

Original paper

# Sample preparation and chromatographic separation for Sr, Nd, and Pb isotope analysis in geological, environmental, and archaeological samples

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In countless modern geochemical studies, diverse biological and geologic samples are analyzed for Sr, Nd, and Pb isotopic composition. Such heterogeneity presents challenges for a “one-size-fits-all” approach to sample preparation, necessitating customization of sample preparation and chromatographic separation methods. We present (1) digestion techniques for low-Nd silicates, carbonatites, carbonates, water, plant and wood material, organic soils, aerosols collected via filtration, as well as archaeological samples (alloys, teeth, and bones) (2) a column chromatographic approach for samples with low concentrations (large amounts of a matrix) and (3) method verification via replicate analyses of a wide variety of isotopic standards.

**Keywords:** strontium, neodymium, lead, chemical separation, isotopic analyses, TIMS

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## 1. Introduction

Since the early use of ion-exchange chromatography in isotope geochemistry (Aldrich et al. 1953), well-established methods have undergone near-constant modification to accommodate a broader range of analyzed sample matrices as to take advantage of innovations in analytical instrumentation as well as newly developed separation media and reagents. Moreover, individual laboratories commonly tailor their approaches, adapting their workflow to best accommodate their sample load and available facilities.

The growing diversity of sample matrices that can now be analyzed, smaller sample sizes, or the ability to analyze lower concentrations due to advances in instrumental sensitivity pose additional challenges in sample preparation. For the same project, it is commonly necessary to prepare and analyze different types of samples: bulk rocks, mineral separates, soils, various aquatic solutions, and biologic samples, each requiring a specialized approach and method of preparation. This is balanced against the benefits of improved efficiency, sample throughput, and more straightforward workflows when using only a limited number of standardized laboratory procedures.

Quality of sample preparation and work done in the laboratory play a critical role in the overall quality of the measured data. An integral part of this process is transparent public documentation that guarantees reproduc-

ibility of the analyses done. While it is common practice to append an outline of the analytical procedure with each dataset published, there is seldom enough space to provide all analytical details.

This paper focuses on specialized digestion and preparation methods for various types of samples (rock samples, plants, ores, and alloys) that have been successfully tested for routine use in the Laboratory of Radiogenic Isotopes of the Czech Geological Survey (CGS). Documentation of repeated Sr, Nd, and Pb isotope analyses of various international reference materials performed over several years ensures the reliability of these techniques and reproducibility of results.

## 2. Materials

### 2.1. Reagents

Sample preparation and chemical separations for Sr, Nd, and Pb isotope analyses were performed in the Ultra-trace Laboratory at CGS (lab cleanliness ISO 7, laminar flow box cleanliness ISO 5). Given the low concentrations of elements of interest in many of the samples, reagents can significantly contribute to overall procedural blanks, and therefore the reagents' purity is critical during sample decomposition and element separation. We employ two-stage sub-boiling distillation for HCl and HNO<sub>3</sub> using a dedicated Savillex DST-1000 PFA Acid Purification Sys-

tem. For HF, HClO<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub>, we use commercial ultra-pure reagents (UpA™) by Romil with certified contents of Sr, Nd, and Pb ≤ 1ppt. Ultra-pure water (resistance 18.2 MΩ cm) is used throughout the laboratory procedure, including acid dilution and final labware cleaning (further referred to as MQ water). It is purified using a two-step process consisting of a first reverse-osmosis filtration step (Merck-Millipore Elix system), followed by further purification in a Merck-Millipore Milli-Q system.

## 2.2. Ion exchange chromatography columns and resins

Bio-Rad AG50W X8 (200–400 mesh) cation exchange resin and Eichrom selective resins (50–100 μm Sr resin, TRU resin, and Ln resin) were used as a stationary phase for Sr, Nd, and Pb separation. Bio-Rad AG50W X8 resin is washed in a Teflon PFA bottle using 50% aqua regia and subsequently with 6M HCl alternating with MQ water. These 6M HCl and MQ water steps are repeated 10 times or more, until the color of water above the resin does not change. Eichrom resins are washed in 60 ml vessels in 6 M HCl alternately with MQ water.

*Bio-Rad AG50W X8* is a strong acid cation exchange resin, formed by sulfonic acid functional groups attached to a copolymer lattice. During the ion exchange procedure, the positively charged counterions on the resin are replaced by sample ions with the same charge. The sample ions are then exchanged and can be eluted by an ion with a higher affinity for the resin or a high concentration of an ion with equivalent or lower affinity. For example, Rb<sup>+</sup> ion can be replaced by Sr<sup>2+</sup> with higher affinity to AG50W X8, which in turn can be eluted by strong acid, i.e., H<sup>+</sup> ions with low affinity but high concentration (see Bio-Rad Laboratories manual for further details). Nelson et al. (1964) first used this resin for Be, Ba, and Sr separation.

*Eichrom Sr resin* is used for specific extraction of Sr and Pb in the form of a cyclic polyether complex. It strongly adsorbs Sr in high concentrations of HNO<sub>3</sub>. Apart from other matrix elements, other alkali and alkaline earth elements also show a much lower affinity for the resin than strontium, therefore, it is well suited for the separation of Sr from Ca. Barium retention is higher than Ca; its uptake peaks at about 3M nitric acid and falls off at higher concentrations. Strontium is eluted by dilute HNO<sub>3</sub> (0.05 M). The selection of the absorbent acid and concentration is very important for good Sr separation (Makishima 2015). This resin can also separate lead due to the high retention of Pb across a broad range of nitric acid concentrations.

*Eichrom TRU resin* is a carbamoyl phosphine-based exchanging chromatographic material. The ion exchange procedure could be performed using HNO<sub>3</sub> (e.g., 2M

HNO<sub>3</sub>) or HCl (e.g., 1M HCl). While originally designated to separate transuranic elements, Horwitz et al. (1993) documented the elution behavior of commonly occurring elements on the TRU resin in 2M HNO<sub>3</sub>. Alkali and alkaline earth elements, together with heavy metals (Fe, Cu, Zn, Cr, Ni, Co) and Ba are fully eluted by the first 5 ml of the solution while the rare earth elements (REE) are retained.

*Eichrom Ln resin* is di-(2-ethylhexyl)phosphoric acid (HDEHP) impregnated onto inert support, used for the separation of REE from each other; they are sequentially eluted by HCl from lighter to heavier elements. Increasing acid strength can accelerate the process of elution. Calibration of the columns and acids is thus highly important for the quality of separation.

## 2.3. Vials and vessels

Separation procedures for isotope geochemistry require high-precision and low-blank preparation methods: the cleanness of vials and vessels used for sample preparation is extremely important. Perfluoroalkoxy-Teflon (PFA) labware is commonly used in isotope laboratories, due to its material characteristics. Most of the PFA vials and vessels used for sample preparation are manufactured by Savillex: 500 ml and 1000 ml jars with screw caps for voluminous water sample evaporation, 60 ml vessels for sample digestion, water sample evaporation and membrane filter leaching; 7 ml and 15 ml vials with a rounded interior for sample digestion and Pb collection; 3 ml octagonal body vials with a rounded interior for Sr and Nd collection; 2 ml and 25 ml beakers for aliquots preparation and Sr–REE fraction collection. For high-temperature processing, we employ buttress threaded vessels. For centrifugation, we use polypropylene (PP) centrifuge tubes with screw caps.

## 2.4. Chromatography columns

The various types of chromatography columns used and the carousel holder are presented in Fig. 1.

For Bio-Rad resin separations, we use Poly-Prep chromatography columns (Bio-Rad). Once filled with resin, the columns are washed with 6M HCl after separation and used repeatedly. If not re-used immediately again, the filled columns are stored in 6M HCl – this is critical to prevent the resin from drying out.

For all Eichrom resins, we employ modified 1 ml Pasteur pipets (Fisherbrand, cat. No 1343-9118), prepared after Míková and Denková (2007). The bottom of the tips of the columns is fitted with 30 μm polyethylene frits cut to the appropriate diameter. Unlike Míková and Denková (2007), we do not cover the Ln resin with an upper frit, because the resin tends to swell and shrink depending on

acid strength, which leads to bubble formation that impedes flow through the column. Instead, Ln resin columns are used repeatedly. For cleaning, we introduce several column volumes of 6M HCl, followed by one column volume of 6M HCl containing a drop of HF. The column is then washed with MQ water and prepared for the next separation (or storage) with 0.22 M HCl. Sr and TRU resins are discarded after each sample. Empty columns with frits are washed with MQ water and stored in 6M HCl.

### 3. Analytical procedures

#### 3.1. Sample sizes

The minimum sample size is given by the need to attain sufficient signal size and corresponding precision during Thermal Ionisation Mass Spectrometry analysis (hereafter TIMS; approximately 200 ng for Sr and Nd). In practice, for high-concentration samples, excess amounts of sample are dissolved to ensure homogeneity; the sample is then aliquoted before column chromatography based on previously measured or estimated concentrations of the element(s) of interest. The minimum amount of Pb for isotope analyses by Inductively-Coupled Plasma Mass Spectrometer (MC-ICP-MS) is approximately 100 ppb if using a quartz dual cyclone spray chamber or ~25 ppb if using an Aridus II desolvating nebulizer (Cetac).

#### 3.2. Sample digestion

##### 3.2.1. Silicate rocks

The first digestion step used for most silicate samples is HF–HNO<sub>3</sub>, whereby typically *c.* 100 mg of powdered sample is dissolved in 7–15 ml vials with 3.5 ml of concentrated (conc.) HF and 1.5 ml conc. HNO<sub>3</sub> at 140 °C on a hot plate for at least 24 hours. The solution

evaporates to dryness. The residue is dissolved in a 2 ml mixture of 6M HCl with a few drops of conc. HClO<sub>4</sub> at 140 °C for 12 h. Then it is evaporated at 180 °C, followed by three repeated dry down steps using 0.5 ml of conc. HNO<sub>3</sub>. The final dissolution step is in 4 ml of 6M HCl.

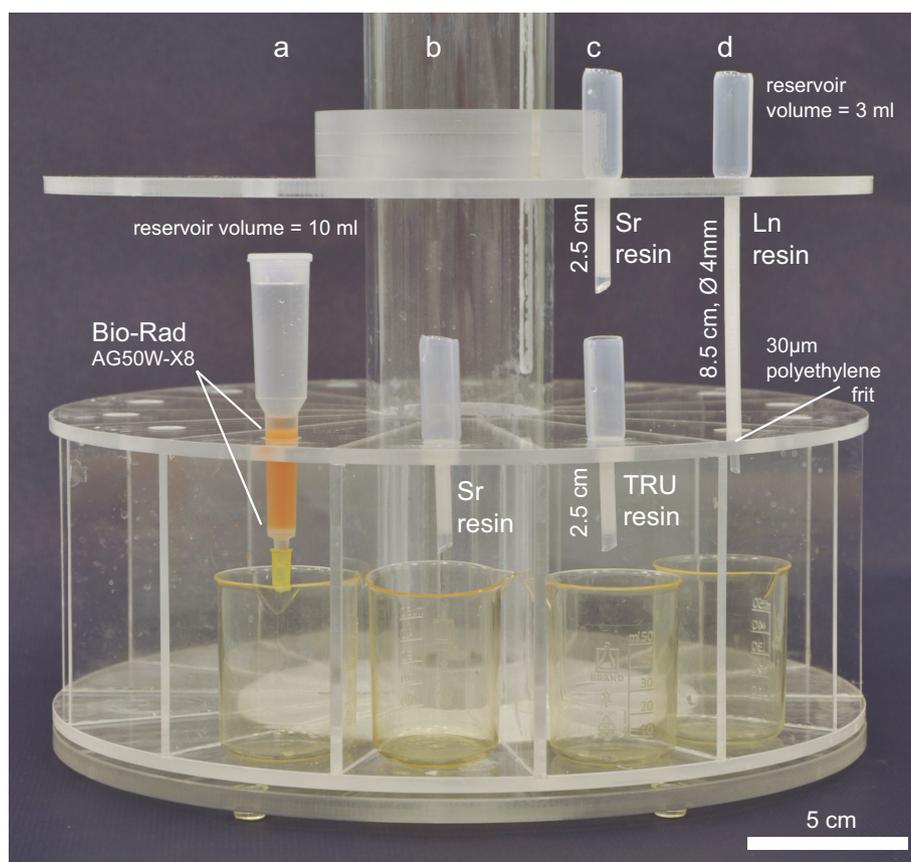
##### 3.2.2. Low-Nd silicate rocks

Neodymium-poor silicate samples (<5 ppm of Nd) require a modified silicate rock digestion protocol adjusted according to correspondingly larger sample weights. We use sample loads up to 1 g and increase the volume of the acid accordingly to maintain dissolution stoichiometry. If undissolved solid-phase residuum persists in the last 6M HCl step, the whole procedure is repeated.

##### 3.2.3. Carbonates

For carbonate samples, digestion using HF–HNO<sub>3</sub> is unsuitable due to the formation of insoluble fluorides. In most cases, digestion in 2.5 M HCl is sufficient.

If silicate impurities are present in the sample – which is often the case of carbonate shell fragments of macroscopic fossil finds – a more careful approach is implemented. Samples, cleaned by mechanical abrasion and rinsed in MQ water, are leached in 4 ml of warm 0.1M



**Fig. 1** Photograph of chromatography separation setups used in this dataset. **a** – Bio-Rad columns used for pre-separation of Sr and Nd and stripping off problematic matrix elements such as Ba, **b** – Sr resin columns for separations only involving Sr and/or Pb, **c** – Tandem separation using both Sr resin and TRU resin columns for obtaining Sr and REE fractions respectively, **d** – Ln resin columns for the separation of Nd from the REE fraction.

acetic acid for 10 min in an ultrasonic bath to dissolve the carbonate phase while avoiding leaching of the silicate phase. Residual silicates are removed by centrifugation.

### 3.2.4. Carbonatites

Carbonatites are distinctly prone to fluoride formation as igneous mixtures of carbonate and silicate matrix. For this reason, we leach separately carbonate part and then dissolve the silicate residuum, following the suggestion of Bizimis et al. (2003).

The powdered sample (~0.5 g) is weighed into beakers (60 ml) and leached in 40 ml of hot 2.5N HCl for 10 min in an ultrasonic bath to dissolve the carbonate phase. Residual silicate phases are removed by centrifugation (10 min, 4 000 rpm), and dissolved in 10 ml of concentrated HF and 5 ml of concentrated HNO<sub>3</sub> at 140 °C for 24 hours. After that, the solution is evaporated to dryness, and the residue is re-dissolved in 10 ml of mixed HClO<sub>4</sub>–6M HCl (1:4 v/v) at 140 °C for 12 hours. Following evaporation at 180 °C, the residue is refluxed three times using 1.5 ml of concentrated HNO<sub>3</sub> and re-dissolved in 4 ml 6M HCl. Finally, the dissolved carbonate fraction evaporates to dryness at 80 °C overnight.

The final solution of the bulk rock sample aliquot could then be recombined from the dissolved carbonate and silicate aliquots, or each fraction could be treated separately.

### 3.2.5. Environmental samples

*Water samples.* Filtered, acidified by HNO<sub>3</sub> water samples are evaporated to dryness. Sample volume depends on the concentration of the element(s) of interest. For Sr isotope analyses, we use 1–2 l of open area precipitation, 1 l of water from catchments or wells, and 10–20 ml of soil water samples. The residue is dissolved in a concentrated H<sub>2</sub>O<sub>2</sub>–HNO<sub>3</sub> (1:9 v/v) mixture, is evaporated to dryness and dissolved in 4 ml of 6 M HCl. It is important to have enough material for at least two repeated isotope analyses in case of measurement failure, as re-sampling is not possible; samples taken in another season will have a different isotopic composition.

*Plant and wood.* To remove dust, plant samples are immersed in de-ionized water and sonicated repeatedly. These are then dried at room temperature and burned in an oven at 800 °C for 16 h. The weighted amount of dried organic samples is approximately 0.4–0.7 g, and the ash weight varies from 0.006 to 0.020 g. The ash is dissolved in 3 ml of concentrated HCl with a few drops of HClO<sub>4</sub> at 140 °C for 48 h; then, the solution was evaporated to dryness. Three repeated dry-down steps are followed using 0.5 ml of concentrated HNO<sub>3</sub>. Finally, the residue is completely dissolved in 4 ml of 6 M HCl.

*Organic soils.* For bulk analyses, organic soil samples are burned in an oven at 800 °C, as with plant samples. This is followed by the silicate rocks digestion with HF–HNO<sub>3</sub>–HClO<sub>4</sub>–HCl attack. To obtain a bio-available soil phase, we use the first step of the BCR-extraction procedure (Sutherland and Tack 2002; Kochergina et al. 2017). Soil samples (1 ± 0.01 g) are leached in 40 ml of 0.11 M acetic acid for 16 h.

*Aerosol-loaded membrane filters.* The plastic ring should be removed from the PTFE filter. Filters with air dust are placed in PFA vessels in an acid mixture (5 ml of conc. HCl and 5 ml of conc. HNO<sub>3</sub>) and left on a hot plate at 80 °C for 48 h. Twice a day, samples are left for 45 minutes in an ultrasonic bath. After cooling, the membrane is removed from the vessel; 2 ml of HF is added to the solution and left at the hotplate at 140 °C for 24 hours. After evaporation, the residue is re-dissolved in 5 ml of 6M HCl with a few drops of HClO<sub>4</sub> at 140 °C for 12 hours. Following evaporation at 180 °C, the residue is refluxed three times using 1.5 ml of concentrated HNO<sub>3</sub> with a few drops of H<sub>2</sub>O<sub>2</sub> and re-dissolved in 4 ml 6M HCl. Finally, the residuum is evaporated to dryness at 80 °C overnight.

### 3.2.6. Archaeological samples

*Alloys.* Samples of alloys used for Pb isotope analyses are dissolved in a mixture of ultrapure (Romil®) HNO<sub>3</sub> and 6M HCl (1:1 v/v) in single-use, pre-cleaned poly vials, and are gently evaporated at 50 °C to dryness. The residue completely dissolves in 4 ml of 6 M HCl.

*Teeth and bones.* Samples with weights of 50 to 150 mg are placed in PFA vials and sonicated in 5 ml of 5% ultrapure acetic acid for 15 min and then rinsed with Milli-Q water. To remove potential secondary minerals and contamination, all samples are left overnight in the 5% ultrapure acetic acid at room temperature, then rinsed three times in Milli-Q water. Samples are dissolved with a mixture of 3.5 ml conc. HF and 1.5 ml of conc. HNO<sub>3</sub> at 140 °C. The solution evaporates to dryness at 60–80 °C, then is treated twice with conc. HNO<sub>3</sub>, in order to dissolve the organic residuum, 3–5 drops of perchloric acid (HClO<sub>4</sub>) are added. Following evaporation at 180 °C, the residue is refluxed three times using 1.5 ml of concentrated HNO<sub>3</sub>. After evaporation, the residue is treated again with a mixture of 0.14 M HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> (9:1). Then, the dry sample is taken up with 1.7 ml of 2M HNO<sub>3</sub> and centrifuged for 10 min at 4000 rpm to check the presence of solid residues.

## 3.3. Ion exchange chromatography

Dissolved samples are stored in 6 M HCl. One day before the first separation step, the solution aliquot is transferred

to a new beaker, evaporated to dryness, and dissolved in 2 ml of 2.5 M HCl. The Bio-Rad columns are prepared for separation: they are removed from storage beakers with 6 M HCl and washed with 15 ml of 6M HCl (3 column reservoir volumes), 5 ml of Milli-Q water and 5 ml of 2.5 M calibrated HCl.

### 3.3.1. Bio-Rad columns

Bio-Rad AG50W-X8 (200–400 mesh) cation exchange resin is used as a pre-separation step before Sr, Nd isolation from silicate rocks, soils, and samples with very low Nd concentrations. We use this step only to separate Sr and REE fractions from the major elements. The Sr fraction is eluted by 2.5 M HCl, whereas REE elution occurs in 6 M HCl (Fig. 2a). For Ba-rich samples, we can use this step to remove Ba via 2.5 M HNO<sub>3</sub> (Fig. 2a). All fractions are collected in Teflon (white) beakers and evaporated to dryness at 60–80 °C overnight. This separation takes less than 4–5 hours. Columns are washed with 20 ml of a mixture of 6M HCl with a few drops of HF and subsequently stored in 6 M HCl for later reuse.

### 3.3.2. Sr and TRU resin columns

Before Sr and Nd separation, the samples are treated with 500 µl of 3M HCl and 0.1 M ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>) (1 : 1) to decrease the amount of Fe<sup>III</sup> and are centrifuged for 10 min at 4000 rpm. After centrifugation, the solution is dried down and the residue dissolved in 2 M HNO<sub>3</sub> (Sr fraction), or 0.22 M HCl (REE fraction for Nd chemistry).

The combination of Bio-Rad and Ln resin columns is sufficient for Nd separation for most silicate samples. However, those with low Nd and correspondingly large sample weights (~1 g) and/or with high Ba amounts, peridotites, carbonatites, high-K calc-alkaline, and ultrapotassic rocks require very precise separation of REE fraction. For these, we use a “long” separation scheme with three sets of columns: Bio-Rad Sr resin (Fig. 2a) – Sr Spec + TRU resin (Fig. 2c) – Ln resin (Fig. 3a).

The Sr and TRU resin steps for REE separation can be done in one day, typically taking less than 6 hours. For Sr, Pb and REE separation, we modified the separation scheme of Míková and Denková (2007) and Pin et al. (2014) (Figs 2b–c, 3). The Sr, Pb, and REE fractions are collected into vials and evaporated to dryness at 60–80 °C overnight.

### 3.3.3. Ln resin columns

To separate Nd from other light REE (e.g., La, Ce, Pr, and Sm) Ln-resin column and 0.22 M HCl are used (Fig.

3a). Unlike Bio-Rad, Sr, and TRU resin columns, the Ln resin columns require individual, precise calibration. Each column has an identification number that is recorded for each processed sample. During Nd isotopic measurement, La, Ce, Pr, and Sm peaks are monitored for quality control. Shifts of the elution curve are corrected by re-calibration of individual columns.

## 3.4. Separation schemes for Sr, Nd, and Pb

### 3.4.1. Sr-only or Sr–Pb separation

For Sr-only or Sr–Pb separation, Sr resin is the best choice (Fig. 3b). However, for Sr-poor samples, where larger sample amounts are used, and/or where Rb concentrations are high, pre-purification via Bio-Rad column is preferred. For the separation of archaeological samples (Cu-alloys, teeth, and bones) and environmental samples (except soils), only Sr resin columns are used (Fig. 3b).

### 3.4.2. Nd separation

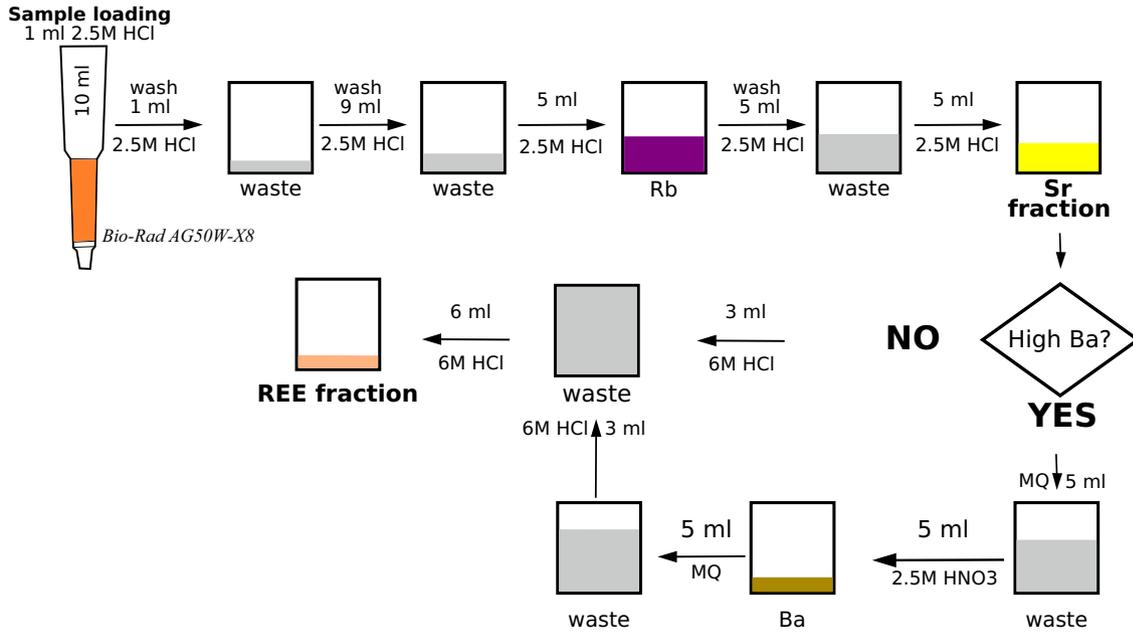
For Nd separation in all samples, we use the Light Rare Earth Elements (LREE) fraction eluted from the Bio-Rad column. For samples not previously identified as potentially problematic for Nd separation, where the diameter of the dry LREE residuum spot is < 1 mm, we use Ln resin columns directly (Figs 2a, 3a). If the size of the dry residuum spot is > 1 mm or we expect problems with separation (e.g., high Ba, low Nd), we first use Sr and TRU resin columns to elute most of the unwanted elements (Figs 2a–c, 3a).

## 3.5. Sr, Nd, and Pb isotopic measurements

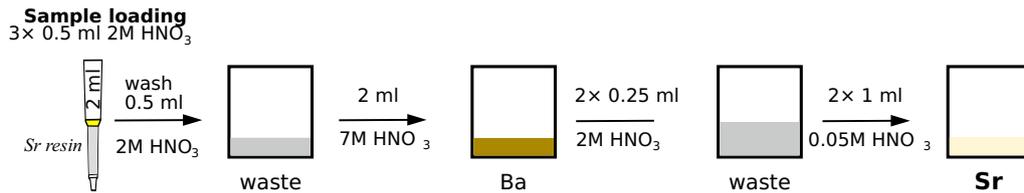
The Sr and Nd isotopic measurements are performed on a Thermo-Fisher Scientific Triton Plus TIMS, whereas procedures for Pb analysis have been developed for the Thermo-Fisher Scientific Neptune MC-ICP-MS, both housed at the Czech Geological Survey. The signals on TIMS generally have much better stability, but ionization yields are low, resulting in less noisy but lower-intensity signals. The MC-ICP-MS signals have higher intensity for a given sample size due to near-complete ionization in the plasma, but come at the cost of much greater plasma source-induced signal instability that provides little-to-no benefit in terms of signal-to-noise ratio over TIMS. Therefore, the TIMS measurements are preferred for isotopic systems where there are two naturally-occurring stable isotopes of the element of interest, meaning that instrumental mass bias can easily be corrected. In the absence of double-spike, isotopic systems with only one non-radiogenic isotope are more readily measured via

## Sr-Nd separation

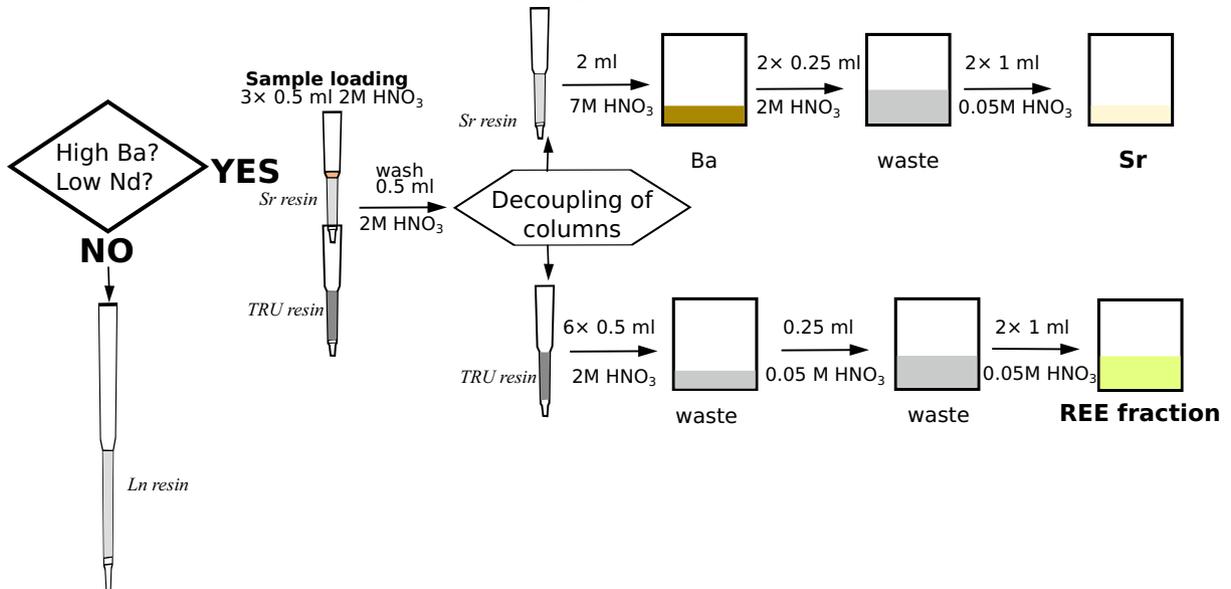
### a. Day 1: Sr- and REE-fraction separation



### b. Day 2a: Sr separation



### c. Day 2b: REE fraction cleaning - "long Nd separation"

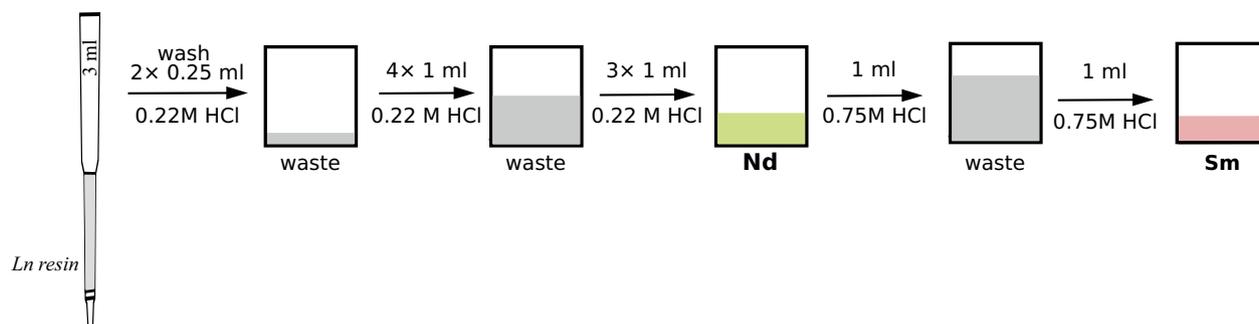


## Sr-Nd-Pb separation

## a. Day 3: Nd separation

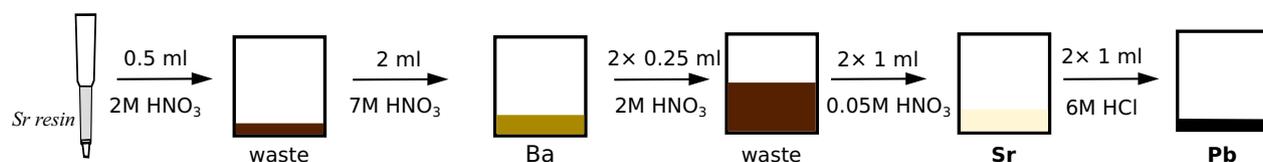
## Sample loading

0.3 ml 0.22M HCl



## b. Sr-Pb separation

## Sample loading

3 x 0.5 ml 2M HNO<sub>3</sub>

**Fig. 3** Strontium, neodymium and lead separation. **a** – Nd separation using Ln resin (modified after Míková and Denková 2007 and Pin et al. 2014); **b** – Sr and Pb separation using Sr resin (modified after Pin et al. 2014).

MC-ICPMS as the instrumental mass bias is less of a factor, approaches steady-state, and can be determined via the addition of a dopant, e.g., Tl, for which two isotopes can be measured.

## 3.5.1. Strontium isotopic measurement

After the Sr resin column separation, the Sr fraction is evaporated to dryness overnight. The residue is treated by addition and subsequent evaporation to dryness of 50  $\mu$ l of 0.05 M H<sub>3</sub>PO<sub>4</sub>, 100  $\mu$ l of 7N HNO<sub>3</sub>, and 100  $\mu$ l of H<sub>2</sub>O<sub>2</sub> before loading onto a single Ta filament. Tantalum filaments were previously degassed under vacuum (Filament Baking Device, Spectromat Massenspektrometer GmbH) and left to oxidize under standard laboratory conditions

for at least one week. Parafilm dams on either side of the heated filament ( $\sim$ 1.1 A) reduce sample spread. The dry Sr fraction is dissolved in 3  $\mu$ l of MQ water and loaded on the centre of the filament between the Parafilm dams and dried slowly (*c.* 3 min at 1.1 A). Then the filament is further heated (1.6–2.0 A) until the phosphoric acid and Parafilm begin to evaporate (white fumes). Temperature is kept at this point for several seconds until the smoke disappears. Then the filament was heated to dull red (2.0–2.5 A) just for a moment and cooled rapidly (based on the manufacturer's recommendation).

Lower Sr amounts can be measured using previously degassed single Re filaments. These need not be oxidized but require the addition of a Ta activator. After separation, Sr residuum is dissolved in 2  $\mu$ l of Ta activator and loaded on the filament.

In case Sr isotopic measurements would be done using MC-ICP-MS, separated dry samples are treated by addition and subsequent evaporation to dryness of 100  $\mu$ l of 7N HNO<sub>3</sub> and 100  $\mu$ l of H<sub>2</sub>O<sub>2</sub> and are dissolved in 2% of HNO<sub>3</sub> at least a few hours before measurement. However, no such analyses are reported in this paper.

↩

**Fig. 2** Strontium and REE separation scheme. **a** – Sr- and REE- fraction separation using Bio-Rad AG50W-X8 resin; **b** – Sr separation using Sr resin (modified after Pin et al. 2014); **c** – “Long” Nd separation procedure. REE-fraction cleaning using Sr- and TRU resins (modified after Míková and Denková 2007 and Pin et al. 2014).

**Tab. 1** Strontium isotopic composition of reference materials measured by TIMS from 3/2017 to 12/2021

Reference material	Type	$^{87}\text{Sr}/^{86}\text{Sr}$	n	2SE	2SD	GeoReM preferred, $\pm 2\sigma$	GeoReM published values <sup>3</sup> , $\pm 2\sigma$
NBS 987 sm		0.710257	109		$\pm 22$		$0.710224 \pm 953$ , $n = 1706^4$
BIR-1	basalt	0.703120	1	$\pm 12$		$0.703116 \pm 52$	
BCR-2	basalt	0.705025	5		$\pm 23$	$0.704920 \pm 1100$	
BHVO-2	basalt	0.703481 0.703490	2	$\pm 13$ $\pm 12$		$0.703478 \pm 68$	
JB-1	basalt	0.704150	1	$\pm 11$			
JB-3	basalt	0.703437	14		$\pm 25$		$0.703449 \pm 145$ , $n = 14$
JSy-1	syenite	0.882981	8		$\pm 2827$		
JA-1	andesite	0.703561	1	$\pm 13$			$0.703577 \pm 50$ , $n = 4$
AGV-2	andesite	0.704000	1	$\pm 07$		$0.703992 \pm 66$	
JG-1a	granodiorite	0.710989	20		$\pm 37$		$0.710979 \pm 37$ , $n = 10$
JG-2	granite	0.759165	1	$\pm 16$			
JG-3	granite	0.705382	1	$\pm 13$			$0.705390 \pm 26$ , $n = 4$
GS-N	granite	1.211946	1	$\pm 01$			
JF-1	feldspar	0.713572	6		$\pm 246$		
COQ-1	carbonatite	0.703293	1	$\pm 09$			
NIST SRM 915b	calcium carbonate	0.707996	1	$\pm 08$			
JLs-1 Sr	limestone	0.707833	4		$\pm 29$		
EN-1 Sr	mollusc shell	0.709171	6		$\pm 29$		
NIST SRM 1515a	apple leaves	0.713997	32		$\pm 10$		
NIST 2709a	San Joaquin Soil	0.708180	22		$\pm 28$		$0.70815$ , $n = 2$
NIST 2709a bio-a Sr <sup>1</sup>	San Joaquin Soil	0.707906	4		$\pm 10$		
NIST SRM 1640a <sup>2</sup>	natural water	0.708866	1	$\pm 26$			

sm = static mode, 2SE = two standard errors, 2SD = two standard deviations ( $\pm 2\sigma$ )

<sup>1</sup> bioavailable Sr, leached sample (Erban-Kochergina et al. 2021, this study)

<sup>2</sup> measured on Re filament with Ta activator

<sup>3</sup> data available at GeoReM on February 10, 2021; GeoReM (Jochum and Nohl 2008), is a Max-Planck-Institute online database of georeference materials (<http://georem.mpch-mainz.gwdg.de>)

<sup>4</sup> TIMS data only

Strontium isotopic ratios are measured in static mode, i.e., abundances of all isotopes are acquired simultaneously by Faraday collectors connected to  $10^{11} \Omega$  amplifiers; the desired  $^{88}\text{Sr}$  beam intensity is  $>3.5$  V (but optimal is  $>5$  V) for 100 ratios and integration time of 8 s. The measured isotopic ratios are corrected for mass-dependent instrumental fractionation using an exponential law and  $^{86}\text{Sr}/^{88}\text{Sr}$  as an internal standard with a presumed natural ratio of 0.1194 (Steiger and Jäger 1977). Isobaric interference of Rb at mass 87 is corrected, assuming the natural value of 0.3857 for  $^{87}\text{Rb}/^{85}\text{Rb}$  (Steiger and Jäger 1977). For well-separated samples the Rb signal is normally negligible,  $<10^{-5}$  V. External reproducibility is estimated from repeated analyses of the NBS 987 isotopic standard [ $^{87}\text{Sr}/^{86}\text{Sr} = 0.710257 \pm 22$  ( $2\sigma$ ,  $n = 109$ ), Tab. 1].

### 3.5.2. Neodymium isotopic measurement

Following Ln resin column chemistry, Nd fractions are evaporated to dryness overnight. The residue is treated by addition and subsequent evaporation to dryness of 100  $\mu\text{l}$  of 7N  $\text{HNO}_3$  before dissolution in 3  $\mu\text{l}$  of 1M  $\text{HNO}_3$  and loading onto the Re double filaments. As for Sr, Parafilm barriers are emplaced on the filament at *c.* 1 A heating,

before the addition of the 2  $\mu\text{l}$  sample load. The sample is allowed to dry on the filament, then briefly ramped to *c.* 1.5 A, which results in boiling off of the Parafilm barriers. The isotopic analyses are performed either in static (see above) or double collector multidynamic mode (i.e., two Faraday collectors backed by  $10^{11}\Omega$  amplifiers are used to measure  $^{146}\text{Nd} - ^{145}\text{Nd}$ ,  $^{145}\text{Nd} - ^{144}\text{Nd}$  and  $^{144}\text{Nd} - ^{143}\text{Nd}$  pairs sequentially) and normalized to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  (Wasserburg et al. 1981). External reproducibility is estimated from repeat analyses of the JNdi-1 isotopic standard [ $^{143}\text{Nd}/^{144}\text{Nd} = 0.512098 \pm 07$  ( $2\sigma$ ,  $n = 60$ ), Tab. 2]. Total procedural blanks are  $<65$  pg Nd, and are considered negligible.

### 3.5.3. Lead isotopic measurement

The MC-ICPMS is run in static low-resolution mode, using Faraday detectors and  $10^{11}\Omega$  amplifiers. Low-Pb concentration samples (air filters, peridotites, some archaeological bronzes) are measured using an Aridus II desolvating nebulizer (Cetac), yielding  $\sim 5$  V at  $^{208}\text{Pb}$  for 25 ppb lead concentration. Otherwise, a quartz dual cyclone spray chamber with micro concentric 50  $\mu\text{l}$  nebulizer is utilized for sample introduction, which provides

**Tab. 2** Neodymium isotopic composition of reference materials measured by TIMS from 3/2017 to 12/2021

Reference material	Type	$^{143}\text{Nd}/^{144}\text{Nd}$	n	2SE	2SD	GeoReM preferred, $\pm 2\sigma$	GeoReM published values <sup>1</sup> , $\pm 2\sigma$
JNdi-1 sm		0.512098	60		$\pm 07$		$0.512108 \pm 219$ , $n = 380^2$
JNdi-1 dm		0.512110	7		$\pm 16$		
BIR-1	basalt	0.513068	1	$\pm 30$		$0.513091 \pm 28$	
BCR-2	basalt	0.512623	5		$\pm 13$	$0.512635 \pm 58$	
BHVO-2	basalt	0.512968	2	$\pm 08$		$0.512979 \pm 28$	
JB-3	basalt	0.512971	2	$\pm 22$			
JB-3	basalt	0.513040	8		$\pm 11$		$0.513055 \pm 28$ , $n = 30$
JSy-1	syenite	0.512395	2	$\pm 07$			
JSy-1	syenite	0.512389	2	$\pm 09$			
JA-1	andesite	0.513087	1	$\pm 09$			$0.513087 \pm 42$ , $n = 9$
AGV-2	andesite	0.512790	2	$\pm 29$		$0.512786 \pm 28$	
AGV-2	andesite	0.512759	2	$\pm 09$			
JG-1a	granodiorite	0.512368	16		$\pm 10$		$0.512323 \pm 279$ , $n = 13$
JG-2	granite	0.512224	2	$\pm 04$			$0.512229 \pm 25$ , $n = 11$
JG-2	granite	0.512222	2	$\pm 09$			
JG-3	granite	0.512617	1	$\pm 05$			$0.512623 \pm 21$ , $n = 11$
GS-N	granite	0.511664	1	$\pm 26$			
RGM-2	rhyolite	0.512783	3		$\pm 12$		$0.512795 \pm 16$ , $n = 4$
JF-1	feldspar	0.512202	1	$\pm 09$			
UB-N	serpentinite	0.512892	1	$\pm 20$			$0.512918 \pm 3$ , $2\sigma$ , $n = 1$
COQ-1	carbonatite	0.512800	5		$\pm 06$		

sm = static mode, dm = multidynamic mode, 2SE = two standard errors, 2SD = two standard deviations

<sup>1</sup> data available at GeoReM site on February 10, 2021<sup>2</sup> TIMS data only**Tab. 3** Lead isotopic composition of reference materials measured by MC-ICP-MS

	Average $\pm 2\sigma$	Pb isotopic ratios							
		206/204	207/204	208/204	208/206		206/204	207/204	208/204
		This study			208/206	207/206	GeoReM database		
NIST SRM 981 (NBS 981)	Average	16.931	15.4909	36.6879	2.1666	0.9146	16.934	15.475	36.6932
$n = 117$	$2\sigma$	0.0505	0.0224	0.124	0.0021	0.0007	0.22	0.85	0.41
BCR-2, basalt	Average	18.7525	15.6257	38.7264			18.754	15.622	38.726
$n = 3$	$2\sigma$	0.003	0.0017	0.0037			0.02	0.01	0.04
JB-3, basalt	Average	18.3	15.542	38.2607			18.297	15.536	38.2475
$n = 6$	$2\sigma$	0.0081	0.0073	0.0193			0.02	0.02	0.03
JG-1a, granodiorite	Average	18.654	15.6302	38.7558			18.601	15.61	38.7216
$n = 14$	$2\sigma$	0.0857	0.0078	0.0264			0.14	0.01	0.05
JG-2, granite	Average	18.633	15.6505	39.0704					
$n = 3$	$2\sigma$	0.0027	0.0018	0.0087					
GS-N, granite	Average	18.357	16.0975	39.5605					
$n = 4$	$2\sigma$	0.0081	0.0083	0.0346					
RGM-2, rhyolite	Average	18.772	15.6135	38.4933			18.955	15.62	38.659
$n = 3$	$2\sigma$	0.0059	0.0054	0.0151			0.005	0.002	0.001
UB-N, serpentinite	Average	18.324	15.6327	38.3598			18.312	15.62	38.322
$n = 3$	$2\sigma$	0.0081	0.0069	0.0287					
COQ-1, carbonatite	Average	22.771	15.7985	39.8817					
$n = 3$	$2\sigma$	0.0118	0.0026	0.0062					
NIST SRM 1515a, apple leaves	Average	18.816	15.7253	38.7211	2.0580	0.8355			
$n = 13$	$2\sigma$	0.0695	0.0762	0.2348	0.0054	0.0012			
NIST SRM 2709a, soil	Average	19.126	15.6838	39.0231	2.0407	0.8198			
$n = 14$	$2\sigma$	0.0144	0.0185	0.0588	0.0016	0.0003			
NIST SRM 1640a, natural water	Average	18.218	15.5922	38.1831	2.0957	0.8555			
$n = 10$	$2\sigma$	0.0671	0.0639	0.1493	0.0011	0.0005			

\*published data from GeoReM database; data for BCR-2 from GeoRem preferred values database

at least 4.5 V at  $^{208}\text{Pb}$  for 100 ppb lead concentration. Samples for Pb isotopic analysis are spiked with NIST SRM 997 thallium reference material and the mass bias is corrected with the generalized power law using  $^{205}\text{Tl}/^{203}\text{Tl} = 2.3871$  (Ridley 2005). Ideally, the signal intensities of  $^{204}\text{Pb}$  and  $^{205}\text{Tl}$  should be equal. The reported data are the uncertainty-weighted mean of at least three replicate measurements and are corrected by a standard-sample bracketing approach relative to NIST declared values for the SRM 981 reference material (Košler 2008). Potential  $^{204}\text{Hg}$  isobaric interference on  $^{204}\text{Pb}$  is monitored at mass 202 ( $^{202}\text{Hg}$ ) and corrected by assuming natural Hg isotope ratios ( $^{202}\text{Hg}/^{204}\text{Hg} = 4.35$ ) (Zadnik et al. 1989).

External reproducibility of Pb isotopic measurements is given by repeat analyses of NIST SRM 981 isotopic standard ( $^{206}\text{Pb}/^{204}\text{Pb} = 16.931 \pm 50$ ;  $^{207}\text{Pb}/^{204}\text{Pb} = 15.490 \pm 22$ ;  $^{208}\text{Pb}/^{204}\text{Pb} = 36.688 \pm 124$ ;  $^{208}\text{Pb}/^{206}\text{Pb} = 2.166 \pm 2$ ;  $^{207}\text{Pb}/^{206}\text{Pb} = 0.9146 \pm 7$ ;  $n = 117$ , Tab. 3). Total procedural blanks are  $< 30$  pg Pb, and are considered negligible.

## 4. Results

The performance and accuracy of our new procedure have been tested by repeated analyses of a variety of sample matrices represented by international reference materials NBS 987, JNdi-1, NBS 981, AGV-2, BCR-2, BIR-1, BHVO-2, COQ-1, EN-1, GS-N, JA-1, JB-1, JB-3, JG-1a, JG-2, JG-3, JF-1, JSy-1, JLS-1, NIST SRM 1515a, NIST SRM 2709a, NIST SRM 1640a, RGM-2, UB-N. The Sr, Nd, and Pb isotopic data for these standards are presented in Tabs 1–3. All analyses were performed on different powder aliquots. The results have been compared with reference values from GeoReM, a Max-Planck-Institute online database (Jochum and Nohl 2008). In the case of BIR-1, BCR-2, BHVO-2, and AGV-2 reference materials, the GeoReM preferred values were chosen for comparison. In other cases, our measured data were compared with the GeoReM published values database. The COQ-1 Sr, Nd, and Pb isotopic ratios in GeoRem, obtained by Ackerman et al. (2017) in our laboratory, were excluded from the comparison. Unlike Ackerman et al. (2017), our new Sr and Nd analyses were performed using TIMS and are in good agreement with MC-ICP-MS data from our lab and MC-ICP-MS Sr isotopic ratios reported by Bellefroid et al. (2018).

For reference materials where the number of measurements is greater than 2, the two standard deviations ( $2\text{SD} = 2\sigma$ ) were calculated (Tab. 1); otherwise (for  $n \leq 2$ ), all measured value(s) are given. The  $^{87}\text{Sr}/^{86}\text{Sr}$  of rock standards are in good agreement with published data: basalt JB-3 = 0.7034 ( $n = 14$ ), granodiorite JG-1a = 0.7111 ( $n = 20$ ). The most radiogenic sample is granite GS-N with  $^{87}\text{Sr}/^{86}\text{Sr} = 1.212$ . The Apple leaf SRM 1515a reference material shows a homogeneous  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of

0.7140 ( $n = 32$ ). Soil sample SRM 2709a has more radiogenic Sr ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7082$ ;  $n = 22$ ), than its leachate (0.7079;  $n = 4$ ). The sample of natural water SRM1640a containing very low amounts of Sr was measured on Re filaments and yielded  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.7089.

The most-measured reference material for Nd isotopic composition is granodiorite JG-1a with  $^{143}\text{Nd}/^{144}\text{Nd} = 0.5124$  ( $n = 16$ ) (Tab. 2). Basalt standard JB-3 shows  $^{143}\text{Nd}/^{144}\text{Nd} = 0.5130$  ( $n = 8$ ), basalt BCR-2 has  $^{143}\text{Nd}/^{144}\text{Nd} = 0.5126$  ( $n = 5$ ), carbonatite sample COQ-1 has  $^{143}\text{Nd}/^{144}\text{Nd} = 0.5128$  ( $n = 5$ ). The serpentinite standard UB-N with the lowest Nd concentration yielded a single  $^{143}\text{Nd}/^{144}\text{Nd}$  value of 0.51289.

The most-measured reference material for Pb isotopic composition is JG-1a ( $n = 14$ ) with  $^{206}\text{Pb}/^{204}\text{Pb} = 18.654$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.630$ ,  $^{208}\text{Pb}/^{204}\text{Pb} = 38.756$  (Tab.3). The apple leaves environmental standard SRM 1515a ( $n = 13$ ) shows  $^{206}\text{Pb}/^{204}\text{Pb} = 18.816$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.725$ ,  $^{208}\text{Pb}/^{204}\text{Pb} = 38.721$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.058$ ,  $^{207}\text{Pb}/^{206}\text{Pb} = 0.836$ ; soil SRM 2709a ( $n = 14$ ) show  $^{206}\text{Pb}/^{204}\text{Pb} = 19.126$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.684$ ,  $^{208}\text{Pb}/^{204}\text{Pb} = 39.023$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.041$ ,  $^{207}\text{Pb}/^{206}\text{Pb} = 0.820$  and water SRM 1640a ( $n = 10$ ) show  $^{206}\text{Pb}/^{204}\text{Pb} = 18.816$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.725$ ,  $^{208}\text{Pb}/^{204}\text{Pb} = 38.721$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.058$ ,  $^{207}\text{Pb}/^{206}\text{Pb} = 0.836$ .

## 5. Discussion

The modern isotope geochemistry laboratory must cope with (1) increasing diversity of sample matrices, (2) large sample sets requiring high throughput, and (3) processing smaller samples and those with lower concentrations of the elements of interest, relative to work done in the past. There are several publications about sample preparation and measurement procedures, among them a comprehensive work by Makishima (2015), describing silicate digestion, separation, and measurement methods for almost all elements of the periodic table. Several publications (Pin et al. 1994; Le Fèvre and Pin 2005; Pin and Rodriguez 2014; Pin et al. 2014) were devoted to the method of separation of Sr, Pb, and Nd isotopes. Rapid simultaneous Sr, Nd, and Pb separation is highly effective if processing a small number of samples with a similar composition. Pin et al. (2014) suggested the separation scheme of Sr, Nd, and Pb isotopes by extraction chromatography without intervening evaporations. However, in our opinion, the tandem column separation method is best suited for small sample sets typical of graduate student theses.

### 5.1. Examples of the described separation methods in use

The methods described here allow simultaneous processing of a wide spectrum of sample types, which has been

tested on large environmental sample suites, consisting of rocks, soils, soil water, precipitation, wood, and leaves (Novák et al. 2020a, b; Erban Kochergina et al. 2021). Aside from representing a broad gamut of sample matrices, the presented standard data span a wide range of isotopic compositions, from non-radiogenic mantle-like signatures up to old, crustal, and extremely radiogenic values, e.g., JSy-1 and GS-N.

Non-element-specific cation exchange resins had historically been the method of choice for separating Sr, Nd, and Pb (Aldrich et al. 1953; Hedge 1966; Richard et al. 1976) prior to the development of specialized resins in the mid-1990s (Pin et al. 1994). However, due to the necessarily small volumes of specialized resin used, they are less effective when processing large sample weights needed for low-concentration work. Using Bio-Rad columns for pre-separation solves the problem of samples with low Nd content. Large sample loads were previously divided among several Sr resin columns, which decreased throughput and increased costs due to the high price of Sr resin. BioRad resin helps effectively separate the REE fraction from the light elements and increases the efficacy of the Sr – TRU – Ln resin separation procedures, and was employed, for instance, for Nd separation in on REE-poor (0.4 to 1.9 ppm) peridotite samples from the Vosges, France (Hora et al. 2021).

Carbonatite samples are complicated due to the non-traditional digestion method, low Nd, and high amount of Ba. The carbonate fraction precludes the use of classic silicate digestion using HF because Nd accumulates in insoluble fluorides. Leaching in 2.5 M HCl helps to separate the carbonate and silicate parts of the sample preventing this problem. This method was used in the study of carbonatites from Tamil Nadu, India (Ackerman et al. 2017) and Roztoky, Czech Republic (Rapprich et al. 2017). Pre-separation using BioRad columns solved two problems: (i) stripping most of the Ba, which was completely removed on Sr resin column, and (ii) separated the REE fraction from the other elements.

The three-column separation procedure using BioRad Sr and Ln resin columns was successfully employed in the isotopic study of plutonic and volcanic rocks (Walther et al. 2016; Mysliveček et al. 2018; Janoušek et al. 2020; Casas-García et al. 2021; Mach et al. 2021; Janoušek et al. 2022) as well as loess samples (Warszewski et al. 2021).

A mixture of HCl and HNO<sub>3</sub> acids is sufficient to dissolve archaeological alloys. In some cases, the reaction can be quite turbulent, necessitating incremental addition of acids. HF is never used to avoid dissolving silicate contamination that may be present in the sample, and centrifugation is necessary following HCl–HNO<sub>3</sub> digestion and before sample separation. The quality of Pb separation is very important for archaeological alloys

due to low Pb concentrations and very small samples (Kmošek et al. 2018, 2020; Odler et al. 2021). Most are very rare and irreplaceable museum samples. In cases of low Pb concentrations where there is a large amount of matrix, it is advantageous to repeat the separation.

## 5.2. Advantages and disadvantages of our method

Pre-separation and carrying out Sr and Nd separations on different days also have disadvantages. Two additional beakers are used for pre-separated Sr- and REE-fractions, increasing potential blank contribution, as well as acid and time used for beaker cleaning. In addition, drying of pre-samples takes up additional space on hotplates. Therefore, adequate planning is essential. That said, splitting the separation among several steps (days) allows for workflow optimization, evaluating the previous step's quality, and making operational changes to the separation procedure.

## 6. Conclusion

The methods described here represent an effective way of handling samples from a wide variety of environmental and geologic samples for isotopic analysis. The specificity of the digestion methods accommodates the challenges presented in diverse sample matrices and ensures complete dissolution of the sample before column chromatography. Pre-separation using cation exchange columns addresses the issue presented by large sample sizes associated with samples where concentrations of Nd are low. The methods presented here are verified using a large variety of isotopic standards.

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