Technical note

Efficient microwave-assisted digestion of geological materials with HBF_4: a reduced-hazard alternative to HF

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Microwave-assisted digestion using tetrafluoroboric acid (HBF_4) was evaluated as a reduced-hazard alternative to hydrofluoric acid (HF) for elemental analysis of geological materials. Six geological reference materials spanning a range of lithologies and compositions relevant to sedimentary paleoenvironmental investigations (BHVO-2, SCo-2, SSAR-1, MESS-4, NOD-A-1, and ShBOQ-1) were digested using an automated microwave system and analysed for elemental concentrations by ICP-MS/MS. Near-quantitative recovery of refractory silicate- and oxide-associated elements, including Cr, Co, and Ni, indicates effective dissolution of resistant mineral phases, although minor under-recovery of Ti and Zr suggests that digestion may not have been fully quantitative for all refractory minerals. In contrast, Mg, Al, Ca, rare earth elements (REEs), and Th exhibited notably reduced recoveries, inferred to result from the precipitation of insoluble fluorides and oxides—a limitation common to fluoride-based digestion methods. Despite this, the method enables efficient microwave-assisted sample processing and is well suited for the determination of REE profiles and concentrations of light transition metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As) and many trace elements (Be, Na, P, S, K, Nb, Sb, Ba, Tl, Pb, U) from geological materials, while presenting lower hazards relative to conventional HF-based digestion procedures.

1 Background

Accurate geochemical analyses of sediments and rocks are essential for developing a robust understanding of geological processes through time for both environmental and economic applications. Conventional digestion protocols for subsequent elemental and isotopic analyses commonly employ hydrofluoric acid (HF) to dissolve silicate matrices, yet its highly toxic nature demands stringent laboratory protocols and specialised infrastructure. Recent studies have demonstrated that HBF_4 can effectively replace HF, acting as a stable and non-lethal in situ source for fluoride ions through the accelerated hydrolysis of HBF_4 at high temperatures which releases HF, thereby enabling the thermo-regulated digestion of geological materials (Chen et al., 2005; Quiroz et al., 2016; Maher et al., 2018; Javed et al., 2020; Zimmermann et al., 2020; Klein et al., 2022; Li et al., 2024). In tandem, the development of microwave-assisted digestion systems provides efficient and reproducible dissolution under elevated temperature and pressure (Javed et al., 2020; Zimmermann et al., 2020; Li et al., 2024).

Despite generally effective dissolution, the presence of free fluoride ions in solution can lead to the precipitation of Al-, Ca- and Mg- fluorides which are resistant to chemical attack and incorporate trace elements (e.g. Rb, Ba, REE, Th, U) by substitution for the major cation (Takei et al., 2001; Muratli et al., 2012; Chen et al., 2017; Karandashev

et al., 2017; Javed et al., 2020; Zimmermann et al., 2020; Kagami and Yokoyama, 2021; Horsburgh et al., 2023). The oxidation and precipitation of fluorophile high field strength elements (HFSE; e.g., Ti, Zr, Nb, Hf, and Ta) can also occur during evaporation when samples approach dryness due to the volatilisation of F^- ions which maintain these species in solution (Karandashev et al., 2017; Okina et al., 2018). Where the accurate determination of absolute element concentrations is required, it is therefore important to minimise the formation of insoluble precipitates or fully redissolve them after digestion. The use of HBF_4 for digestion achieves this through the complexation of free F^- ions with aqueous B in solution to reform HBF_4, reducing the amount of fluoride ions available for precipitate formation (Krachler et al., 2002; Zimmermann et al., 2020).

While previous studies have demonstrated the utility of HBF_4-based microwave digestion for trace element analysis, these have predominantly focused on soils, peat, coal and deep marine sediments (Krachler et al., 2002; Javed et al., 2020; Zimmermann et al., 2020; Li et al., 2024), with limited evaluation of REE pattern fidelity or broader elemental suite recovery across the lithological diversity typical of paleoenvironmental investigations. Here, we address these gaps by characterising elemental recovery and REE pattern integrity across six compositionally diverse geological reference materials using an automated high-throughput microwave system, validating HBF_4 digestion as a practical, low-hazard routine method for paleoenvironmental geochemistry.

Digests were analysed for elemental concentrations by ICP-MS/MS to assess: (1) effectiveness of bulk sample dissolution, (2) elemental recovery for major and trace elements, and (3) accuracy of REE profiles. We explore elemental recovery at two stages, first immediately post-digestion, and secondly following total evaporation to dryness and redissolution—an essential step preceding isotopic analyses and high-precision concentration analyses. We then briefly discuss mechanisms which drive differential recovery across element groups. The method was developed for efficient sample throughput (40 samples in $\sim$3 h) and reduced handling of highly hazardous reagents relative to conventional open-vial and HF-based digestion approaches.

2 Method details

2.1 Sample preparation and digestion

The digestion protocol was tested on six certified reference materials; BHVO-2 (Hawaiian basalt, USGS), NOD-A-1 (Atlantic ferromanganese nodule, USGS), ShBOQ-1 (Boquillas Shale, USGS), SCo-2 (Cody Shale, USGS), SSAR-1 (Animas River sediment, USGS), and MESS-4 (Beaufort Sea marine sediment, NRC Canada). First, 40–60 mg of each reference material was weighed into 8 mL PFA digestion vials, with six replicates for each material and three procedural blanks (39 samples in total). Samples were acidified with 6 mL of HNO_3 (65 % w/w, trace metal analysis grade, VWR) and left to react for 2 h to dissolve easily soluble phases such as carbonates. Subsequently, 1 mL HBF_4 (38 % w/w ultra-pure grade, AnalytiChem Belgium) was added to each vial before loading them into a Milestone ultraCLAVE automated microwave digestion system with a Single Reaction Chamber. A baseload solution in the reactor consisted of 300 mL 18.2 MΩ cm ultrapure water, 10 mL H_2O_2 (30 % w/w, trace analysis grade, VWR) and 5 mL H_2SO_4 (95 % w/w, trace metal analysis grade, VWR), which served to absorb excess microwave energy and ensure uniform heat distribution among reaction vials. The chamber was initially pressurised with N_2 gas to 4 MPa to prevent sample boiling during heating. Variable microwave power was applied up to a maximum of 1000 W to sustain a temperature ramp of 4 °C min^{-1} for 45 min until 180 °C, corresponding to a reaction pressure of $\sim$10 MPa, which was maintained for 105 min. Total operational duration, including heating, cooling and depressurisation was approximately 3 h, with capacity for the digestion of up to 40 samples in each run.

Following digestion, vials were removed from the microwave digestion system and left cooling in a fume hood for 1 h prior to further processing. Immediately after opening each vial, an aliquot of 70 µL was pipetted from close to the surface of the digested solution and diluted into 6.93 mL 0.5 mol L^{-1} HNO_3 for elemental analysis; these aliquots are hereafter referred to as the T1 aliquots. The remaining $\sim$6.93 mL of sample in each digestion vial were transferred into 14 mL PFA vials, and the original digestion vials were rinsed twice with 18.2 MΩ cm ultrapure water into their corresponding PFA vial. The combined solution was evaporated to dryness overnight at 120 °C on a hotplate within a fume hood, then redissolved in 10 mL 0.5 mol L^{-1} HNO_3, hereafter referred to as the T2 aliquots. For elemental analyses, both the T1 aliquots and T2 aliquots were further diluted in 0.5 mol L^{-1} HNO_3 to a total dilution factor of 10 000 relative to the initial average sample mass. A flowchart overview of the total procedure is provided as Figure S5 in the Supplementary Material.

2.2 Elemental concentration measurements

Elemental concentrations were analysed on an Agilent 8900 Triple Quadrupole ICP-MS/MS at the Faculty of Geosciences and the Environment, University of Lausanne. Measurements were conducted under various gas modes (He, H_2, O_2 and no gas) using both single and triple quadrupole configurations to minimise polyatomic and isobaric interferences for each element. An internal standard solution containing Rh and Bi was introduced via in-line addition. Calibration standards were prepared gravimetrically from multi-element reference solution (CMS-1, CMS-3, CMS-4, CMS-5; Inorganic Ventures). Details of gas modes, isotope selection, internal standard correction, and mass-shifts parameters are provided in Supporting Table S1 (Bollen et al., 2026).

Data reduction was performed in Agilent MassHunter, applying blank subtraction and internal standard correction. Limits of detection (DL) were defined as three times the standard deviation of blank replicates, corresponding to a <1 % probability that the signal arises from instrument

noise. Limits of quantification (LOQ) were set to three times the DL. Concentrations below the LOQ were excluded for further analyses. To monitor for analytical accuracy, reproducibility, two secondary reference solutions (NOD-A-1, USGS—digested in aqua regia; DRIFT, in-house multi-element solution gravimetrically diluted to 1 ppb) were each measured after every 10 samples (Fig. S1, Supplementary Material).

Element recovery was evaluated using certified and information values for each reference material (Fig. 1). Where such values were incomplete, they were supplemented by community-based reference data compiled in the GeoReM database (Jochum et al., 2005). For certain elements, MESS-3 and SCo-1 values were used to supplement MESS-4 and SCo-2, respectively, ensuring a consistent comparison across the widest possible array of elements and lithologies, though there may be slight compositional differences between these editions. The complete dataset of certified/accepted/community values for each reference material are presented in Supporting Table S2 (Bollen et al., 2026). REE profiles were normalised to Post-Archean Australian Shale (PAAS; Pourmand et al., 2012). To account for variable element recovery, each REE concentration was further normalised to the mean REE concentration of the corresponding sample. This approach preserves the shape of PAAS-normalised REE pattern while compensating for overall recovery offsets, thereby allowing the detection of any systematic fractionation trends across the lanthanide group.

2.3 Analytical uncertainty and blank assessment

Instrumental reproducibility was assessed using two reference solutions; NOD-A-1 digested in aqua regia, and DRIFT, an in-house mixture of elemental concentration standards at 1 ppb (uncertainty expressed as two relative standard deviations, 2RSD; Fig. S1 in the Supplementary Material). The 2RSD is < 10 % for S, V, Mn, Fe, Co, Ni, Cu, Zn, Sr, Y, Zr, Nb, Ba, La, Ce, Tb, Tl, Pb, and U and < 20 % for all other measured elements (Na, Mg, Al, Ti, Cr, As, Sb, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, W) except for Hf (∼ 25 %) and Th (∼ 45 %). The potential for contamination during sample processing was evaluated by normalising the average signal intensity of procedural blanks to the mean signal of reference material samples (Fig. S2, Supplementary Material). For most elements, the procedural blank contribution was < 1 % of the total signal. Only Si and Ta exceeded 10 %, though Si concentrations were below the LOQ in both blanks and T2 aliquots. Considering the negligible impact of blanks relative to the ± 10 % ICP-MS/MS analytical uncertainty, no procedural blank correction was applied to the reported concentrations. Seven outlying measurements were removed, with poor data quality attributed to erroneous sample dilution and handling. There are thus four and three replicates of the T1 and T2 aliquots from MESS-4, respectively, and four replicates of the SSAR-1 T2 aliquots. All other materials retain six replicates for each of the processing stages.

3 Results

After the microwave digestion, no original sample residue was observed in the reaction vials. However, white flaky precipitates and slight turbidity were observed in several digests, varying in quantity between reference materials and samples. The most pronounced precipitation occurred in Al-rich samples (MESS-4), while the ferromanganese oxide nodule (NOD-A-1) exhibited the clearest solutions.

The elemental recovery immediately post-digestion (T1) ranged from 80–120 % for most transition metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As) and several other elements (Be, Na, P, S, K, Nb, Sb, Ba, Tl, Pb and U; Fig. 1a). Moderate recoveries (50–80 %) were observed for K, Ca, Ti, Zr, and REE, whereas Mg, Al, Si, Y, and Th showed poor recoveries (< 50 %). Recoveries of Ta and W occasionally exceeded 120 %.

Elemental recoveries after drying and redissolution (T2) were 50–120 % for most elements (Fig. 1b), with recovery of 80–100 % for Na, P, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Nb, and Ba. Consistently low yield occurred for Al (< 50 %) and Si (below LOQ; < 2 %) (Fig. 1b). W yield was highly variable (75–220 %). Relative increases in elemental recovery were observed for Al, Mg, Y, W, Th and REE compared to T1 samples, while Si expressed near-total or total loss.

4 Discussion

4.1 Assessment of initial digestion effectiveness

Elemental recoveries of the transition metals Cr, Co and Ni in the T1 aliquot were within analytical uncertainty of certified values across all reference materials (Fig. 1a). Complete recovery of these elements suggests that all mineral phases containing these elements were effectively digested, including refractory phases such as Cr_2O_3. Recoveries were not significantly different from accepted values in three or more of the reference materials for Be, S, V, Mn, Fe, Cu, Zn, As, Se, Cs, Ta, W, Tl, and Pb. Based on total recovery of these presented elements, we infer that near-complete digestion of all reference materials was achieved during the microwave digestion protocol. However, we concede that the under-recovery of Ti and Zr (which can be present as refractory oxides) may suggest limited decomposition of associated minerals occurred, wherefore we suggest near-complete rather than complete digestion.

In contrast, we observe low recoveries of Mg, Al, Ca, REE, and Th in the T1 aliquots (Fig. 1a), which are consistent with the co-precipitation with insoluble fluorides during or after digestion, as previously reported for HF-based methods (Yokoyama et al., 1999). We infer that the majority of Al (80–95 %) reacted with F^- ions during digestion to form fluoroaluminate precipitates, such as insoluble AlF_3. Figure 2 explores the relationship between the abundance of Al and the recovery of light REE (LREE; La, Ce, Pr, Nd) and Th following digestion (Fig. 2a,b), revealing an inverse correlation in which Al-rich materials show poorer LREE and Th recoveries. This observation suggests that the loss

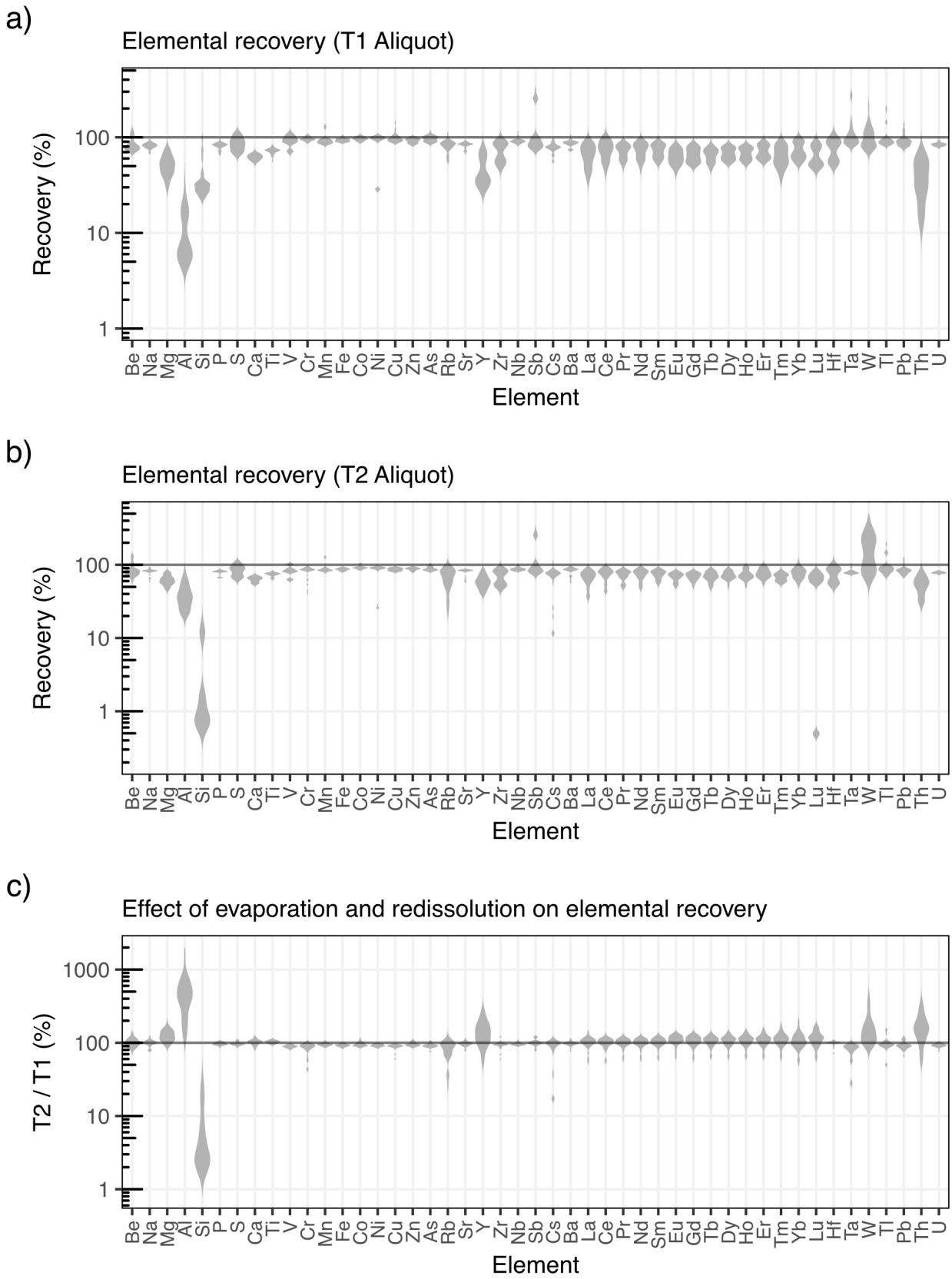

Figure 1. (a) Elemental recovery for T1 aliquots which were sampled immediately post-digestion, and (b) T2 aliquots which were evaporated to dryness and redissolved. (c) The relative change in recovery between T2 and T1, indicating a gain or loss of elements in solution during drying and redissolution. Violin plots identify the distribution of elemental recovery across all measured samples from all reference materials.

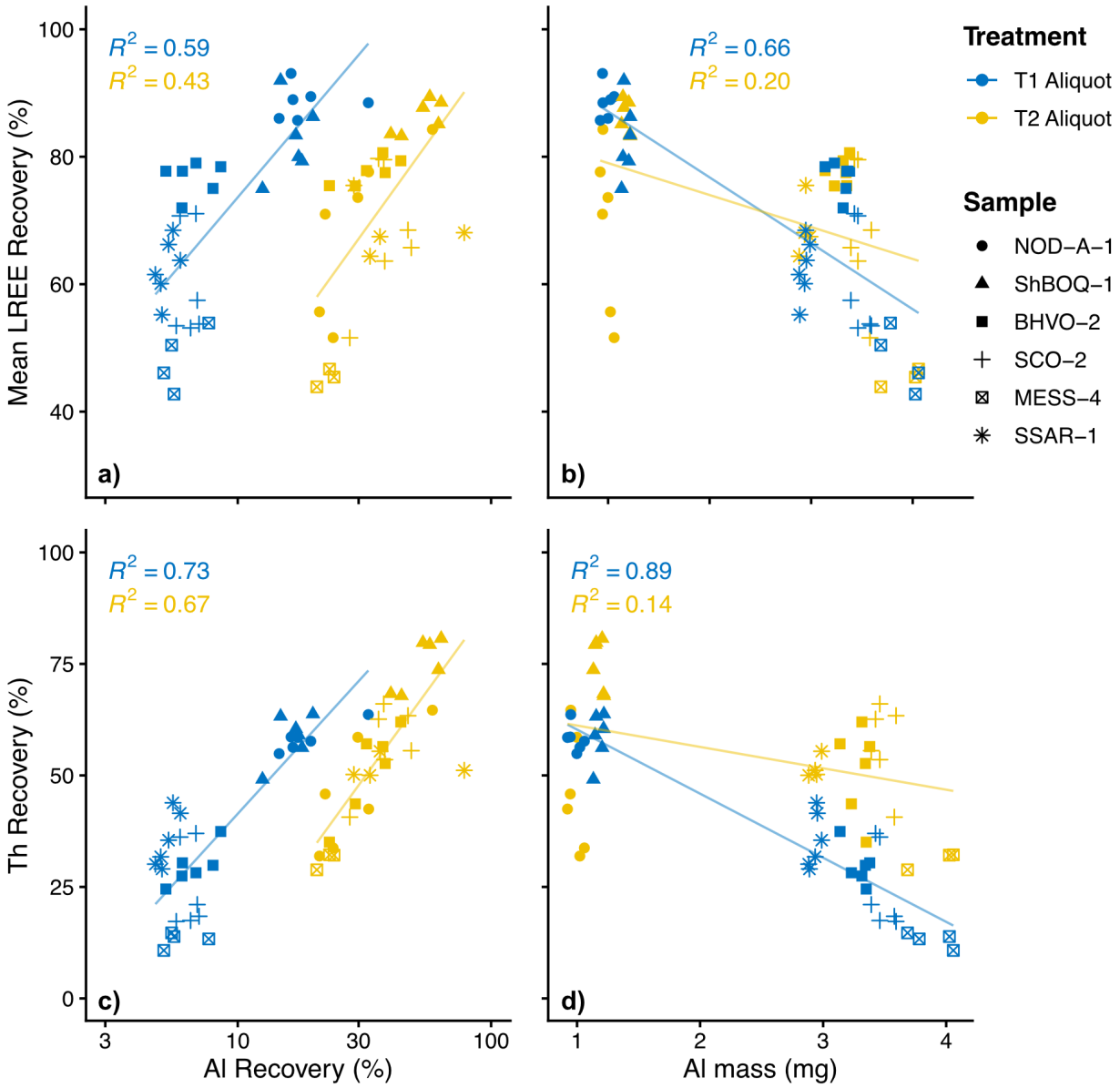

Figure 2. (a, b) Relationship of mean LREE recovery to a) Al recovery and b) total actual Al mass in the sample prior to digestion. (c, d) Relationship of Th recovery to c) Al recovery and d) actual Al mass in the sample prior to digestion. T1 aliquots (immediately post-digestion) are shown in blue and T2 aliquots (evaporated to dryness and redissolved) are displayed in yellow. Note that the linear trendlines and R^2 values are calculated from the $\log^{10}$ of Al recovery in panels a) and c).

of LREE and Th from solution is at least partly governed by Al abundance, hypothesised to result from increased aluminium fluoride precipitation.

4.2 Effects of open-vial evaporation to dryness

Substantial increases in recovery, up to four-fold, were observed in the T2 aliquot for Mg and Al (Fig. 1c), indicating at least partial breakdown of soluble precipitates occurred during evaporation and redissolution. Concurrent increases in REE, Y, and Th recoveries (Fig. 2c) indicate that while these elements may have been initially incorporated into precipitated phases, they were released during evaporation and redissolution. In contrast, the near total loss of Si is attributed to the volatilisation of SiF_4 during evaporation to dryness (Arslan and Lowers, 2024). Such a loss of volatile species (including Si, B, and halogens) is a well-known limitation of open-vial drying in digestion protocols (Vlastelic and Piro, 2022). Although volatilisation is minimised during high-pressure and high-temperature microwave digestion (Zimmermann et al., 2020), it persists during any subsequent open-vial evaporation steps.

4.3 Fractionation of rare earth elements

The precipitation of insoluble fluorides can lead to the reduced recovery of REEs due to their incorporation in Al-, Ca-, and Mg- fluorides, where the relative concentrations of those major ions in solution determine the composition, mineralogy and solubility of the precipitated fluorides (Yokoyama et al., 1999). A negative correlation observed between the total Al content in samples and LREE recovery (Fig. 2b)

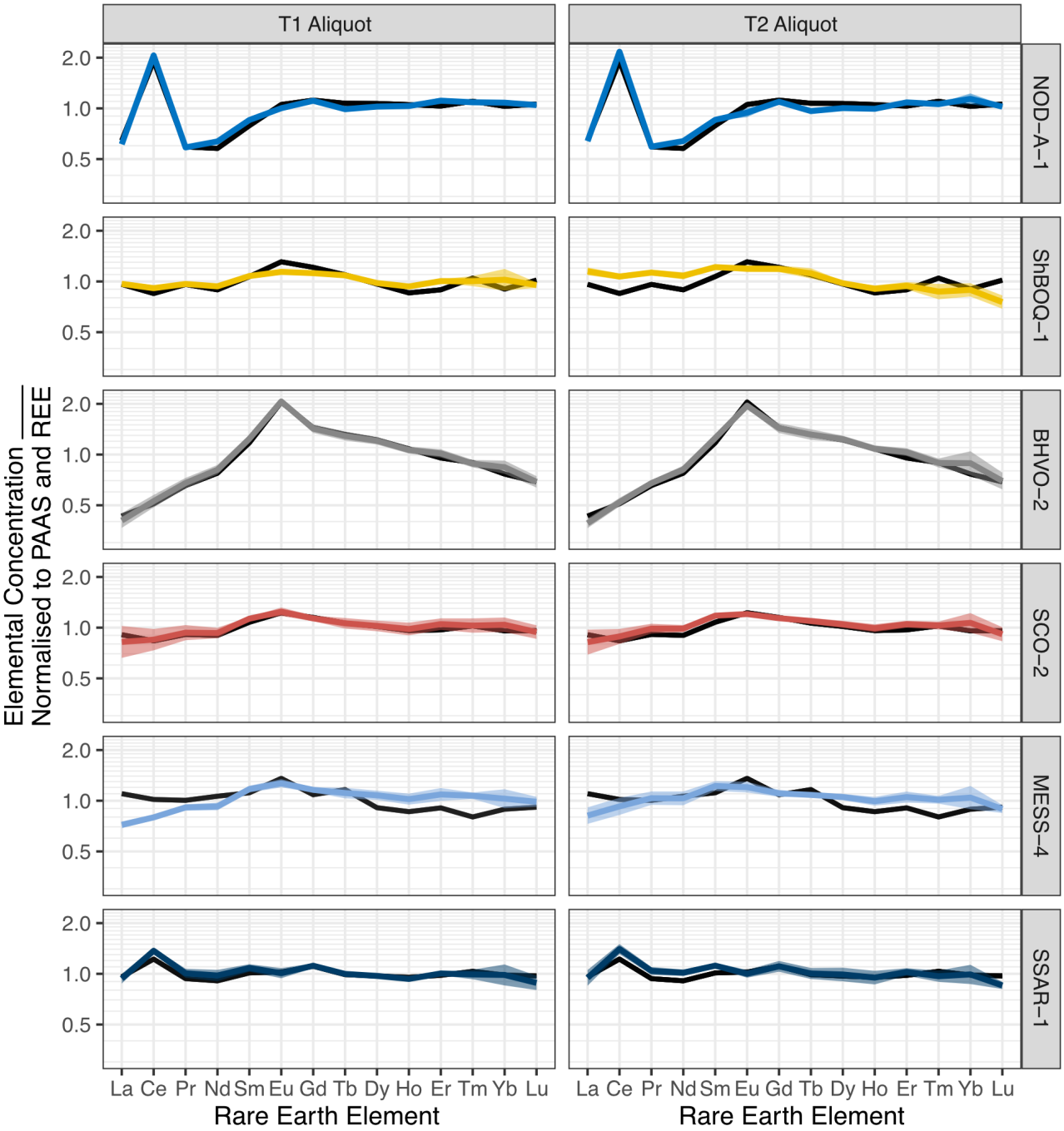

Figure 3. REE concentration profiles, normalised to PAAS and the mean concentration of REE, for geological reference materials, comparing T1 aliquots (immediately post-digestion) and T2 aliquots (evaporated to dryness). The black lines represent the accepted/certified values for each reference material, normalised to PAAS and mean REE concentration (not including uncertainty). Solid colored lines indicate the average of replicate measurements, and the shaded areas show the 2RSD range for the measured data, normalised to PAAS and REE concentration.

indicates that LREE may be preferentially uptaken in an Al-rich environment. There is also a positive correlation between the recoveries of Al with LREE and Th (Fig. 2a, c), suggesting a causal link between their under-recoveries. Interestingly, while both Al and Th recovery increased following evaporation and redissolution, LREE recovery is not seen to follow suit for most reference materials (except SCo-2; Fig. 2a, c). This suggests that LREE may be preferentially concentrated into the least soluble alumino-fluoride precipitate forms.

The shale-normalised REE patterns, corrected for absolute recovery, are broadly comparable to the accepted reference patterns for each material (Fig. 3; uncorrected patterns are shown in Fig. S3 of the Supplementary Material), with BHVO-2, NOD-A-1, SCo-2, and SSAR-1 generally reproducing the expected REE profiles in both T1 aliquots and T2 aliquots (Fig. 3). The only notable deviations from accepted profiles occur for MESS-4 and ShBOQ-1 (Fig. 3). In MESS-4, there is a minor depletion of LREE and enrichment in heavy REE (HREE, Dy–Yb) relative to

middle REE (MREE; Sm–Tb; Fig. S3 in Supplementary Material). Following evaporation and redissolution, ShBOQ-1 shows a greater degree of LREE enrichment and slight HREE depletion (Tm and Lu; Fig. 3).

Despite the under-recovery of REE, fractionation across the Lanthanide group remains minor even where recoveries are only above 50 % (Fig. S4, Supplementary Material). This result indicates that fluoride precipitation is not inherently problematic for geochemical studies focused on relative REE patterns rather than their absolute concentrations. Indeed, the distinct and accurate REE profiles reproduced in basaltic, ferro-manganese, shale, and riverine matrices (BHVO-2, NOD-A-1, SCo-2, and SSAR-1) demonstrate that HBF_4-based microwave digestion may preserve the geochemical integrity of REE distributions across diverse lithologies. Our results emphasise that fluoride precipitates may form even for sample compositions previously deemed favorable (Takei et al., 2001; Kagami and Yokoyama, 2021). The potential for REE fractionation thus warrants the careful evaluation of potential effects using matrix-matched reference materials.

4.4 Applications and recommended use

The presented HBF_4-based microwave digestion method yields generally satisfactory elemental recoveries for most elements, achieving acceptable recovery for most light transition metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn) immediately after digestion (T1 aliquot), and obtaining representative REE profile forms despite under-recovery of the Lanthanide elements. We find that this method is fit for purpose for the determination of light transition metal concentrations, and applications where complete elemental recovery is not essential, or where fractionation effects can be identified and corrected for—including sedimentary U-Th, Nd, Sr and Pb isotopes (Zimmermann et al., 2020; Hallmaier et al., 2025; Lee et al., 2026). For new materials, we recommend the use of matrix-matched reference materials to evaluate elemental recovery and assess potential fractionation. Where total recovery of HFSE or REE is required, this method should be combined with complementary protocols that either prevent the formation of insoluble mineral phases or ensure their subsequent total dissolution (e.g. Yokoyama et al., 1999; Muratli et al., 2012; Chen et al., 2017).

5 Conclusions

We demonstrated and verified a simple, low-hazard, and efficient (40 samples in $\sim$3 h) method for the digestion of geological materials relevant for sedimentological applications, leveraging HBF_4 as an in-situ source of HF within a closed single reaction chamber microwave-assisted digestion system. By eliminating the hazards associated with HF use and open-vessel processing, this approach offers substantial safety and operational advantages. The protocol achieved near-complete digestion of six geological reference materials, evidenced by the complete recovery of light transition metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn). Consistent with other high-pressure, high-temperature HF digestion methods, the formation of insoluble fluoride precipitates during digestion was found to reduce the absolute recovery of REE and some trace elements. The degree of REE fractionation varies according to matrix composition, emphasising the importance of testing the approach with certified materials of similar mineralogy and composition. Despite modest under-recovery, REE patterns for four out of six reference materials agree with expected values, confirming that the relative REE distributions can remain reliable despite incomplete elemental recovery. The method is shown capable of providing accurate REE patterning and robust total concentrations for transition metals. Further refinements, such as post-digestion treatments to dissolve precipitates, could be applied to enhance quantitative recovery. Overall, the HBF_4 microwave digestion offers a low-hazard, efficient and reproducible alternative for routine geochemical analyses.

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Data, code, and outputs availability

Figures S1–S6 are available in the accompanying Supplementary Material. Supporting Table S1 and S2 are available in Bollen et al. (2026, https://doi.org/10.57744/LDLDB1186369). Main text figures are available for download in the online version of this article.

Competing interests

The authors declare no competing interests.

Licence agreement

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