F}$  for zircon (Fig. 3).  $\text{NH}_4\text{F}$  is a neutral solid reagent. In a closed digestion environment,  $\text{NH}_4\text{F}$  alone is incapable of digesting silicate samples due to its nearly neutral attribution (Hu et al., 2010). It is possible that the addition of  $\text{HNO}_3$  releases HF rapidly from  $\text{NH}_4\text{F}$  by the reaction  $\text{NH}_4\text{F} + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 + \text{HF}$ , which subsequently facilitates the digestion of silicate samples in a closed digestion environment. Unlike in closed-vessel acid digestion, the likely decomposition reaction of  $\text{NH}_4\text{F} \rightarrow \text{NH}_3\uparrow + \text{HF}$  can continue to proceed slowly at high temperatures because of the loss of the reaction product  $\text{NH}_3$  gas in open-vessel digestion. Thus, in open-vessel digestion,  $\text{NH}_4\text{F}$  can digest rock samples alone. As previously mentioned, the added  $\text{HNO}_3$  will react with  $\text{NH}_4\text{F}$ , and release HF rapidly. In open-vessel digestion, the produced HF will be rapidly lost by evaporation at elevated digestion temperatures (relative to  $\text{HNO}_3$ , HF will be preferably lost due to its lower boiling point), which would significantly reduce the digestion capability of  $\text{NH}_4\text{F}$  in open-vessels. This point may explain the substantially

low recoveries of Zr in  $\text{NH}_4\text{F}$ –open-vessel acid digestion after the addition of  $\text{HNO}_3$ .

### 3.3. Correlation between test portion mass and amount of $\text{NH}_4\text{F}$ added

Fig. 4 shows the recoveries of 37 elements for the digestion of 50–100 mg of GSP-2 as a function of the added  $\text{NH}_4\text{F}$  amount from 100 mg to 800 mg. The digestion temperature and time are 250 °C and 2 h, respectively. The final sample dilution factors are all held constant at 2000 for the various tested mass proportions. There is a positive correlation between test sample mass and the amount of  $\text{NH}_4\text{F}$  required for complete recovery of Zr, Hf, Nb, Ta, and heavy rare earth elements in GSP-2. For the full recoveries of these elements in 50 mg or 100 mg of GSP-2, at least 300 mg or 600 mg of  $\text{NH}_4\text{F}$  is required, respectively (Fig. 4). The poor recoveries of Zr, Hf, and heavy REEs, when using a proportion of  $\text{NH}_4\text{F}$  to mass of GSP-2 of less than 6 are due to the incomplete dissolution of the refractory mineral zircon. The lower recoveries

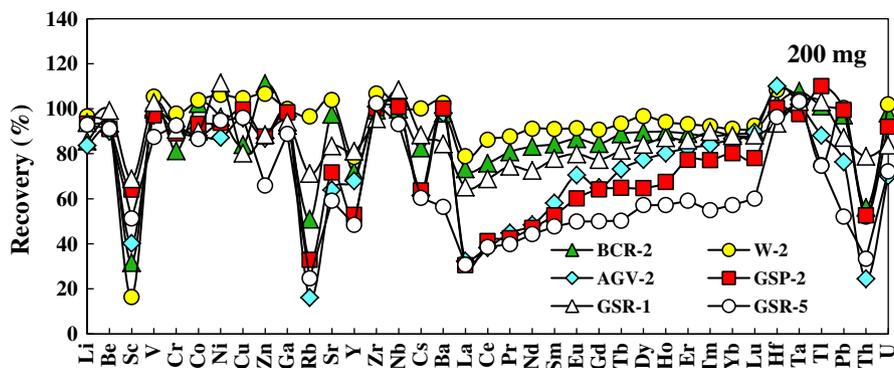


Fig. 6. Effect of the presence of insoluble fluorides on the recoveries of elements for the digestion of 200 mg of BCR-2 (basalt), W-2 (diabase), AGV-2 (andesite), GSP-2 (granodiorite), GSR-1 (granite), and GSR-5 (shale) by using conventional high-pressure digestion bomb method.

**Table 2**

Procedure blank and method limits of quantitation (LOQ, ten times the standard deviation of 11 analyses of the procedural blank). The LOQ is expressed as the concentration in the samples, thereby taking into account the dilution factor (2000).

	Procedure blank (ng g <sup>-1</sup> ), n = 8			LOQ (μg g <sup>-1</sup> )		
	NH <sub>4</sub> F		Purified	NH <sub>4</sub> F		Purified
	HF + HNO <sub>3</sub>	Unpurified		HF + HNO <sub>3</sub>	Unpurified	
Li	0.010	0.030	0.021	0.023	0.052	0.020
Be	0.0095	0.010	0.0057	0.072	0.074	0.049
Sc	0.32	0.36	0.16	0.34	0.57	0.14
V	0.0038	0.054	0.0051	0.013	0.074	0.022
Cr	0.16	8.80	0.17	0.30	4.08	0.44
Co	0.0051	0.069	0.0069	0.019	0.080	0.016
Ni	0.079	2.88	0.089	0.21	1.17	0.33
Cu	0.022	0.49	0.052	0.082	0.40	0.12
Zn	0.15	0.58	0.39	0.52	0.79	0.52
Ga	0.0069	0.011	0.009	0.018	0.065	0.012
Rb	0.0022	0.029	0.0041	0.011	0.062	0.015
Sr	0.0031	0.17	0.0068	0.0094	0.044	0.015
Y	0.0011	0.0031	0.0020	0.010	0.017	0.0076
Zr	0.011	0.083	0.033	0.036	0.11	0.038
Nb	0.0010	0.014	0.0014	0.0091	0.021	0.0067
Cs	0.00071	0.0040	0.0060	0.0052	0.011	0.0068
Ba	0.0095	0.52	0.014	0.045	0.37	0.051
La	0.00070	0.0058	0.0015	0.0046	0.013	0.0043
Ce	0.00049	0.017	0.0029	0.0052	0.018	0.0064
Pr	0.00042	0.0017	0.00066	0.0053	0.0056	0.0029
Nd	0.0030	0.0063	0.0031	0.024	0.026	0.022
Sm	0.0031	0.0038	0.0025	0.022	0.025	0.018
Eu	0.00067	0.0012	0.00070	0.0067	0.012	0.0075
Gd	0.0014	0.0021	0.0016	0.012	0.019	0.015
Tb	0.00047	0.00054	0.00040	0.0018	0.0014	0.0019
Dy	0.0020	0.0023	0.0015	0.013	0.018	0.010
Ho	0.00039	0.00052	0.00038	0.0029	0.0050	0.0030
Er	0.0012	0.0010	0.0010	0.013	0.0069	0.0094
Tm	0.00042	0.00033	0.00031	0.0031	0.0023	0.0033
Yb	0.0015	0.0020	0.0020	0.019	0.019	0.0074
Lu	0.00042	0.00054	0.00044	0.0041	0.0021	0.0035
Hf	0.0014	0.0037	0.0023	0.0074	0.0057	0.0078
Ta	0.0022	0.0055	0.00074	0.0019	0.026	0.0026
Ti	0.0015	0.0022	0.0038	0.0094	0.0069	0.0070
Pb	0.017	0.29	0.016	0.016	0.34	0.023
Th	0.00043	0.0020	0.0010	0.0017	0.0022	0.0018
U	0.00025	0.0011	0.00066	0.0014	0.0016	0.0014

of Nb and Ta in the presence of a small amount of NH<sub>4</sub>F may be related to their strong tendency to hydrolyze or polymerize at low F<sup>-</sup> concentrations. The other elements were almost completely recovered under all digestion conditions studied (50–100 mg of GSP-2, 100–800 mg of NH<sub>4</sub>F). In our routine sample digestion, the adopted proportion of NH<sub>4</sub>F relative to the amount of sample powder required for complete element recovery is 6:1.

### 3.4. Effect of insoluble fluorides

Besides difficulties related to the dissolution of resistant minerals such as zircon in geological samples, the formation of insoluble fluorides, which incorporate large proportions of trace elements, represents another complication during sample decomposition using HF (Boer et al., 1993; Yokoyama et al., 1999; Makishima et al., 2009). Therefore, it is very important to suppress the formation of insoluble fluorides, but this is not always straightforward and is often difficult to accomplish. The repeated evaporation of sample solutions with HClO<sub>4</sub> is a commonly used method to prevent fluoride formation (Langmyhr, 1967; Yokoyama et al., 1999; Zhang et al., 2012a). Yokoyama et al. (1999) obtained 100% recovery of the incompatible elements Rb, Sr, Y, Cs, Ba, REE, Pb, Th, and U by using large amounts of HClO<sub>4</sub> and evaporating the sample to dryness in a stepwise fashion. However, the high field strength elements (HFSE), such as Ti, Zr, Nb, Hf, and Ta, were lost as insoluble oxides. Takei et al. (2001) and Tanaka et al. (2003) observed that the precipitation of fluorides during HF/HNO<sub>3</sub> sample dissolution is controlled by the

relative proportions of Al:Mg:Ca in the sample. According to a study by Takei et al. (2001), AlF<sub>3</sub> was formed when Al-rich felsic samples with (Mg + Ca)/Al < 1 were decomposed by a high-pressure digestion method, incorporating some trace elements and cannot be decomposed by evaporation with HClO<sub>4</sub>. Zhang et al. (2012a) also observed insoluble fluorides after the evaporation of sample solutions (granodiorite GSP-2) with HClO<sub>4</sub>, which may incorporate trace elements such as Li, Sc, and Rb. Using a novel “Mg-addition” and “Al-addition” method, Takei et al. (2001) and Tanaka et al. (2003) were able to overcome these problems. However, these methods are not very suitable for the analysis of unknown samples of different matrix compositions. It has also been suggested that during sample digestion, treated powder after acid attack should not be allowed to dry completely, a step that can apparently minimize the formation of insoluble compounds (Dulski, 2001; Navarro et al., 2008). However, this method is empirical and uncontrollable. Zhang et al. (2012a) reported that insoluble fluorides were observed in the final solution for test portion mass > 100 mg (GSP-2) regardless of which of five different digestion solutions was used (1 ml HF, 2 ml HF, 1 ml HF + 0.5 ml HNO<sub>3</sub>, 1 ml HF + 1 ml HNO<sub>3</sub> and 1.5 ml HF + 1.5 ml HNO<sub>3</sub>). To prevent the formation of insoluble fluorides, the use of small quantities of a sample (not exceeding 100 mg) is recommended (Yokoyama et al., 1999; Potts and Robinson, 2003; Hu et al., 2010; Zhang et al., 2012a). However, Takei et al. (2001) reported the formation of AlF<sub>3</sub> during the decomposition of test portions as small as 20 mg. The results of Cotta and Enzweiler (2012) were also affected by the precipitation of AlF<sub>3</sub> during the dissolution of 50 mg of GPS-2 at 200 °C and 260 °C under 13 MPa. Additionally, the use of very small test portions is not recommended, because few reference materials (RMs) have had their homogeneity tested at the milligram scale (Cotta et al., 2007). The formation of insoluble fluorides and the coprecipitation of trace elements when small test portions (8–40 mg) are dissolved were also investigated by Makishima et al. (2002). It seems that further investigations are still required to clarify the formation and dissolution mechanism of these insoluble fluorides.

Fig. 5 shows the recoveries of elements as a function of the test portion size of BCR-2 (basalt), W-2 (diabase), AGV-2 (andesite), GSP-2 (granodiorite), GSR-1 (granite), and GSR-5 (shale) from 50 mg to 200 mg using the NH<sub>4</sub>F–open-vessel acid digestion method developed here. It is very interesting to note that no insoluble fluorides are observed by the naked eye, even when the test portion size of these rock samples is increased to 200 mg, and the agreements among our determined values for different sample portion masses and between our determined values and the reference values are generally better than 10% for all of these elements. It is possible that some insoluble fluorides are present but semitransparent and not easily visible to the naked eye, but the excellent agreement between our determined values and the reference values shows that if these semitransparent insoluble fluorides are present, they do not have a significant effect on the recoveries of the elements analyzed. In contrast, white precipitates were observed in all the final solutions of these rock samples for 200 mg test portions using the conventional high-pressure digestion bomb method. The morphology and topography of these collected white precipitates vary substantially by rock sample (SFig. 1), although the change of recoveries of analyzed elements are quite similar (Fig. 6). Environmental scanning electron microscopy showed that these precipitates were mainly composed of F + Al + O + Mg + Ca + K + Na (SFig. 1). The recoveries of Sc, Rb, Y, Cs, REEs and Th are consistently lower in the presence of insoluble fluorides in these samples (Fig. 6). It is thus clear that the analysis of trace elements in the presence of insoluble fluorides will yield misleading conclusions, especially in Rb–Sr, La–Ce, Sm–Nd, and U–Th–Pb systematics, and REE patterns. Compared to the conventional high-pressure digestion bomb method, this feature is another important advantage of the NH<sub>4</sub>F open-vessel digestion method. Unlike in the NH<sub>4</sub>F open-vessel digestion method, we observed insoluble fluorides in 150–200 mg of GSR-1 (granite) in the NH<sub>4</sub>F-assisted high pressure digestion bomb method (Hu et al., 2010). The main differences between

**Table 3**Data for thirty-seven trace elements in twelve rock reference materials digested by the NH<sub>4</sub>F digestion method. The uncertainty represents one standard deviation.

	BHVO-2		BCR-2		W-2		AGV-2		GSP-2		GSR-1	
	n = 4	Ref.	n = 4	Ref.	n = 4	Ref.	n = 4	Ref.	n = 8	Ref.	n = 8	Ref.
Li	4.57 ± 0.10	4.8	8.78 ± 0.49	9	8.78 ± 0.10	9.3	11 ± 0.7	11	35.3 ± 0.9	36	132 ± 5	131
Be	1.07 ± 0.06	1	2.06 ± 0.06	2.08	0.67 ± 0.01	0.71	2.24 ± 0.24	2.3	1.50 ± 0.04	1.5	12.9 ± 0.8	12.4
Sc	30.8 ± 0.4	32	32.1 ± 0.1	33	35.1 ± 0.7	35.9	12.7 ± 0.4	13	6.40 ± 0.25	6.3	5.86 ± 0.24	6.1
V	303 ± 8	317	417 ± 5	416	257 ± 5	268	118 ± 7	122	50.5 ± 1.4	52	20.9 ± 0.8	21 <sup>c</sup>
Cr	274 ± 5	280	19.1 ± 0.8	18	99.1 ± 1.4	93	16.4 ± 1.4	16	19.2 ± 0.7	20	2.98 ± 0.32	5
Co	43.5 ± 2.3	45	36.5 ± 0.1	37	45.2 ± 0.4	45	15.8 ± 1.1	16	7.41 ± 0.39	7.3	2.74 ± 0.17	2.7 <sup>c</sup>
Ni	124 ± 6	119	14.3 ± 0.4	18	77.5 ± 1.1	72.0	18.8 ± 1.1	20	17.4 ± 0.7	17	0.91 ± 0.23	1.1 <sup>c</sup>
Cu	124 ± 4	127	17.9 ± 0.4	21	105 ± 3	105	50.9 ± 3.7	53	44.4 ± 1.6	43	2.20 ± 0.11	3.2
Zn	97.6 ± 8.0	103	125 ± 7	127	74.5 ± 4.6	77	86.7 ± 6.9	86	114 ± 2	120	24.4 ± 1.3	28
Ga	21.4 ± 0.6	22	21.6 ± 0.3	23	17.5 ± 0.1	18	20.4 ± 2.1	20	23.1 ± 0.5	22	18.7 ± 0.4	19
Rb	8.86 ± 0.22	9.11	45.5 ± 4.1	46.9	19.5 ± 0.3	21	65.9 ± 6.9	66.3	243 ± 7	245	465 ± 10	466
Sr	389 ± 11	396	321 ± 7	340	188 ± 6	196	665 ± 55	661	235 ± 8	240	106 ± 3	106
Y	26.1 ± 0.8	26	36.2 ± 0.4	37	21.9 ± 0.2	22	19.7 ± 1.3	19	27.2 ± 1.0	28	68.4 ± 1.9	67 <sup>c</sup>
Zr	163 ± 4	172	178 ± 5	184	92.3 ± 3.9	92	229 ± 13	230	572 ± 12	550	164 ± 16	167
Nb	17.8 ± 0.5	18.1	12.1 ± 0.27	12.6	7.24 ± 0.15	7.5	14.1 ± 1.3	14.5	25.8 ± 0.8	27	42.7 ± 0.6	40
Cs	0.11 ± 0.01	0.1	1.07 ± 0.15	1.1	0.84 ± 0.01	0.92	1.12 ± 0.08	1.2	1.14 ± 0.04	1.2	38.2 ± 1.4	38.4
Ba	124 ± 2	131	652 ± 18	677	163 ± 2	172	1136 ± 81	1130	1339 ± 32	1340	315 ± 10	343
La	14.6 ± 0.2	15.2	24.2 ± 0.4	24.9	10.3 ± 0.3	10.8	37.8 ± 2.6	37.9	187 ± 5	180	52.2 ± 1.36	54
Ce	35.9 ± 0.7	37.5	51.4 ± 0.3	52.9	22.4 ± 0.4	23.4	69. ± 6.1	68.6	424 ± 11	410	107 ± 4	108
Pr	5.01 ± 0.06	5.35	6.58 ± 0.33	6.7	2.87 ± 0.02	3	8.06 ± 0.77	7.84	54.1 ± 2.4	54 <sup>c</sup>	12.1 ± 0.3	12.7
Nd	23.2 ± 0.6	24.5	27.4 ± 0.3	28.7	12.8 ± 0.1	13	30.6 ± 2.5	30.5	201 ± 7	200	43.6 ± 1.7	47
Sm	5.99 ± 0.09	6.07	6.56 ± 0.16	6.58	3.27 ± 0.05	3.3	5.53 ± 0.37	5.49	26.5 ± 0.8	27	9.58 ± 0.31	9.7
Eu	1.96 ± 0.04	2.07	1.87 ± 0.01	1.96	1.03 ± 0.01	1.08	1.62 ± 0.11	1.53	2.31 ± 0.08	2.3	0.81 ± 0.04	0.85
Gd	6.01 ± 0.13	6.24	6.50 ± 0.08	6.75	3.55 ± 0.15	3.66	4.62 ± 0.40	4.52	12.7 ± 0.2	12	8.51 ± 0.36	9.3
Tb	0.91 ± 0.02	0.92	1.06 ± 0.01	1.07	0.61 ± 0.01	0.62	0.66 ± 0.04	0.64	1.39 ± 0.07	1.36 <sup>c</sup>	1.59 ± 0.04	1.65
Dy	5.28 ± 0.18	5.31	6.48 ± 0.11	6.41	3.85 ± 0.12	3.79	3.53 ± 0.37	3.47	5.94 ± 0.16	6.1	10.0 ± 0.6	10.2
Ho	0.95 ± 0.03	0.98	1.26 ± 0.01	1.28	0.80 ± 0.02	0.79	0.68 ± 0.05	0.65	0.96 ± 0.03	1	2.02 ± 0.10	2.05
Er	2.45 ± 0.11	2.54	3.61 ± 0.06	3.66	2.18 ± 0.01	2.22	1.81 ± 0.13	1.81	2.47 ± 0.09	2.37 <sup>c</sup>	6.36 ± 0.41	6.5
Tm	0.32 ± 0.01	0.33	0.53 ± 0.01	0.54	0.31 ± 0.01	0.33	0.27 ± 0.02	0.26	0.30 ± 0.02	0.29	1.08 ± 0.06	1.06
Yb	1.91 ± 0.01	2	3.33 ± 0.02	3.38	1.98 ± 0.04	2.05	1.68 ± 0.08	1.62	1.69 ± 0.09	1.6	7.34 ± 0.42	7.4
Lu	0.27 ± 0.01	0.274	0.49 ± 0.01	0.503	0.30 ± 0.01	0.31	0.25 ± 0.02	0.247	0.24 ± 0.01	0.23	1.14 ± 0.08	1.15
Hf	4.25 ± 0.09	4.36	4.75 ± 0.28	4.9	2.42 ± 0.11	2.45	5.32 ± 0.44	5	14.4 ± 0.4	14	5.84 ± 0.53	6.3
Ta	1.13 ± 0.03	1.14	0.76 ± 0.01	0.74	0.45 ± 0.01	0.47	0.88 ± 0.07	0.87	0.83 ± 0.04	0.9 <sup>c</sup>	6.95 ± 0.47	7.2
Tl	0.030 ± 0.001	0.028 <sup>a</sup>	0.27 ± 0.02	0.254 <sup>b</sup>	0.10 ± 0.01	0.13	0.29 ± 0.03	0.27	1.14 ± 0.17	1.1	2.13 ± 0.26	1.93
Pb	1.70 ± 0.05	1.6	10.2 ± 0.81	11	7.84 ± 0.01	7.7	13.1 ± 1.4	13.2	43.2 ± 1.9	42	31.0 ± 1.4	31
Th	1.16 ± 0.02	1.22	5.76 ± 0.28	5.7	2.10 ± 0.02	2.17	6.01 ± 0.4	6.1	106 ± 6	105	53.9 ± 2.3	54
U	0.40 ± 0.01	0.403	1.65 ± 0.09	1.69	0.49 ± 0.01	0.5	1.86 ± 0.14	1.86	2.38 ± 0.17	2.4	19.0 ± 0.5	18.8
	G-2		RGM-1		GSR-5		SCo-1		GSS-4		GSS-25	
	n = 6	Ref.	n = 4	Ref.	n = 4	Ref.	n = 4	Ref.	n = 3	Ref.	n = 3	Ref.
Li	30.4 ± 0.8	34	58.6 ± 5.5	57	46.7 ± 0.3	44	43.5 ± 0.1	45	55.5 ± 4.1	55	30.0 ± 1.4	32
Be	2.38 ± 0.12	2.5	2.49 ± 0.06	2.37	2.95 ± 0.07	3	1.85 ± 0.01	1.84	1.62 ± 0.08	1.85	1.92 ± 0.06	1.9
Sc	3.48 ± 0.15	3.5	4.82 ± 0.18	4.4	19.1 ± 0.1	18.5	11.0 ± 0.1	10.8	20.0 ± 0.1	20	11.1 ± 0.3	11.6
V	32.7 ± 0.7	36	11.7 ± 0.6	13	82.6 ± 0.9	87	123 ± 1	131	239 ± 2	247	69.9 ± 3.5	77
Cr	7.86 ± 1.73	8.7	13.2 ± 0.8	3.7	100 ± 3	99	70.7 ± 0.2	68	366 ± 12	370	61.7 ± 0.2	66
Co	4.25 ± 0.14	4.6	2.09 ± 0.05	2	21.1 ± 0.1	21	10.8 ± 0.1	10.5	21.7 ± 0.1	22	11.5 ± 0.5	12
Ni	1.85 ± 0.54	5	4.52 ± 0.38	4.4	40.0 ± 0.9	36.8	27.3 ± 1.6	27	66.7 ± 4.6	64	28.5 ± 0.3	30
Cu	9.68 ± 0.36	11	11.9 ± 0.4	11.6	44.2 ± 0.2	42	27.9 ± 0.4	28.7	39.8 ± 0.2	40	22.8 ± 2.1	23.6
Zn	79.4 ± 1.9	86	32.4 ± 4.5	32	53.5 ± 0.3	55	97.1 ± 0.3	103	202 ± 5	210	61.3 ± 4.1	66
Ga	23.0 ± 0.6	23	16.1 ± 0.3	15	25.8 ± 0.1	25.6	16.5 ± 0.1	16.4 <sup>f</sup>	30.9 ± 0.2	31	14.2 ± 0.7	14.9
Rb	164 ± 3	170	150 ± 8	149	214 ± 4	205	111 ± 3	112	73.3 ± 1.0	75	92.0 ± 5.1	95
Sr	461 ± 14	478	101 ± 3	108	91.5 ± 0.6	90	168 ± 4	174	71.3 ± 0.5	77	192 ± 8	192
Y	10.0 ± 0.1	10.2 <sup>d</sup>	23.7 ± 1.4	21.8	28.5 ± 0.3	26	24.9 ± 0.1	26	41.9 ± 2.0	39	26.1 ± 2.1	27
Zr	310 ± 18	309	222 ± 5	219	100 ± 6	96	148 ± 4	160	527 ± 28	500	265 ± 11	254
Nb	12.3 ± 0.3	12	9.02 ± 0.27	8.9	13.4 ± 0.1	14.3	11.9 ± 0.2	11	38.1 ± 0.1	38	12.8 ± 0.5	14.2
Cs	1.37 ± 0.05	1.34	9.52 ± 0.50	9.6	14.1 ± 0.1	14	7.43 ± 0.1	7.8	21.7 ± 0.1	21.4	6.60 ± 0.32	7.2
Ba	1867 ± 48	1882	814 ± 26	807	431 ± 9	450	544 ± 10	570	211 ± 2	213	480 ± 25	495
La	89.2 ± 1.9	89	23.2 ± 0.8	24	59.2 ± 0.2	62	29.1 ± 0.2	29.5	52.4 ± 2.0	53	33.8 ± 1.8	35
Ce	163 ± 3	160	46.4 ± 2.3	47	113 ± 3	109	58.3 ± 0.2	62	144 ± 3	136	66.2 ± 3.6	71
Pr	16.4 ± 0.3	18	5.25 ± 0.03	5.32	13.1 ± 0.1	13.6	6.72 ± 0.07	6.6	8.19 ± 0.39	8.4	7.84 ± 0.37	8
Nd	53.6 ± 1.5	55	19.2 ± 0.3	19	48.0 ± 0.3	48	25.5 ± 0.2	26	26.3 ± 1.1	27	31.0 ± 1.7	31
Sm	7.21 ± 0.21	7.2	4.01 ± 0.26	4.3	8.36 ± 0.07	8.4	5.10 ± 0.09	5.3	4.26 ± 0.08	4.4	5.82 ± 0.29	5.8
Eu	1.50 ± 0.06	1.4	0.64 ± 0.01	0.66	1.66 ± 0.01	1.7	1.13 ± 0.01	1.19	0.84 ± 0.04	0.85	1.11 ± 0.05	1.2
Gd	3.75 ± 0.07	3.8 <sup>e</sup>	3.72 ± 0.18	3.7	6.72 ± 0.01	6.7	4.54 ± 0.11	4.6	4.77 ± 0.02	4.7	5.16 ± 0.26	5.3
Tb	0.46 ± 0.01	0.48	0.61 ± 0.01	0.66	0.97 ± 0.01	1.02	0.70 ± 0.01	0.7	0.94 ± 0.05	0.94	0.81 ± 0.04	0.86
Dy	2.23 ± 0.07	2.4	3.89 ± 0.31	4.08	5.37 ± 0.02	5.1	4.11 ± 0.06	4.2	6.56 ± 0.17	6.6	4.75 ± 0.18	5
Ho	0.36 ± 0.02	0.4	0.77 ± 0.01	0.81	1.01 ± 0.01	0.98	0.81 ± 0.01	0.86 <sup>g</sup>	1.46 ± 0.01	1.46	0.93 ± 0.07	1.02
Er	0.90 ± 0.06	0.92	2.34 ± 0.06	2.42	2.83 ± 0.09	2.7	2.36 ± 0.01	2.5	4.51 ± 0.21	4.5	2.68 ± 0.12	2.8
Tm	0.12 ± 0.01	0.12 <sup>d</sup>	0.36 ± 0.04	0.37	0.40 ± 0.01	0.43	0.35 ± 0.01	0.36 <sup>g</sup>	0.72 ± 0.001	0.7	0.40 ± 0.02	0.46
Yb	0.72 ± 0.06	0.72 <sup>d</sup>	2.48 ± 0.12	2.6	2.52 ± 0.01	2.6	2.31 ± 0.03	2.27	4.85 ± 0.20	4.8	3.01 ± 0.14	3.3
Lu	0.11 ± 0.01	0.11	0.39 ± 0.01	0.41	0.38 ± 0.01	0.38 <sup>d</sup>	0.34 ± 0.01	0.34	0.76 ± 0.02	0.75	0.41 ± 0.03	0.45
Hf	7.57 ± 0.38	7.9	5.98 ± 0.38	6.2	2.80 ± 0.02	2.9	4.50 ± 0.06	4.6	14.5 ± 0.51	14	6.80 ± 0.30	7

Table 3 (continued)

	G-2		RGM-1		GSR-5		SCo-1		GSS-4		GSS-25	
	n = 6	Ref.	n = 4	Ref.	n = 4	Ref.	n = 4	Ref.	n = 3	Ref.	n = 3	Ref.
Ta	0.90 ± 0.11	0.88	0.93 ± 0.03	0.95	0.86 ± 0.01	0.82 <sup>d</sup>	0.85 ± 0.01	0.92	3.12 ± 0.01	3.1	1.03 ± 0.05	1.1
Tl	0.87 ± 0.04	0.91	0.99 ± 0.02	0.93	0.75 ± 0.03	0.71	0.78 ± 0.01	0.72	1.00 ± 0.01	0.94	0.54 ± 0.01	0.59
Pb	29.5 ± 1.0	30	24.4 ± 1.8	24	8.15 ± 0.03	7.98 <sup>d</sup>	32.2 ± 0.2	31	57.9 ± 0.6	58	20.1 ± 1.8	22
Th	24.5 ± 0.9	24.7	14.2 ± 0.3	15.1	13.1 ± 0.1	12.8	9.26 ± 0.05	9.7	27.9 ± 1.2	27	10.9 ± 1.0	11.5
U	1.95 ± 0.22	2.07	5.57 ± 0.49	5.80	1.61 ± 0.01	1.5	3.02 ± 0.01	3	7.28 ± 0.04	6.70	2.36 ± 0.10	2.40

The reference values of BHVO-2, BCR-2 and AGV-2 are taken from the preferred values in GeoRem (<http://georem.mpch-mainz.gwdg.de/>). In the absence of preferred values, published results were used:

<sup>a</sup> Chauvel et al. (2011),

<sup>b</sup> Marx et al. (2010). The reference values of GSP-2 are taken from USGS (Wilson, 1998). Pr, Tb, Er and Ta in GSP-2 are exceptions, which are taken from

<sup>c</sup> Cotta and Enzweiler (2012). The reference values of other reference materials are taken from Govindaraju (1994) and published results:

<sup>d</sup> Qi and Grégoire (2000),

<sup>e</sup> Pretorius et al. (2006),

<sup>f</sup> Hu and Gao (2008) and

<sup>g</sup> Meisel et al. (2002), respectively.

these methods are the different digestion pressures in their vessels. It is therefore possible that the low-pressure environment prevents the formation of insoluble fluorides. It has also been reported by Takei et al. (2001) that using the Teflon beaker method (low pressure) to digest rhyolite (JR-2) tends to form decomposable fluorides. Further work on the formation and influence of fluorides is needed to identify the specific mechanisms.

### 3.5. Procedural blank and limit of quantitation

Modern ICP-MS instrumentation enables the measurement of extremely low concentrations of elements in geological samples. The influence of the reagent blank on the analytical results becomes increasingly important with decreasing elemental concentrations, which determines the lower limit of quantitation in many cases. The limit of quantitation (LOQ, ten times the standard deviation of 11 analyses of the procedural blank) and procedural blank for both the NH<sub>4</sub>F digestion method and the conventional HF-HNO<sub>3</sub> high-pressure digestion method are illustrated in Table 2. The LOQ is expressed as the concentration in the samples, thereby taking into account the dilution factor (2000). The HF-HNO<sub>3</sub> high-pressure digestion method was described in detail by Hu and Gao (2008). For unpurified NH<sub>4</sub>F, the procedure blanks for trace elements range from 0.00033 to 0.49 ng g<sup>-1</sup>, with the exception of Cr (8.80 μg g<sup>-1</sup>) and Ni (2.88 μg g<sup>-1</sup>), and the LOQs range from 0.0021 μg g<sup>-1</sup> to 0.79 μg g<sup>-1</sup>, which are acceptable for the determination of these trace elements in most of geological samples. Compared to those of the unpurified NH<sub>4</sub>F, the procedure blanks for V, Cr, Co, Ni, Cu, Rb, Sr, Ba, La, Ce and Pr are reduced by a factor of 4–55 using the purified NH<sub>4</sub>F. The purified NH<sub>4</sub>F is therefore recommended for the digestion of geological samples for ultratrace determination of these elements. For purified NH<sub>4</sub>F, the LOQ values ranged from 0.14 μg g<sup>-1</sup> to 0.52 μg g<sup>-1</sup> for Sc, Cr, Ni, Cu, and Zn and from 0.0014 μg g<sup>-1</sup> to 0.051 μg g<sup>-1</sup> for the other elements, which are similar to those obtained using the HF-HNO<sub>3</sub> high-pressure method. Compared to the conventional alkali fusion method, the easy production of ultrapure NH<sub>4</sub>F reagent using sub-boiling distillation is an important advantage of this proposed method, which guarantees its wide applicability for the digestion of various geological samples for ultra-trace multi-element determinations.

### 3.6. Analytical results for reference materials

To further investigate the precision and bias of the proposed NH<sub>4</sub>F digestion method, we analyzed a series of rock reference materials: BHVO-2, BCR-2, W-2, AGV-2, GSP-2, GSR-1, G-2, RGM-1, GSR-5, SCo-1, GSS-4, and GSS-25. Our measured values for these international reference materials are compared with the values from the GeoRem database (<http://georem.mpch-mainz.gwdg.de/>) and Govindaraju (1994) in Table 3. We have replaced some obviously incorrect reference values

from Govindaraju (1994) with the latest published data in GeoRem (<http://georem.mpch-mainz.gwdg.de/>) (Table 3). The analytical precision under our given instrumental operating conditions, reported as 1 RSD (%), is generally better than 10% for most elements, except for Cs (10–14%) in BCR-2 and AGV-2, Tl (12–15%) in GSP-2 and GSR-1, Ta (12.2%) in G-2, and Cr and Ni (11–30%) in GSR-1 and G-2, which are mainly due to the low analyte concentrations in these samples. The agreement between our data and the reference values is better than 10% for most of the elements in these geological reference samples. The observed discrepancies (a bias between the determined data and the reference values of greater than 10%) for the analyzed reference materials are as follows: BCR-2 (Ni, Cu), W-2 (Tl), RGM-1 (V, Cr), GSR-1 (Cr, Ni, Cu, Zn), G-2 (V, Cr, Ni, Cu, Ho), GSS-4 (Be), and GSS-25 (V, Nb, Tm). Most of these elements are transition metals. The interferences of polyatomic ions are potential problems for the accurate determination of transitional elements using quadruple ICP-MS. It is not always easy to evaluate the accuracy of an analytical method by simply comparing the obtained data with reference values. Further work on the determination of these elements in these reference materials is needed to identify the reasons for the discrepancies. These results demonstrate that the presented NH<sub>4</sub>F digestion technique is well suitable for the digestion of a range of silicate geological materials.

## 4. Conclusions

The developed NH<sub>4</sub>F–open-vessel acid digestion combines the advantages of the open- and closed-vessel digestion methods, providing an effective, straightforward, economical, and comparatively safe dissolution method, and is well suited for the digestion of a range of geological materials, including felsic rocks and other materials that contain refractory minerals such as zircon.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2013.06.024>.

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