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## ARTICLE

## Evaluation of two methods allowing the full preparation in a single day of silicate rocks in view of radiogenic isotopes (Nd, Sr, Pb) analyses.

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In this paper, two approaches are described aiming to circumvent the bottle-neck associated to sample decomposition of silicate samples and subsequent isolation of three elements (Nd, Sr, and Pb) of major interest for their radiogenic isotope compositions. These new methods alleviate the need for any evaporation and repeated dissolution steps, and make it possible to achieve in a single day the complete preparation of a batch of 10 samples. Specifically, samples are decomposed either by alkaline fusion with a LiBO<sub>2</sub> flux followed by quenching in nitric acid, or by quick dissolution in an HF-HNO<sub>3</sub> mixture immediately followed by reaction with an aqueous solution of boric acid to neutralize excess HF and dissolve sparingly soluble fluorides. In both cases, the resulting sample solutions are directly loaded onto small chromatographic columns filled with RE and Sr resins, respectively, used in tandem, in order to achieve the concomitant separation of the LREE, Sr, and Pb from matrix elements. While Sr and Pb fractions suitable for isotopic analyses are directly stripped from the Sr resin, an additional column of DGA resin is used, in tandem with the RE resin column, to obtain a Nd fraction isolated from the other LREE. The potential of these most straightforward approaches is demonstrated by repeated analyses of eleven geological reference materials (RMs) spanning a wide range of major element concentrations.

### 1. Introduction

The variations of radiogenic isotopes of Sr, Pb, and Nd, caused by radioactive decay of <sup>87</sup>Rb, <sup>235,238</sup>U+<sup>232</sup>Th, and <sup>147</sup>Sm, respectively, provide a powerful means for tracing the origin and evolution of natural systems. Accordingly, these three isotopic systems, used separately or preferably in combination, make part of the standard tool box of scientists involved in environmental, geological, and planetary sciences. By virtue of the direct sample introduction at atmospheric pressure inherent to this technique, MC-ICP-MS has greatly simplified the isotope ratio measurement step, increased the overall analytical throughput and, in the case of lead, made it possible to correct more accurately instrumental mass fractionation. However, wherever direct solid sampling by laser ablation is not possible, that is, in all cases but a few accessory minerals containing the elements of interest at high concentrations (e.g., Sr in apatite or some plagioclase, Nd in phosphate phases), it is necessary to greatly concentrate and purify the element to be analyzed from sample matrix. This is generally achieved by using liquid chromatography techniques, which in turn requires decomposing the sample and then putting it in the form of a solution appropriate for the separation process. These steps

involve lengthy dissolution and evaporation steps typically requiring several days, much longer than the chromatographic separation proper.

In this paper, we describe two new procedures, differing by their sample decomposition steps (viz., alkaline fusion with LiBO<sub>2</sub> vs. modified version of acid dissolution with HF), but using the same separation scheme, based on the adaptation of well-established extraction chromatographic techniques. Because they do not involve any evaporation or repeated acid treatments, and use miniaturized columns filled with fairly selective extraction chromatographic materials, these protocols make it possible to prepare in a single day a set of 10 samples for measuring <sup>143</sup>Nd/<sup>144</sup>Nd, <sup>87</sup>Sr/<sup>86</sup>Sr, and <sup>208,207,206</sup>Pb/<sup>204</sup>Pb ratios.

### 2. Experimental

#### 2.1 Chemicals

Water was first deionized with conventional ion-exchange resins and then further purified to a resistivity of 18.2 MOhm cm with an Aqua System Distribution (Bondoufle, France) device. Reagent grade hydrofluoric, nitric and hydrochloric acids (Fluka, Seelze, Germany) were purified by subboiling distillation in PFA DST-100 systems (Savillex, Eden Prairie, MN, USA). Orthoboric acid (Merck, Suprapur, 99.9999%) and ascorbic acid (Sigma, analytical grade, >99%) were used without further purification. The LiBO<sub>2</sub> flux used for sample decomposition by fusion was prepared in-house by sintering at 550°C a mixture in stoichiometric proportions of high-purity Li<sub>2</sub>CO<sub>3</sub> and H<sub>3</sub>BO<sub>3</sub>, both of Suprapur grade (supplied by Merck).

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Eleven geological materials were investigated during the course of this work, eight were provided by United State Geological survey (USGS), namely AGV-2 (andesite), BCR-2, BHVO-2 and BIR-1a (basalts), G-2 (granite), GSP-2 (granodiorite), RGM-1 (rhyolite), STM-1 (nepheline syenite). We analysed also two RMs from the Geological Survey of Japan, namely JA-1 (andesite) and JB-3 (basalt) and finally one basalt (BE-N) from the "Centre de Recherches Pétrographiques et Géochimiques" (CRPG, Nancy, France).

### 2.2 Extraction chromatographic materials

Three extraction chromatography (EXC) materials obtained from Triskem International (Bruz, France) were used in this work, respectively the RE resin, based on octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) dissolved in tributyl phosphate,<sup>1,2</sup> the DGA resin, based on tetra(n-octyl)diglycolamide,<sup>3</sup> and the Sr resin, based on the crown ether di-tertbutylcyclohexano-18 crown-6 (DtBuCH<sub>18</sub>C<sub>6</sub>) in 1-octanol.<sup>4</sup> In every case, these ligands were sorbed onto Amberchrom CG-71 acrylic ester beads of 50-100 µm particle size.

### 2.3 Instrumentation

Except for the alkaline fusion stage, all chemical handlings were made under Class 10 vertical laminar flow hoods in a laboratory supplied with an overpressure of filtered air, at a temperature of 20 °C.

A 2.4 kW EasyHeat induction heater (Ambrell Co., Rochester, NY, USA) was used for sample decomposition by fusion with a LiBO<sub>2</sub> flux, in home-made, graphite crucibles with a rounded bottom machined from 25 mm diameter high-purity graphite rods (Ringsdorff, Bonn, Germany) covered with a flat graphite disk during RF heating.

Screw cap 15 ml PFA vessels (Savillex, Eden Prairie, MN, USA) were used for sample dissolution. The separated fractions of Sr, Pb, and Nd were collected in 5 ml screw cap PFA vials with a conical bottom (Savillex) and evaporated to dryness.

Three different columns, fitted with polyethylene frits at the bottom and at the top of the resin bed, were involved. The first short column, ca. 5 mm i.d., is prepared from a "Fine tip, large bulb", model 234 (Samco Scientific) obtained from ThermoScientific. It contains 100 mg of RE resin, slurry-packed in dilute HNO<sub>3</sub>, making a ca. 10 mm high resin bed. The second short column, ca. 5 mm i.d., is made of silica glass and contains 83 mg of Sr resin.

The third, longer column is made of a ca. 4 mm i.d. transfer pipette (model 235 (Samco Scientific) filled with a slurry containing 500 mg of DGA resin, corresponding to a resin height of ca. 80 mm. These are depicted in Fig. 1.

Two quadrupole ICP-MS (Agilent 7500 and 8900, Agilent Technologies, Les Ulis, France) were used for setting up the separation method and further characterization of the protocol, respectively. All isotope ratio measurements were made with a Neptune Plus MC-ICP-MS (Thermo Scientific) with a conventional sample introduction system, and operating parameters given in Table 1.

### 2.4 Sample digestion

#### 2.4.1 Digestion by alkaline fusion

An aliquot of ca. 50 mg of finely powdered sample is added to a ca. three-fold weight of LiBO<sub>2</sub>, and intimately mixed in a porcelain dish with a small stainless steel spatula. Then, the sample-flux blend is carefully transferred to the graphite crucible, covered with a graphite lid, placed in the coil of the induction heater with a pneumatic piston, and fused for 5 min at ca. 1150 °C. The resulting melt is gently swirled in the graphite crucible to recover any droplet on the walls, and quenched into a pre-cleaned, single-use polystyrene jar (model 2835, Caubère, Paris) containing 5 ml of 2 mol.L<sup>-1</sup> HNO<sub>3</sub> stirred with a magnetic bar. After complete dissolution of the glass droplets, requiring 5-10 min, the sample solution is centrifuged at 4000 rpm during 10 min to remove graphite particles detached from the crucible during the fusion process. The next steps must be made promptly, because the stability of the sample solution is limited due to the very small volume of acid used for quenching and dissolving the melt. Otherwise, especially in case of high-silica samples, the first column may get plugged by the precipitation of gelatinous products. The supernatant solution is transferred to a pre-cleaned polypropylene tube, with rinsing of the quenching jar and magnetic bar with 1 ml 2 mol.L<sup>-1</sup> HNO<sub>3</sub>. Then, 40-50 mg of ascorbic acid and 25 µl of mass fraction of 48 % HF are added in order to reduce Fe(III) and help stabilizing the high field strength elements prone to hydrolysis, respectively. After 5-10 min in an ultrasonic bath, the solution is ready for the next, column separation step.

#### 2.4.2 Digestion by acid dissolution

The sample powder (ca. 50 mg) is weighed on a small sheet of weighing paper, and gently poured into a 15 ml PFA vial (Savillex) with a flat or rounded bottom in which 1 ml of 14 mol.L<sup>-1</sup> HNO<sub>3</sub> has been put beforehand. The powder is carefully wetted by nitric acid before addition of 0.5 ml of 48 % HF. The vial is tightly closed by hand, and the mixture swirled and/or agitated ultrasonically a few minutes to prevent the formation of any powder agglomerate. Then, the vial is placed on a hot plate at 100 °C for a short-duration attack ("flash digestion") during no more than 20 minutes. The vial, still lukewarm, is opened in a fume hood, and 4 ml of mass fraction of 4 % aqueous solution of boric acid are promptly added to the sample. The vial is quickly closed and placed in a heated ultrasonic bath for a few minutes at ca. 50 °C to hasten the reaction of boric acid with the fluorides formed during the attack and obtain a clear solution. This solution is poured into a centrifuge tube with an additional 0.5 ml of 2 mol.L<sup>-1</sup> HNO<sub>3</sub> to rinse the PFA vial. After centrifugation (4 min at 4000 rpm), some 30-50 mg (depending on the iron concentration of the sample) of ascorbic acid are added to the solution and dissolved in an ultrasonic bath. After 10 min, the solution is ready for EXC separation.

### 2.5 Chemical Separations

Whatever the digestion technique used, the ca. 6 ml sample solution in 2 mol.L<sup>-1</sup> HNO<sub>3</sub> containing ascorbic acid is loaded onto the RE column placed over the Sr column (both preconditioned in 2 mol.L<sup>-1</sup> HNO<sub>3</sub>). The loading is made as 6 portions of 1 ml each, in order to keep to a minimum the surface of the column reservoir in contact with the solution. After complete draining, the two columns, still in tandem, are rinsed twice with 0.5 ml of 2 mol.L<sup>-1</sup> HNO<sub>3</sub>-0.145 mol.L<sup>-1</sup> HF. Then, the RE and Sr columns are decoupled. The RE column is further rinsed with 0.5 ml of 1 mol.L<sup>-1</sup> HNO<sub>3</sub>. Following this, the rest of unwanted matrix elements and the heavy REE are stripped by using a suite of small fractions of nitric acid of decreasing strength, specifically, 2 x 0.25 ml of 0.5 mol.L<sup>-1</sup> HNO<sub>3</sub>, 2 x 0.25 ml of 0.25 mol.L<sup>-1</sup> HNO<sub>3</sub>, 2 x 0.25 ml of 0.125 mol.L<sup>-1</sup> HNO<sub>3</sub>, and finally 0.15 ml of 0.05 mol.L<sup>-1</sup> HNO<sub>3</sub>. At this stage, the DGA column (preconditioned with 3 mol.L<sup>-1</sup> HCl) is placed below the RE column, and the LREE are eluted from the RE resin, and simultaneously loaded onto the DGA column by means of 2 ml of 3 mol.L<sup>-1</sup> HCl. Then, the columns are decoupled and the lightest lanthanides (La-Ce-Pr) are eluted from the DGA column with 3.55 ml of 2 mol.L<sup>-1</sup> HCl. Finally, the Nd fraction is recovered with 2.75 ml of 1 mol.L<sup>-1</sup> HCl.

After decoupling from the RE column, the Sr column is rinsed with 0.5 ml of 2 mol.L<sup>-1</sup> HNO<sub>3</sub>, and then 2 ml of 7 mol.L<sup>-1</sup> HNO<sub>3</sub> to get rid of matrix elements left in the free column volume and Ba, respectively. A small, intermediate fraction of 0.5 ml of 2 mol.L<sup>-1</sup> HNO<sub>3</sub> precedes the elution of the Sr fraction with 2 ml of 0.05 mol.L<sup>-1</sup> HNO<sub>3</sub>. Finally, Pb is stripped with 2 ml of 6 mol.L<sup>-1</sup> HCl. The whole procedure of chemical separation is outlined in Table 2.

The total duration of the whole procedure, for a batch of 10 samples, including weighings is about 12 hours.

### 3. Results

The elution profiles of the elements of interest on the RE and DGA columns used in tandem are compared in Fig. 2 in order to evaluate the potential effect of the alternative sample digestion modes on chromatographic separation. Although a subtly earlier breakthrough of La can be noticed in the fusion-digested profile, there is no significant shift of the LREE peaks, in spite of the fact that the HFSE elements, including titanium, display contrasting behaviours in F-bearing and F-free contexts. Indeed, if the RE resin does not extract HFSE when these elements are complexed by fluorine - as is the case when the sample has been dissolved with HF, it has a distinct affinity for these elements in the absence of fluoride ( $D_{Zr} > 400$  and  $D_{Ti}$  ca. 25 in 2 mol.L<sup>-1</sup> HNO<sub>3</sub>).<sup>2</sup> As a result, the effective column capacity for the LREE might have been somewhat reduced when processing samples digested by fusion. However, the similarity of the elution profiles shows that the combined RE-DGA EXC approach is robust enough to make such effects negligible, and can handle sample solutions prepared by contrasting methods, even when micro-columns are used.

The ranges of chemical recoveries measured for the three elements are listed in Table 3 for both sample digestion methods. While essentially identical values around 90 % were

obtained for Nd, it can be observed that slightly lower recoveries (in the 80-90% range) were achieved for Sr and Pb when the samples were digested by fusion. The cause for this difference is not clear at present. However, because the LiBO<sub>2</sub> flux is likely to contain non negligible amounts of potassium, the only element (besides Ba, Sr and Pb) to be significantly extracted by the Sr resin,<sup>4</sup> it is tentatively suggested that this element might have reduced the capacity of the column, and caused a partial loss of Sr and Pb during sample loading. If this explanation proves to be true, this problem could be circumvented by using a slightly greater amount of resin, or obtaining a flux cleaner in K. Nevertheless, it is noteworthy that good chemical recoveries can be obtained from both expeditious silicate sample digestion procedures investigated. The analytical contamination associated with the reagents and columns used in this work can be evaluated from the data given in Table 4, together with the total procedural blanks measured for the two, HF-based, and LiBO<sub>2</sub>-based methods. Not surprisingly, total procedural blanks achieved for the procedure based on sample digestion by fusion are significantly larger than those obtained with the acid dissolution. However, the results do not differ by a factor greater than three for Sr, and even two for Pb and Nd, thus indicating that - contrary to a widespread opinion - the sample digestion approach by fusion does not suffer from an intrinsic, irremediable flaw. Indeed, from a practical point of view, such levels of contamination would not be excessive for processing a wide range of common samples, in which a 50 mg sample portion typically contains several µg of Sr, and several tens of ng of Pb and Nd.

In order to demonstrate the potential of these two single day preparation methods prior to radiogenic isotope measurements, eleven reference materials have been processed by using both protocols, and the Nd, Sr, and Pb fractions isolated in this way analyzed by MC-ICP-MS for <sup>143</sup>Nd/<sup>144</sup>Nd, <sup>87</sup>Sr/<sup>86</sup>Sr, and <sup>208,207,206</sup>Pb/<sup>204</sup>Pb ratios. The results for Nd are listed in Table 5, along with the average value of the isotopic standard JNdi-1, and the net values measured for the ion beams at m/z 140 and 147, which are used to monitor Ce and Sm, the two elements having isobaric interferences with Nd at mass 142 and 144, respectively. These values document that Nd was very well isolated from these two troublesome elements, although the significantly higher signal for <sup>147</sup>Sm<sup>+</sup> than for <sup>140</sup>Ce<sup>+</sup> (73 +/- 48 (SD) µV against 9 +/- 25 µV, respectively) suggests that, unless a very minor polyatomic interference occurred at m/z 147, the volume of 1 mol.L<sup>-1</sup> HCl used to recover the Nd fraction could be slightly reduced. The overall accuracy of our results can be judged from a comparison with the ranges of values obtained worldwide for these geostandards, as compiled by GeoReM.<sup>5</sup> It can be seen that the <sup>143</sup>Nd/<sup>144</sup>Nd ratios measured by both modes of digestion agree very well within analytical precision. The only possibly significant difference is observed for GSP-2, a ca. 1.4 Ga old granodiorite, for which the two subsamples digested by fusion are very slightly less radiogenic than that dissolved with HF. This might suggest that a refractory phase with an even less radiogenic signature was not entirely opened during the HF attack. However, all the three data are well within the range of

values of the GeoReM compilation and the isotopic dispersion might equally well be interpreted in terms of subtle heterogeneity of that RM, prepared from a coarse-grained igneous rock prone to “nugget effect” for trace elements such as Nd. It is concluded from these data that a swift HF dissolution promptly followed by treatment with boric acid does not introduce any perceptible bias, as far as Nd isotopes are concerned, in part because the highly refractory phase zircon generally does not play a major role in the mass balance of that element.

Lead isotope data do not show clear discrepancy between those samples decomposed by fusion and those dissolved with HF (Table 6). Only the results for GSP-2 digested by fusion display slightly more radiogenic  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  and less radiogenic  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios, consistent with a more complete opening of an ancient, accessory mineral with a high U/Th ratio, presumably zircon, as commonly found in crustal plutonic rocks. The fusion data for JA-1 display more radiogenic signatures of both uranium and thorium ratios than those of the acid dissolution ones, but an interpretation in terms of an ancient component rich in U and Th is not much attractive in this volcanic sample. More work would be required to get further insights into this difference. The agreement of our data with the  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios compiled by GeoReM documents the overall accuracy of the method. Based on the similar ion beam sizes obtained for both digestion modes, no evidence was found for any significant loss of lead as a volatile species during fusion, in contrast with the observation of Totland et al.<sup>6</sup> who used much longer (20 min.) fusions in a muffle furnace.

Although the results for Sr (Table 6) do not show a large bias between the values obtained after fusion and HF dissolution, respectively, it can be observed that, in most cases, slightly higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were measured for those samples digested by fusion. The largest offset of  $8 \times 10^{-5}$  is observed for the most radiogenic ratios measured in GSP-2, a very ancient rock, which developed large isotopic differences among its rock-forming minerals, and is therefore not likely to be perfectly homogeneous at the 50 mg subsample scale, as far as radiogenic isotopes are concerned. In the other cases, the higher  $^{87}\text{Sr}/^{86}\text{Sr}$  might be interpreted to reflect the effect of the higher procedural blank inherent to the fusion method. However, this explanation would not account for the conspicuous absence of negative correlation between the offset of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and the amount of sample Sr processed; indeed, samples with the highest Sr mass fraction (STM-1:  $700 \mu\text{g g}^{-1}$  Sr, and BE-N:  $1370 \mu\text{g g}^{-1}$  Sr)<sup>8</sup> show the same positive bias ( $3 \times 10^{-5}$  and  $2 \times 10^{-5}$ , respectively) than the much poorer BIR-1 basalt ( $110 \mu\text{g g}^{-1}$  Sr,  $2 \times 10^{-5}$ ), while RGM-1 ( $110 \mu\text{g g}^{-1}$  Sr) has a negative bias of the same amplitude. It is therefore suspected that the observed differences might be due to a limited accuracy, not adequately reflected by the quoted within-run precision, of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios measured by MC-ICP-MS. It is tentatively suggested that residual amounts of Li left in the Sr fraction, quite likely to occur after a single pass separation, might have subtle effects on instrumental mass bias which is the Achilles' heel of that technique. Further work involving

measurements by TIMS would be required to get clearer insights into this question.

Whatever the reasons for these small discrepancies, it is emphasized that our Sr and Pb isotope data are encompassed by those compiled by GeoReM, thereby documenting an overall satisfactory accuracy. This is noteworthy because the fusion method is generally deemed “dirty”, not only because of the use of the alkaline flux, but also because it involves sample handling in a HT environment not easy to keep under very clean conditions.

## 4. Discussion

### 4.1 Sample size

A nominal sample size of 50 mg was chosen because, in most cases, this provides more than enough of the three target elements to measure radiogenic isotope ratios. Besides this, processing as small a sample mass as possible facilitates the digestion process, and keeps to a minimum the amount of expensive and/or hazardous high-purity reagents involved in the subsequent steps. Certainly, such a mass is on the lower end of the acceptable range of sample quantity to keep powder in-homogeneity issues at a low level. These are particularly acute in the case of granitic (*s.l.*) samples, where many trace elements (REE, HFSE, radiogenic Pb) are mostly hosted by accessory minerals, which are not evenly distributed. The size of the final powder portion taken for analysis can be significantly reduced by adding a further step to the standard powder preparation procedure. Specifically, a subsample of *ca.* 1 gram of the powder obtained following the conventional grinding is taken, poured in a small (*ca.* 5 ml) agate-lined jar together with a few small agate balls, placed in a “Mixer Mill” apparatus, and submitted to vigorous shaking for half an hour or so. This treatment produces a final powder that is both very finely ground and well homogenized, thereby allowing the analyst to use sample aliquots as small as a few tens of mg.

### 4.2 Sample digestion

The two methods used in this work share a crucial common feature, namely, enabling the analyst to decompose silicate rocks and obtain a solution suitable for chemical separations in a few tens of minutes. This compares very favourably to the conventional HF dissolution procedure which requires several days, starting from digestion proper – often made during tens of hours – to final dissolution in a medium adapted to the isolation of the element(s) of interest, through repeated evaporation and conversion steps to remove un-reacted HF and destroy sparingly soluble fluorides formed during attack.

#### 4.2.1 Digestion based on alkaline fusion with lithium metaborate

Following its introduction by Ingamells in the 1960's,<sup>9,10</sup> lithium metaborate has become the preferred flux for decomposing powdered silicate rocks by fusion, because it combines rapidity and effectiveness (including for refractory minerals<sup>11,12</sup>) to prepare clear homogeneous solutions suitable for major and

trace element analyses by ICP-AES and ICP-MS. However, in spite of a few successful examples<sup>13-15</sup>, its application to the field of radiogenic isotopes is much less popular. This is because special pieces of equipment (high temperature furnace, and possibly, very expensive platinum crucibles) are required, and also because the method suffers from a real or alleged poor image concerning analytical contamination. It is indeed not so easy to achieve sufficiently low blank levels for a solid compound such as  $\text{LiBO}_2$ , compared to an HF aqueous solution which can be conveniently purified from a wide range of non-volatile impurities by sub-boiling distillation. More specifically, commercially available products used to be severely contaminated by LREE due to the concomitant production, in the same facilities, of lithium tetraborate containing large quantities (mass fraction of 15-20 %) of lanthanum oxide used as a strong absorber in the fused disks beads prepared for XRF spectrometric analyses.<sup>16</sup> In order to minimize blank problems,  $\text{LiBO}_2$  can be dissolved in hot water and purified by recrystallization,<sup>10</sup> but this method is relatively tedious.<sup>17</sup> Alternatively,  $\text{LiBO}_2$  can be dissolved in 3 mol.L<sup>-1</sup>  $\text{HNO}_3$  and passed through EXC cartridges of DGA resin to get rid of the REE, Sc, and Y, before the flux is recovered by evaporation followed by a high T (720°C) treatment to remove residual nitric acid and water.<sup>18</sup> However, this method is also time-consuming and hampered by the reduced solubility of  $\text{LiBO}_2$ , limiting this approach to the purification of relatively small quantities of flux. Alternatively, it is possible to prepare  $\text{LiBO}_2$  in a clean environment, starting from high-purity precursors. In this work, batches of several hundred grams were prepared by sintering at 550°C overnight an appropriate mixture of solid boric acid and lithium carbonate.<sup>10,19,20</sup> As shown by the data listed in Table 4, the flux produced in this way contains the target elements at a level which is sufficiently low to make the contribution of the digestion blank process negligible, at least for a large range of samples. However, it is acknowledged that the digestion by fusion with  $\text{LiBO}_2$  is not yet optimal for those samples particularly depleted in Nd, Sr and/or Pb, such as ultramafic rocks which would require an even higher excess of flux to obtain clear solutions.

In order to obviate the need for prohibitively expensive fusion vessels made of platinum, relatively low-cost crucibles machined in-house from high-purity graphite were used throughout this study.<sup>10,14,15</sup> Cost-effective digestions with adequate blank levels are achieved in this way, at the price of the introduction in the quenching solution of inert graphite particles which need to be removed by filtration and/or centrifugation before chromatographic separation.

#### 4.2.2 Digestion based on reaction with HF

Due to the extreme strength of its chemical bond with silicon, fluorine reacts strongly with silicate materials, thus offering a very practical agent to carry out their digestion. Conventionally, a large excess of an aqueous solution of HF, high temperatures, and protracted digestion times are used. Among numerous examples, methods have been reported using 2 ml 69%  $\text{HNO}_3$  and 10 ml 48% HF at 225°C then 100°C during 2-3 days,<sup>21</sup> or 10

ml HF and 8 ml  $\text{HClO}_4$  at 200°C for 0.2 g of sample.<sup>22</sup> However, based on reviews of literature data<sup>23,24</sup> and the senior author's 40 years experience, an overwhelming proportion of silicate rocks can be decomposed within a few tens of minutes under milder conditions, in so far as finely ground powders are processed. This is especially true for those volcanic rocks (basalt, rhyolite) largely composed of glassy or cryptocrystalline, devitrified material which can be dissolved easily at room temperature. In general, it can be seen that the attack is carried out when the sample powder turns into a sort of white fluff. Therefore, maintaining for a long time the sample powder in contact with HF at high temperature not only does not improve the opening of silicates – particularly zircon which, anyway, would require much more stringent conditions in HP bombs – but instead promotes the growth of sparingly soluble fluorides, at least in those samples containing alkaline earth elements in non negligible amount, that is, in most situations. The proportion of such insoluble material is very variable, depending not only on sample composition, but also on the experimental conditions (e.g., temperature path, even at a subtle level, volume of reagents used).<sup>25</sup> In these precipitates, larger crystals tend to grow with time from those of smaller size through the process known as Ostwald ripening. Accordingly, as the solution-precipitate system is ageing, coarser and stronger grains form which are more difficult to destroy subsequently. Unfortunately, these fluorides are not merely simple calcium and magnesium fluorides, but are highly variable in composition, with numerous species referred to as “complex fluorides” built from a wide spectrum of major elements, including Fe, Al, Na, etc.<sup>21,24,26</sup> Almost invariably, they sequester most of the trace elements of radiogenic isotope interest in significant, albeit highly variable, proportions (e.g.<sup>21,27</sup>). As an example, the percentage of several selected trace elements found in precipitates formed during conventional HF dissolution (ca. 90°C, overnight) of basaltic samples are listed in Table 7. These data show that 10 to 30 % (and even up to 50 % for Th and the HREE) may be occluded in these poorly soluble, fluoride compounds, at least in case perchloric acid was not used. The addition of an excess of Al solution to the sample before decomposition has been proposed to suppress the formation of calcium fluoride,<sup>28</sup> but in general, tedious treatments with accompanying acids having a high boiling temperature (perchloric or sulfuric,<sup>29</sup> m-benzene disulfonic<sup>30</sup>) are required to remove HF and convert – with variable success – these fluorides into soluble salts. Although more efficient owing to its very high boiling point (337°C), sulfuric acid is not favoured in practice for several reasons: (i) it is very difficult to remove by evaporation, (ii) it produces insoluble calcium and barium sulfates, and (iii) it has strong complexing properties for several elements of interest. With the exception of potassium when present in relatively high quantities, perchloric acid (boiling temperature 203°C) produces soluble salts, and it is therefore very widely used. However, if evaporated too completely, it leads to the formation of insoluble compounds of Ti and other HFSE.<sup>31,32</sup> When the use of  $\text{HClO}_4$  is prohibited because of safety concerns, nitric or hydrochloric acids, or a mixture thereof (*aqua regia s.l.*) provide a commonly used, but less effective, alternative.

Irrespective of the accompanying acid, the progressive evaporation causes the various unwanted fluoride species to reach their saturation, unless a large excess of perchloric acid has been added at start or, alternatively, the sample solution is continuously diluted by the addition of HNO<sub>3</sub>, HCl, or both, a time-consuming process. In all cases, it is most advisable not to bring the solution to complete dryness, thus implying close monitoring of the evaporation process, a demanding task for the analyst.

In order to circumvent the problems related to digestion proper, and to the subsequent solution handlings, two radical measures have been investigated in this work.

Firstly, a short dissolution time of ca. 15 minutes (hereafter referred to as "flash attack") was used. Admittedly, highly refractory minerals such as zircon are not fully digested under these conditions, particularly if the rock powder was not very finely ground. Accordingly, those samples containing zircon in significant amount – as far as the LREE and uraniumogenic Pb budgets are concerned – would require either a further step of isolation of the undissolved residue and its treatment in a steel jacketed high pressure PTFE bomb<sup>33</sup>, or alternatively, to be decomposed by alkaline fusion, as described above, thereby preserving the advantage of a single stage, rapid process.

Secondly, the evaporation steps were purely and simply eliminated. Following the digestion step, the sample solution is immediately treated with a slight excess of a 4 wt. % boric acid solution in order to neutralize any un-reacted HF and dissolve the "young" fluorides formed during the attack. This approach avoids the heating and evaporation steps involved for the removal of HF and the difficult conversion of fluorides to soluble species. It was developed in the 1960's and 1970's to prepare solutions in view of major – including silica – and trace element determinations by AAS or ICP-AES and widely used<sup>34-41</sup> but, to our knowledge, it was not yet applied prior to separation chemistry in view of radiogenic isotope work. In the scope of isotopic analyses, its outstanding advantage is to produce in a very straightforward way sample solutions ready – at least for the three target elements of this study – for separation by EXC, thereby obviating the need for the time-consuming evaporation and conversion steps which put the strongest limitation to the overall analytical throughput.

Provided that the digestion process starts the evening before the rest of the procedure, a variant of HF-based digestion could be used, in which ammonium acid bifluoride (NH<sub>4</sub>HF<sub>2</sub>, a compound with melting and boiling/decomposition temperatures of 125 °C and 240 °C, respectively<sup>42</sup>) is employed in the molten state instead of the usual aqueous solution of HF<sup>43,44</sup>. Because it involves a reagent with a much higher boiling point than 48% HF, this method does not require high pressure devices, but can be used in simple screw cap PFA vessels, and it is claimed to better dissolve zircon by virtue of working temperatures around 220-230 °C. In this case, the digestion would be made overnight. After cooling to room temperature, the solid residue produced by this mode of attack is taken up with HNO<sub>3</sub> and immediately diluted with boric acid. This method was not used to produce the results given in this study, but preliminary experiments suggest that solutions prepared in

such manner are compatible with subsequent separations based on our protocol.

It is emphasized that these modes of digestion are not appropriate for a concomitant determination of Sm/Nd ratios by isotope dilution, which would require some further steps. In the case of fusion with LiBO<sub>2</sub>, a total spiking approach with a mixed <sup>149</sup>Sm-<sup>145</sup>Nd tracer could be used by adding the tracer before fusion, as described elsewhere.<sup>15</sup> By virtue of the very high temperatures reached during the melting process, this method is likely to ensure a perfect isotopic equilibration between sample and tracer, and it would allow the determination of both Nd concentration and <sup>143</sup>Nd/<sup>144</sup>Nd ratio to be made through a single mass spectrometric run. In all the other cases, a precisely weighed, small aliquot portion of the solution left after fusion and quenching, or boric acid treatment of the sample dissolved in HF-HNO<sub>3</sub>, should be taken, mixed with a weighed amount of isotopic tracer, e.g. a <sup>149</sup>Sm-<sup>150</sup>Nd mixed spike. Then, the sample-tracer blend should be evaporated to dryness (after addition of HF to get rid of Si as volatile fluoride, in the case of fusion), and submitted to a thorough treatment with HCl and/or HNO<sub>3</sub> and preferably HClO<sub>4</sub> to promote isotopic equilibration between sample and tracer. Finally, the dry residue left after this treatment could be taken up in 1 mol.L<sup>-1</sup> HNO<sub>3</sub> and passed through a small column of TRU or RE resin to get rid of matrix elements and obtain a LREE fraction suitable for the simultaneous measurement of <sup>145</sup>Nd/<sup>146</sup>Nd and <sup>149</sup>Sm/<sup>147</sup>Sm isotope ratios by MC-ICP-MS. Bearing in mind the small sample quantities and volumes of acids involved, it is suggested that these steps might be made in parallel with the processing of the main solution used for unspiked, isotope composition measurements.

#### 4.2.3 Comparative assessment

Because of its intrinsic advantages (completeness of attack, no hazard related to the use of HF, no problem caused by fluoride complexing and precipitation), alkaline fusion appears to offer the best approach. However, the digestion by fusion is not free of problems. First, it involves a large (threefold or even more) excess of flux, implying a significantly larger volume of the quenching solution which is used to start the separation process. This in turn necessitates to up-scale the size of chromatographic columns, even in the case where highly specific EXC materials are used. Indeed, the slow flow rate inherent to narrow-bore, miniaturized columns would make loading such large volumes on the columns too long. The second problematic issue of fusion is the degree of purity of the flux which, as a solid compound prepared from solid precursors, is much less easy to obtain with extremely low levels of a wide range of elements (as required for a multi-isotopic method) than acids purified by sub-boiling distillation. For these reasons, it is believed that the best analytical strategy is to use either LiBO<sub>2</sub> fusion or flash dissolution with HF, depending on the presence or absence, respectively, of those refractory minerals hosting a significant proportion of the target elements. Thus, the two silicate sample

digestion procedures studied in this work must be considered by the analyst as complementary rather than opposing tools.

### 4.3 Separation chemistry

The separation stages are based on well-established EXC methods which were found, after very minor adaptations, to be fully compatible with the two swift sample digestion methods used in this study. The first stage achieves the on-line separation of LREE, Sr and Pb from matrix elements. Following earlier work,<sup>45</sup> two EXC columns in tandem configuration are used to isolate, in a single step, the analytes from matrix elements, specifically, a first column filled with a CMPO-based resin coupled to a second column of Sr resin, similar to those used previously<sup>46,47</sup> for the concomitant extraction of the LREE, Sr and Pb. Here, the RE resin was used instead of the TRU resin because it features higher weight distribution ratios of the LREE in 2-3 mol.L<sup>-1</sup> HNO<sub>3</sub>, specifically,  $D_w$  of Nd ca 230<sup>48</sup> vs. ca 150 for TRU,<sup>2</sup> thereby permitting to use significantly larger volumes during the column loading step - as required by the two methods of attack used - without a risk of incipient breakthrough of Nd. The sample solution is loaded onto the RE column and Sr column in tandem, thereby achieving the extraction of the LREE by the upper column, and of Sr and Pb (plus Ba) by the lower one.

After rinsing, the two columns are decoupled and further processed separately. The Sr column is treated as described previously,<sup>47</sup> that is, further rinsed with 7 mol.L<sup>-1</sup> HNO<sub>3</sub> to get rid of Ba, followed by the sequential elution of Sr and Pb with very dilute (0.05 mol.L<sup>-1</sup>) nitric acid and strong (6 mol.L<sup>-1</sup>) HCl, respectively.

The second stage is required to isolate Nd from adjacent REE. As described in an earlier contribution,<sup>49</sup> the LREE fraction is stripped from the RE column with 3 mol.L<sup>-1</sup> HCl and directly loaded onto an on-line column of DGA resin. This lower column allows the lanthanides to be sequentially separated from the lighter to the heavier ones by using a gradient of decreasing HCl molarity. In this way, Nd fractions are easily obtained that are essentially free of Ce and Sm which would produce isobaric interferences at  $m/z$  142 and 144, respectively.

On a wider scope, this study highlights the great flexibility and robustness of extraction chromatography, which proves to be able to accommodate solutions prepared by a variety of methods. Indeed, unlike the small volumes of final solutions obtained after repeated evaporation and conversion stages of the conventional digestion methods, larger volumes were involved, consisting either of pure nitric acid with a high charge of salts, or a more complex mixture of fluoboric and nitric acids. In either case, the extraction of the nitrate species of the three target elements was not significantly impeded, thereby documenting the efficiency and high selectivity of the CMPO and crown ether ligands used to impregnate an inert support with good chromatographic characteristics to produce the RE and Sr resins, respectively.

## Conclusions

The alternative protocols investigated in this work of fast digestion of silicate rocks and further prompt treatment of the sample solution without any evaporation and conversion step are compatible with a straightforward separation of the LREE, Sr, and Pb from matrix elements by miniaturized extraction chromatography. Good chemical recoveries of the three target elements and blank levels adequate for routine work on common rocks are achieved, and the isotope ratios measured on several geological SRMs spanning a range of bulk compositions agree well with published values obtained by using conventional methods, thus documenting the overall validity of these new, single day approaches. With a minor adaptation of the final DGA column, these protocols could include Ce in view of isotope analyses. Last but not least, the solutions obtained from both sample digestion methods would allow, at the price of a precise splitting of the overall starting solution into appropriate aliquots, the concomitant determination of major (including silica) and many trace elements concentrations to be made on one and the same sample. This would require that ICP-AES and ICP-QMS instruments are available in the laboratory, and that a well-functioning organization of the technical staff involved is achieved. In this case, a rather complete chemical and radiogenic isotope characterization of silicate samples could be obtained in a very short amount of time, with minimal cost and analyst time and effort.

## Author Contributions

Both authors designed the analytical procedure, carried out the chemical separation, performed the measurements on mass spectrometers and wrote the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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when he was retiring from the CNRS after 40 years of work in this laboratory.

## References

- 1 E. P. Horwitz, M. L. Dietz, R. Chiarizia, H. Diamond and D. M. Nelson, *Anal. Chim. Acta*, 1993, **281**, 361-372.
- 2 E. A. Huff and D. R. Huff, presented at 34<sup>th</sup> ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tennessee, October, 1993.
- 3 E. P. Horwitz, D. R. McAlister, A. H. Bond and R. E. Barrans Jr., *Solv. Extr. Ion Exch.*, 2005, **23**, 319-344.
- 4 E. P. Horwitz, R. Chiarizia and M. Dietz, *Solvent Extr. Ion Exch.*, 1992, **10**, 313-336.
- 5 GeoReM Data Base, <http://georem.mpch-mainz.gwdg.de> (accessed July 2023).
- 6 M. Totland, I. Jarvis and K. E. Jarvis, *Chem. Geol.*, 1992, **95**, 35-62.
- 7 S. J. G. Galer and W. Abouchami, *Mineral. Mag.*, 1998, **A62**, 491-492.
- 8 K. Govindaraju, *Geostand. Newsl.*, 1994, **XVIII**, 158 p.
- 9 C. O. Ingamells, *Talanta*, 1964, **11**, 665-666.
- 10 C. O. Ingamells, *Anal. Chim. Acta*, 1970, **52**, 323-334.
- 11 M. Cremer and J. Schlocker, *Amer. Miner.*, 1976, **61**, 318-321.
- 12 C. Feldman, *Anal. Chem.*, 1983, **55**, 2451-2453.
- 13 S. Shirey and G. N. Hanson, *Geochim. Cosmochim. Acta*, 1986, **50**, 2631-2651.
- 14 B. Le Fèvre and C. Pin, *Anal. Chem.*, 2001, **73**, 2453-2460.
- 15 B. Le Fèvre and C. Pin, *Anal. Chim. Acta*, 2005, **543**, 209-221.
- 16 P. J. Potts, *A Handbook of Silicate Rock analysis*. Blackie, Glasgow & London, 1987.
- 17 R. B. Vocke, G. N. Hanson and M. Grünenfelder, *Contrib. Mineral. Petrol.*, 1987, **95**, 145-154.
- 18 A. Pourmand, N. Dauphas and T. J. Ireland, *Chem. Geol.*, 2012, **291**, 38-54.
- 19 N. H. Suhr and C. O. Ingamells, *Anal. Chem.*, 1966, **38**, 730-734.
- 20 J. Carignan, CRPG-CNRS Nancy (France), pers. comm.
- 21 R. H. Boer, G. J. Beukes, F. M. Meyer and C. B. Smith, *Chem. Geol.*, 1993, **104**, 93-98.
- 22 K. E. Jarvis, *Chem. Geol.*, 1990, **83**, 89-103.
- 23 R. Bock, *A Handbook of Decomposition Methods in Analytical Chemistry*. International Textbook Co., 1979.
- 24 Z. Sulcek and P. Povondra, *Methods of Decomposition in Inorganic analysis*, CRC Press, Boca Raton, Florida, 1989.
- 25 I. W. Croudace, *Chem. Geol.*, 1980, **31**, 153-155.
- 26 F. J. Langmyhr and K. Kringstad, *Anal. Chim. Acta*, 1966, **35**, 135-137.
- 27 T. Yokoyama, A. Makishima and E. Nakamura, *Chem. Geol.*, 1999, **157**, 175-187.
- 28 R. Tanaka, A. Makishima, H. Kitagawa and E. Nakamura, *J. Anal. Atom. Spectrom.*, 2003, **18**, 1458-1463.
- 29 F. J. Langmyhr, *Anal. Chim. Acta*, 1967, **39**, 516-518.
- 30 R. S. Cohen, P. Hemmes and J. H. Puffer, *Chem. Geol.*, 1975, **16**, 307-309.
- 31 C. O. Ingamells and F. F. Pitard, *Applied Geochemical Analysis*, Wiley Interscience, New York, 1986.
- 32 D. M. Unruh, P. Stille, P. J. Patchett and M. Tatsumoto, 1984, Lunar and Planetary Science Conference, 14th, Houston, TX, J. Geophys. Res., 1984, **89**, B459-B477.
- 33 C. Pin and J. F. Santos Zalduegui, *Anal. Chim. Acta*, 1997, **339**, 79-89.
- 34 B. Bernas, *Anal. Chem.*, 1968, **40**, 1682-1686
- 35 D. E. Buckley and R. E. Cranston, *Chem. Geol.*, 1971, **7**, 273-284.
- 36 N. T. Bailey and S. J. Wood, *Anal. Chim. Acta*, 1974, **69**, 19-25.
- 37 H. Agemian and A. S. Y. Chau, *Anal. Chim. Acta*, 1975, **80**, 61-66.
- 38 W. J. Price and P. J. Whiteside, *Analyst*, 1977, **102**, 664-671.
- 39 H. Uchida, T. Uchida and C. Iida, *Anal. Chim. Acta*, 1979, **108**, 87-92.
- 40 D. Silberman and G. Fisher, *Anal. Chim. Acta*, 1979, **106**, 299-307.
- 41 C. R. M Rao and G. S. Reddi, 1990, *Anal. Chim. Acta*, 1990, **237**, 251-252.
- 42 National Library of medicine Online, <https://pubchem.ncbi.nlm.nih.gov/compound/Ammonium-bifluoride>, (accessed June 2023).
- 43 W. Zhang, Z. Hu, Y. Liu, H. Chen, S. Gao and R. M. Gashnig, *Anal. Chem.*, 2012, **84**, 10686-10693.
- 44 G. Újvári1, U. Klötzli, M. Horschinegg, W. Wegner, D. Hippler, G. I. Kiss, L. Palcsu, *Rapid Commun. Mass Spectrom.*, 2021, **35**, 9081.
- 45 C. Pin, D. Briot, C. Bassin and F. Poitrasson, *Anal. Chim. Acta*, 1994, **298**, 209-217.
- 46 C. Deniel and C. Pin, *Anal. Chim. Acta*, 2001, **426**, 95-103.
- 47 C. Pin, A. Gannoun and A. Dupont, *J. Anal. Atom. Spectrom.*, 2014, **29**, 1858-1870.
- 48 B. Le Fèvre, PhD Thesis, Blaise Pascal University, Clermont-Ferrand, 2002.
- 49 C. Pin and A. Gannoun, *J. Anal. At. Spectrom.*, 2019, **34**, 2136-2146.

## Figure Captions

**Fig. 1** Summary of the geometry and resins of the three extraction chromatography columns used in this work.

**Fig. 2** Elution profiles on the RE and DGA columns for the SRM AGV-2 digested by  $\text{LiBO}_2$  fusion and HF dissolution. The detailed protocol including the volumes and types of acid used is shown in Table 2.

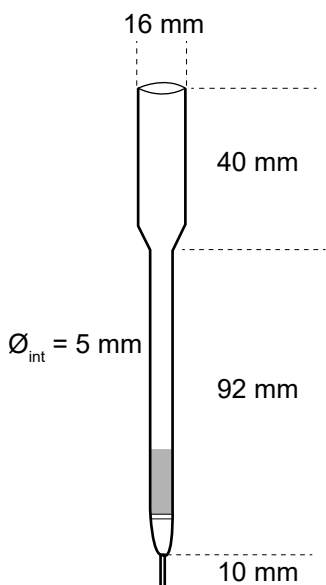
**RE**50 - 100  $\mu\text{m}$ 

100 mg of resin

Samco disposable transfer pipets

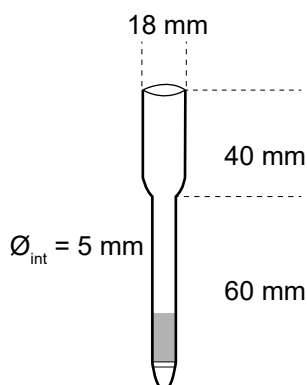
Samco Scientific 234 Fine tip

large bulb

**SR-Spec**50 - 100  $\mu\text{m}$ 

83 mg of resin

Silica glass column

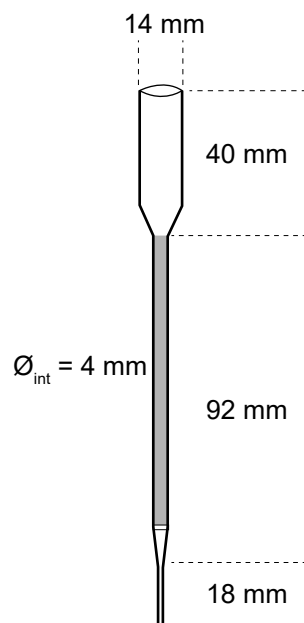
**DGA**50 - 100  $\mu\text{m}$ 

500 mg of resin

Samco disposable transfer pipets

Samco Scientific 235 Fine tip

large bulb

**Fig. 1**

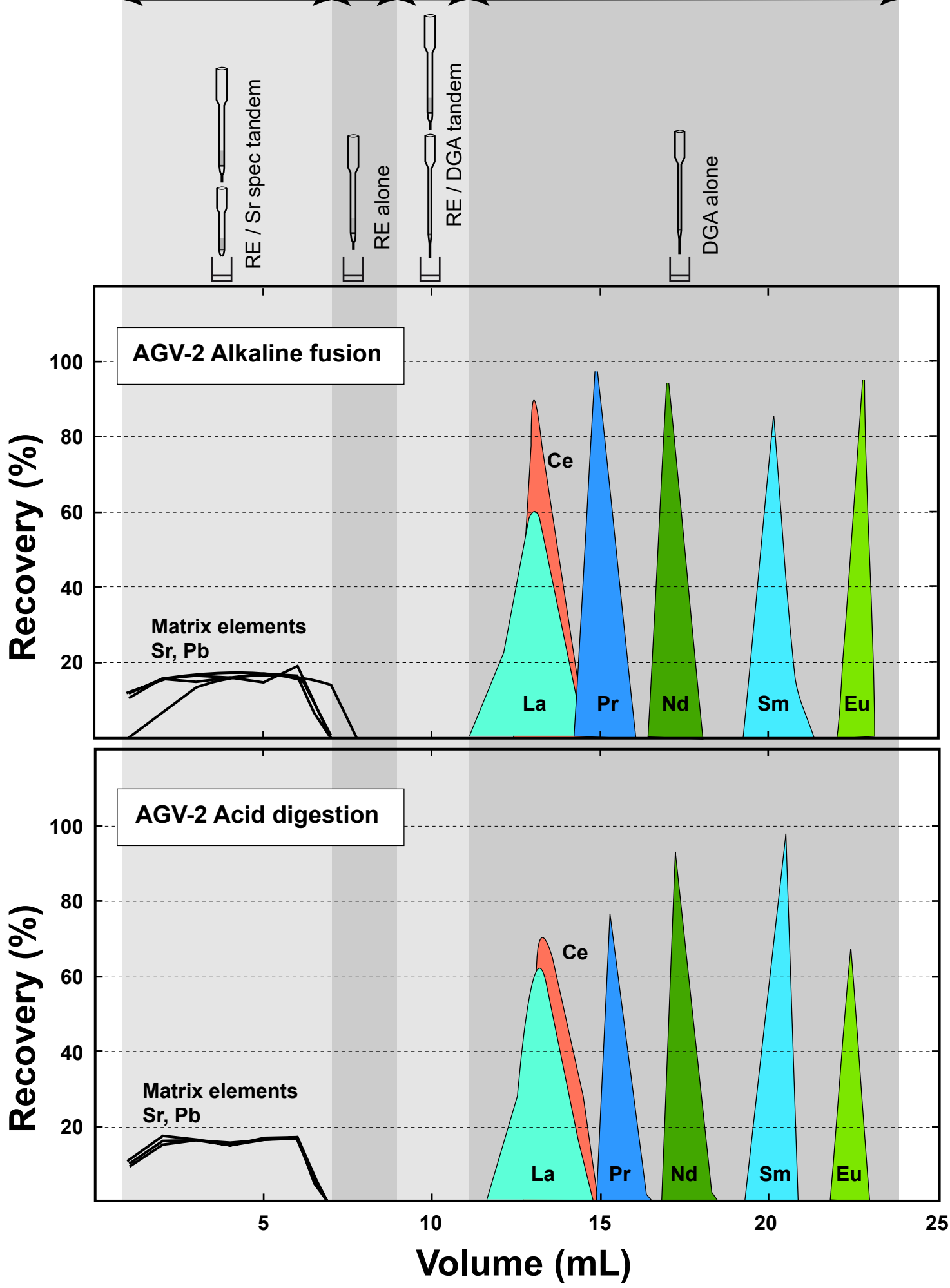


Fig. 2

**Table 1** Instrument settings and data acquisition parameters for isotope ratio measurements of Sr, Nd and Pb by MC-ICP-MS (Neptune Plus, Thermo Fisher Scientific). The Faraday cups configuration is also reported at the bottom of the table.

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Analysis	Sr, Nd and Pb isotopes
Laboratory	Magmas et Volcans
MC-ICP-MS model	Thermo Neptune Plus
Plasma condition	Wet (cyclonic spray chamber)
RF power	1200 W
Resistors	10 <sup>11</sup> Ohms
Resolution	Low ( $M/\Delta M \sim 400$ )
Cool gas flow (Ar) <sup>a</sup>	15 - 16 L.min <sup>-1</sup>
Auxiliary gas (Ar) <sup>a</sup>	0.7 - 0.8 L.min <sup>-1</sup>
Sample gas (Ar) <sup>a</sup>	0.9 - 1.1 L.min <sup>-1</sup>
Sample uptake	100 $\mu$ L.min <sup>-1</sup>
Sample cone	standard
Skimmer cone	H
Sensitivity (V per $\mu$ g.g <sup>-1</sup> )	~60
Scanning mode	Static multi-collection
Integration time	8.4 s
Number of cycles	60
Number of blocks	1

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<sup>a</sup> optimized daily for maximum Sr, Nd or Pb sensitivity

**Table 2** Outline of the full separation procedure enabling the isolation of Sr, Pb and Nd.

	Reagent	Volume (mL)	Step Duration <sup>c</sup> (min)
<b>Column pre-cleaning and preconditioning <sup>a</sup></b>			
Sr-spec column (83 mg of Sr-spec resin)	6 mol.L <sup>-1</sup> HCl	5	
	0.05 mol.L <sup>-1</sup> HNO <sub>3</sub>	5	
preconditioning	2 mol.L <sup>-1</sup> HNO <sub>3</sub>	0.5	
RE column (100 mg of RE resin)	3 mol.L <sup>-1</sup> HCl	4	
	0.05 mol.L <sup>-1</sup> HNO <sub>3</sub>	4	
preconditioning	2 mol.L <sup>-1</sup> HNO <sub>3</sub>	0.5	
DGA column (500 mg of DGA resin)	0.1 mol.L <sup>-1</sup> HCl - 0.29 mol.L <sup>-1</sup> HF	4	
	0.05 mol.L <sup>-1</sup> HCl	4	
preconditioning	3 mol.L <sup>-1</sup> HCl	0.5	
<b>RE and Sr-spec columns in tandem</b>			~90
Sample loading	2 mol.L <sup>-1</sup> HNO <sub>3</sub> - C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	6 x 1	
reservoir and column rinsing	2 mol.L <sup>-1</sup> HNO <sub>3</sub> - 0.145 mol.L <sup>-1</sup> HF	2 x 0.5	
<b>Columns decoupling and further elution <sup>b</sup></b>			~120
<b>Sr Spec column</b>			
Elution of Ba	7 mol.L <sup>-1</sup> HNO <sub>3</sub>	2	
Rinse	2 mol.L <sup>-1</sup> HNO <sub>3</sub>	0.5	
Sr stripping	0.05 mol.L <sup>-1</sup> HNO <sub>3</sub>	2	
Transition	3 mol.L <sup>-1</sup> HCl	4	
Pb stripping	6 mol.L <sup>-1</sup> HCl	2	
<b>RE column</b>			
Stripping of unwanted elements	1 mol.L <sup>-1</sup> HNO <sub>3</sub>	0.5	
(residual major and minor elements, HREE)	0.5 mol.L <sup>-1</sup> HNO <sub>3</sub>	0.5	
	0.25 mol.L <sup>-1</sup> HNO <sub>3</sub>	0.5	
	0.125 mol.L <sup>-1</sup> HNO <sub>3</sub>	0.5	
	0.05 mol.L <sup>-1</sup> HNO <sub>3</sub>	0.15	
<b>RE and DGA columns in tandem</b>			~60
Elution / Loading of the LREE	3 mol.L <sup>-1</sup> HCl	2	
<b>Columns decoupling and further elution</b>			~240
<b>DGA column</b>			
Reservoir and column rinsing	3 mol.L <sup>-1</sup> HCl	0.5	
Pre-Nd fraction (La-Ce-Pr)	2 mol.L <sup>-1</sup> HCl	3.55	
Nd stripping	1 mol.L <sup>-1</sup> HCl	2.75	
Sm stripping	0.5 mol.L <sup>-1</sup> HCl	1.5	

<sup>a</sup> The column pre-cleaning is performed the day before processing the samples. The duration of sample preparation and digestion was ~120 min.

<sup>b</sup> The duration time reported here is for the whole step after decoupling Sr-spec and RE columns, since they were processed in parallel on separate column supports.

<sup>c</sup> The duration time given here is for a set of 10 columns.

**Table 3** Chemical recoveries (%) for the three target elements, measured by ICP-QQQ Agilent 8900.

Yields (%)	Alkaline fusion method		HF Flash method	
	Min	Max	Min	Max
<b>Sr</b>	80	88	85	93
<b>Pb</b>	79	94	95	100
<b>Nd</b>	85	95	82	93

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**Table 4** Analytical blanks of selected acids, EXC columns, and total procedural blanks, as measured by Agilent 8900 ICP-QQQ

	7 mol.L <sup>-1</sup> HNO <sub>3</sub>	6 mol.L <sup>-1</sup> HCl	Column blank	Total Blank (Fusion)	Total Blank (HF Flash)
	(pg.mL <sup>-1</sup> )	(pg.mL <sup>-1</sup> )	(pg)	(pg)	(pg)
<b>Sr</b>	5.1 ± 1.0	4.3 ± 1.2	14.1 ± 3.2	125 ± 37	45 ± 17
<b>Pb</b>	3.1 ± 0.7	1.5 ± 0.4	7.8 ± 2.1	95 ± 28	42 ± 15
<b>Nd</b>	0.9 ± 0.2	1.1 ± 0.3	6.3 ± 1.9	21 ± 6	13 ± 5
	(n=4)	(n=4)	(n=6)	(n=3)	(n=3)



**Table 5** Nd isotope ratios measured by static multi-collection for eleven international SRMs of silicate rocks, digested either by alkaline fusion or by HF dissolution. The net signals measured at m/z 140 and 147 (monitoring isobaric interferences) and m/z 144 are also indicated, along with the range of values listed by the GeoRem compilation.<sup>5</sup>

Geostandards	Method	<sup>140</sup> Ce	<sup>144</sup> Nd	<sup>147</sup> Sm	<sup>143</sup> Nd/ <sup>144</sup> Nd <sup>§</sup>	<sup>143</sup> Nd/ <sup>144</sup> Nd	
		(V)	(V)	(V)	(± 2 s.e)	Min. GEOREM	Max. GEOREM
JA-1	Fusion	4.0E <sup>-05</sup>	3.52	2.8E <sup>-05</sup>	0.513095 ± 0.000006	0.513047	0.513112
JA-1	Flash HF	-1.3E <sup>-05</sup>	2.99	4.8E <sup>-05</sup>	0.513096 ± 0.000007		
BHVO-2	Fusion	1.5E <sup>-05</sup>	6.01	8.2E <sup>-05</sup>	0.512990 ± 0.000005	0.512115	0.513013
BHVO-2	Flash HF	-2.9E <sup>-05</sup>	2.95	3.5E <sup>-05</sup>	0.512990 ± 0.000007		
BIR-1a	Fusion	-2.2E <sup>-05</sup>	0.78	3.0E <sup>-05</sup>	0.513086 ± 0.000013	0.513088	0.513106
BIR-1a	Flash HF	-1.8E <sup>-05</sup>	0.47	7.7E <sup>-06</sup>	0.513092 ± 0.000018		
JB-3	Fusion	2.1E <sup>-05</sup>	3.34	3.5E <sup>-05</sup>	0.513063 ± 0.000006	0.513024	0.513091
JB-3	Flash HF	1.8E <sup>-06</sup>	2.49	4.4E <sup>-05</sup>	0.513066 ± 0.000007		
BE-N	Fusion	2.8E <sup>-06</sup>	7.01	7.7E <sup>-05</sup>	0.512882 ± 0.000005	0.512862	0.512895
BE-N	Flash HF	3.1E <sup>-05</sup>	5.24	6.1E <sup>-05</sup>	0.512883 ± 0.000006		
BCR-2	Fusion	-9.8E <sup>-06</sup>	5.14	9.5E <sup>-05</sup>	0.512642 ± 0.000006	0.5126	0.5129
BCR-2	Flash HF	3.8E <sup>-05</sup>	3.11	3.5E <sup>-05</sup>	0.512638 ± 0.000007		
BCR-2	Flash HF	3.9E <sup>-06</sup>	0.29	6.5E <sup>-05</sup>	0.512649 ± 0.000010		
STM-1	Fusion	1.5E <sup>-06</sup>	8.41	1.1E <sup>-04</sup>	0.512916 ± 0.000005	0.512908	0.512939
STM-1	Flash HF	9.9E <sup>-06</sup>	4.38	6.7E <sup>-05</sup>	0.512919 ± 0.000005		
RGM-1	Fusion	-1.1E <sup>-05</sup>	4.10	4.3E <sup>-05</sup>	0.512800 ± 0.000006	0.512784	0.512816
RGM-1	Fusion	1.6E <sup>-05</sup>	4.39	5.0E <sup>-05</sup>	0.512797 ± 0.000006		
RGM-1	Flash HF	5.3E <sup>-06</sup>	1.91	3.9E <sup>-05</sup>	0.512812 ± 0.000009		
RGM-1	Flash HF	-2.3E <sup>-05</sup>	2.19	3.6E <sup>-05</sup>	0.512807 ± 0.000009		
GSP-2	Fusion	5.1E <sup>-05</sup>	6.65	1.4E <sup>-04</sup>	0.511362 ± 0.000004	0.511348	0.511389
GSP-2	Fusion	3.9E <sup>-05</sup>	11.09	2.5E <sup>-04</sup>	0.511354 ± 0.000003		
GSP-2	Flash HF	6.3E <sup>-05</sup>	3.86	1.1E <sup>-04</sup>	0.511373 ± 0.000005		
AGV-2	Fusion	-2.0E <sup>-05</sup>	7.44	8.6E <sup>-05</sup>	0.512788 ± 0.000004	0.512755	0.512802
AGV-2	Flash HF	1.6E <sup>-05</sup>	2.66	6.1E <sup>-05</sup>	0.512778 ± 0.000007		
G-2	Flash HF	1.5E <sup>-05</sup>	5.66	1.2E <sup>-04</sup>	0.512232 ± 0.000006	0.512215	0.512258

<sup>§</sup> the mean <sup>143</sup>Nd/<sup>144</sup>Nd of JNdi-1 standard is 0.512116 ± 0.000008 (2 S.D; N=7)

**Table 6** Pb and Sr isotope ratios measured by static multi-collection for eleven international SRMs of silicate rocks, digested either by alkaline fusion or by HF dissolution. The net signals measured at  $m/z$  208(Pb) and 88 (Sr) are also indicated, along with the range of values listed by the GeoRem compilation.<sup>5</sup>

Geostandards	Method	<sup>208</sup> Pb	<sup>206</sup> Pb/ <sup>204</sup> Pb <sup>§</sup>	<sup>207</sup> Pb/ <sup>204</sup> Pb <sup>§</sup>	<sup>208</sup> Pb/ <sup>204</sup> Pb <sup>§</sup>	<sup>206</sup> Pb/ <sup>204</sup> Pb		<sup>88</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr <sup>‡</sup>	<sup>87</sup> Sr/ <sup>86</sup> Sr	
		(V)	This study	This study	This study	Min. GEOREM	Max. GEOREM	(V)	This study	Min. GEOREM	Max. GEOREM
JA-1	Fusion	10.7	18.3259 ± 0.0003	15.5654 ± 0.0003	38.3481 ± 0.0009	18.267	18.320	6.9	0.703592 ± 0.000010	0.70350	0.07036
JA-1	Flash HF	8.6	18.3189 ± 0.0006	15.5416 ± 0.0005	38.2675 ± 0.0013			8.1	0.703522 ± 0.000009		
BHVO-2	Fusion	10.3	18.6412 ± 0.0004	15.5517 ± 0.0004	38.2966 ± 0.0011	18.620	18.662	9.3	0.703503 ± 0.000005	0.70349	0.70502
BHVO-2	Flash HF	10.4	18.6400 ± 0.0004	15.5457 ± 0.0004	38.2721 ± 0.0012			6.6	0.703492 ± 0.000006		
BIR-1a	Fusion	11.1	18.8378 ± 0.0004	15.6263 ± 0.0005	38.3613 ± 0.0013	18.674	18.853	3.0	0.703120 ± 0.000013	0.70307	0.70311
BIR-1a	Flash HF	10.8	18.8529 ± 0.0004	15.6456 ± 0.0004	38.4494 ± 0.0011			2.1	0.703108 ± 0.000012		
JB-3	Fusion	9.0	18.2838 ± 0.0003	15.5310 ± 0.0003	38.2226 ± 0.0010	18.287	18.296	8.1	0.703486 ± 0.000008	0.70338	0.70367
JB-3	Flash HF	7.6	18.2868 ± 0.0012	15.5307 ± 0.0010	38.2331 ± 0.0026			9.3	0.703445 ± 0.000008		
BE-N	Fusion	10.9	19.1857 ± 0.0005	15.6001 ± 0.0004	38.9198 ± 0.0011	19.172	19.249	10.5	0.703791 ± 0.000006	0.70328	0.70403
BE-N	Flash HF	10.3	19.1849 ± 0.0004	15.6046 ± 0.0005	38.9110 ± 0.0014			9.5	0.703770 ± 0.000005		
BCR-2	Fusion	5.0	18.7584 ± 0.0008	15.6243 ± 0.0007	38.7300 ± 0.0018	18.740	18.790	9.4	0.705167 ± 0.000008	0.70350	0.70517
BCR-2	Flash HF	6.0	18.7539 ± 0.0007	15.6218 ± 0.0007	38.7123 ± 0.0019			9.8	0.705160 ± 0.000009		
STM-1	Fusion	4.9	19.5158 ± 0.0010	15.6298 ± 0.0009	39.2506 ± 0.0025	19.515	19.519	7.0	0.703818 ± 0.000006	0.70374	0.70382
STM-1	Flash HF	6.0	19.5134 ± 0.0007	15.6295 ± 0.0006	39.1793 ± 0.0018			9.3	0.703792 ± 0.000005		
RGM-1	Fusion	6.1	19.0032 ± 0.0007	15.6321 ± 0.0007	38.7028 ± 0.0018	18.988	19.005	6.8	0.704166 ± 0.000010	0.70419	0.70426
RGM-1	Fusion	6.0	18.9952 ± 0.0007	15.6298 ± 0.0007	38.6480 ± 0.0020			5.8	0.704183 ± 0.000010		
RGM-1	Flash HF	6.3	19.0012 ± 0.0007	15.6293 ± 0.0007	38.6932 ± 0.0018			5.7	0.704208 ± 0.000012		
RGM-1	Flash HF	6.1	18.9965 ± 0.0006	15.6289 ± 0.0006	38.6868 ± 0.0016			4.3	0.704177 ± 0.000015		
GSP-2	Fusion	6.1	17.5966 ± 0.0007	15.5257 ± 0.0007	50.1153 ± 0.0025	17.527	17.615	9.3	0.765136 ± 0.000009	0.76500	0.76522
GSP-2	Flash HF	7.3	17.5728 ± 0.0007	15.5147 ± 0.0007	50.3088 ± 0.0022			8.5	0.765062 ± 0.000008		
AGV-2	Flash HF	6.0	18.8612 ± 0.0007	15.6104 ± 0.0006	38.5662 ± 0.0017	18.851	18.907	10.5	0.703942 ± 0.000006	0.70393	0.70408
G-2	Flash HF	6.2	18.3777 ± 0.0005	15.6314 ± 0.0005	38.8778 ± 0.0015	18.370	18.422	9.9	0.709727 ± 0.000005	0.70830	0.70990

<sup>§</sup> The Pb instrumental mass fractionation was corrected during measurement by doping the Pb solutions with the Tl NBS 997 standard. The NBS 981 standard was measured between every two samples to correct Pb ratios for instrumental drift and the slight difference in mass fractionation between Pb and Tl. Data were normalized to the NBS981 standard using the values of Galer et al.<sup>6</sup> (<sup>206</sup>Pb/<sup>204</sup>Pb = 16.9405, <sup>207</sup>Pb/<sup>204</sup>Pb = 15.4963, <sup>208</sup>Pb/<sup>204</sup>Pb = 36.7219. Repeated analysis of the NBS 981 standard (N = 25) every two samples yielded average intra-session 2SD reproducibility of 119 ppm for both the <sup>206</sup>Pb/<sup>204</sup>Pb and <sup>207</sup>Pb/<sup>204</sup>Pb ratios and 128 ppm for <sup>208</sup>Pb/<sup>204</sup>Pb ratio.

<sup>‡</sup> Strontium isotope compositions were corrected for mass fractionation using <sup>88</sup>Sr/<sup>86</sup>Sr=8.375209. Repeated measurement of the NBS SRM 987 standard (N=12) during the course of the study yielded <sup>87</sup>Sr/<sup>86</sup>Sr=0.710167 ± 25 (2SD). Sample data were renormalized to the accepted value of 0.710245.

**Table 7** Percentage of some trace elements found in fluoride precipitates left after conventional HF dissolution of three basaltic SRMs. The precipitates were isolated by centrifugation and dissolved in HNO<sub>3</sub> with the help of saturated solutions of Al nitrate or boric acid as complexing agents, and analysed by ICP-QMS.

% in precipitate	Ti	Rb	Sr	Ba	Cs	Zr	Nb	Y
<b>BE-N</b>	15	16	27	9	7	19	25	23
<b>BHVO-2</b>	1	49	11	13	82	5	6	14
<b>BHVO-2</b>	5	68	34	20	76	16		46

% in precipitate	La	Ce	Nd	Sm	Eu	Dy	Yb	Lu
<b>BE-N</b>	12	12	11	12	14	17	22	24
<b>BHVO-2</b>	5	5	6	6			12	13
<b>BHVO-2</b>	26	24	29	36		45	48	55

% in precipitate	Hf	Ta	W	Pb	Th	U
<b>BE-N</b>	21	36	1	28	42	4
<b>BHVO-2</b>	6			13	20	3
<b>BHVO-2</b>	18			19	43	7