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Rapid, simultaneous separation of Sr, Pb, and Nd by extraction chromatography prior to isotope ratios determination by TIMS and MC-ICP-MS.

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Abstract

A straightforward separation scheme is described for the separation of Sr, Pb, and Nd from silicate rocks. It allows the concomitant isolation, without any intervening evaporation, of these three elements of great interest in radiogenic isotope geology and cosmochemistry. Following digestion with HF-HNO_3, the sample residue is dissolved in 1M HNO_3. After addition of ascorbic acid to reduce Fe(III) to Fe(II), this solution is passed through two tandem columns containing 250 µL of Sr Spec and TRU Spec extraction chromatography resins, respectively. The upper Sr Spec column extracts Sr and Pb, while the lower TRU Spec column extracts the LREE. Sr and Pb are back-extracted with 0.05M HNO_3 and 6M HCl, respectively. The LREE are eluted directly onto a longer column containing 300 mg of the HDEHP-based EXC material Ln Spec, to obtain, through sequential elution with 0.25M HCl, a Nd fraction free of any Sm contribution. The whole procedure is achieved within a single working day. The Sr and Nd fractions separated in this way are ready for isotope ratio measurements by TIMS (Sr, Nd) or MC-ICP-MS (Nd). The Pb fraction is converted to the nitrate form before isotopic analysis by MC-ICP-MS. The potential of this method is exemplified by analysis of different powder aliquots of several iron-rich, international standard rocks of basaltic composition.

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1. Introduction

Sr, Pb, and Nd are the three basic elements of the radiogenic isotope geochemist's and cosmochemist's "tool box", and their isotope compositions are widely used for tracing petrogenetic processes and for providing chronological information. This is because the abundances of ^{87}Sr, ^{206}Pb, ^{207}Pb, ^{208}Pb, and ^{143}Nd vary in natural samples as a consequence of the long-lived radioactive decay of their respective parent isotopes ^{87}Rb, ^{238}U, ^{235}U, ^{232}Th, and ^{147}Sm. As a result, ^{87}Sr/^{86}Sr, $^{206, 207, 208}$Pb/^{204}Pb, and ^{143}Nd/^{144}Nd ratios in a geological sample reflect the time-integrated parent-daughter elemental ratios of its source. Therefore, these ratios offer a set of geological chronometers and a unique way to study ancient fractionation processes that occurred between trace elements spanning a large range of chemical behaviour during the evolution of the Earth and extra-terrestrial objects. In many circumstances, the measurement of these isotope ratios cannot be made with an adequate degree of precision by using *in situ* analytical techniques such as Secondary Ion Mass Spectrometry (SIMS) or Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS), for simple counting statistics reasons because the elements of interest occur at trace level in most rocks or minerals. As a result, a crucial step of the whole analytical procedure involves the pre-concentration of these trace elements and matrix elements removal from a bulk digested sample, prior to isotope ratio determination by high-precision mass spectrometric methods: Thermal Ionization Mass Spectrometry (TIMS) or Multiple Collection-ICP-Mass Spectrometry (MC-ICP-MS).

For this reason, development of integrated separation schemes enabling the analyst to obtain sufficiently pure fractions of the three elements Sr, Pb, and Nd from single sample dissolutions in a straightforward manner is important. This is so not only to save time and effort, but also to measure all these three radiogenic isotope systems from the same sample aliquot, an interesting possibility when the samples are scarce, or potentially heterogeneous at a given sampling scale. Strontium and a REE fraction can be isolated from most matrix elements by standard cation-exchange chromatography in hydrochloric and/or nitric acid medium (at the cost of using relatively large columns and eluting acid volumes). In contrast, Pb has distribution coefficients with cation-exchange resins which are almost similar to those of major elements (Ca, Fe, Al), and requires a separate treatment. Anion-exchange in hydrochloric acid medium offers a great selectivity, but the low maximum value of the distribution coefficient of Pb (D ~27 in 1.5M HCl [1]) allows only limited amounts of solution to be passed through a column before Pb appears in the effluent [2]. Based on the observation that lead is absorbed by anion-exchange resins from bromide much more strongly than from chloride solution (D max ~500 in *ca.* 0.5M HBr [3]), Strelow and von Toerien [4] developed a method for the isolation of traces of lead from large amounts of other elements. Following this pioneering work, most subsequent studies of lead isotopes in geological materials have relied on this “bromide method” (*e.g.,* references [5-6] and a wealth of subsequent geochemical papers). Therefore, if Sr, Pb and Nd are to be separated from a single solution, at least one evaporation step and conversion of the sample salts to the appropriate chemical form is required. Moreover, it usually proves difficult to bring geological sample into a clear solution by using dilute HBr instead of HCl or HNO_3. A relatively large solid residue is often left behind, which then needs to be repeatedly leached with HBr in an attempt to recover as much Pb as possible, although nearly quantitative yields are seldom achieved.

Extraction chromatography (EXC) offers an attractive alternative, by virtue of its selectivity, inherently much better than that of cation-exchange, allowing a great degree of miniaturization, and the use of efficient acids such as HCl and HNO_3 for sample dissolution prior to column work. For these reasons, a wealth of geochemical methods based on this technique has been developed during the last decades.[7]

In this work, we further elaborate on this EXC approach to set up a straightforward separation scheme, based on the use of three small columns used in tandem configuration, enabling us to separate from the same starting solution Sr and Pb, and then the LREE and Nd, without any intervening evaporation step. The analytes separated in this way are obtained with good chemical yields and procedural blanks, and in a sufficiently pure form for high-precision isotope ratio measurements by TIMS (Sr, Nd) and MC-ICP-MS (Pb, Nd). The potential of this method is demonstrated by analyses of three independent sample powder aliquots, of several international standard rocks of basaltic composition.

2. Experimental

2.1. Chemicals and chromatographic materials

Water with a resistivity of 18.2 MOhm cm, prepared by several steps of ion-exchange followed by final purification using a Milli-Q (Millipore, St Quentin, France) or a PURELAB ClassicUV (Elga LabWater, Antony, France) apparatus, was used throughout. Nitric and hydrochloric acids were purified by subboiling distillation in silica glass stills (Quartex, Paris), or in PFA DST-100 acid purification systems (Savillex, Eden Prairie, MN, USA). Analytical grade HF was purified by subboiling distillation in FEP bottles. Orthoboric acid (Merck, Suprapur) and ascorbic acid (obtained as powders from Merck or Prolabo, Analytical grade) were used as received. The three extraction chromatography (EXC) materials used in this work, and referred to as Sr resin (previously known as Sr Spec), TRU resin (previously TRU Spec), and Ln resin, respectively, were obtained from Eichrom Europe (now Triskem international, Bruz, France). In all cases, the 50-100 µm fine-grained resin was used.

2.2. Instrumentation

All chemical handlings were made under Class 10 vertical laminar flow hoods in a laboratory supplied with an overpressure of filtered air. Vessels made in PFA (Savillex, Eden Prairie, MN, USA) were used for sample dissolution, and for collecting separated Pb fractions. Strontium and Neodymium fractions were collected in pre-cleaned disposable polystyrene vials with a conical bottom. Small columns (ca. 4 mm i.d.) made of silica glass, and fitted with polyethylene frits (*ca.* 25 µm porosity, *ca.* 2 mm thick), were used throughout. The two first columns, filled with 83 mg (corresponding to *ca.* 250 µL of resin bed) of Sr Spec and TRU Spec extracting chromatography materials, respectively, were short (ca. 2 cm), while the third column, used to isolate a Nd fraction from the REE previously separated from matrix elements, was longer (ca. 6 cm) and filled with 300 mg of the Ln resin.

A quadrupole ICP-MS (model PQII+, VG Elemental, Winsford, UK) was used in the semi-quantitative mode for setting up the method. For blank measurements, a switchable additional pumping of the interface (so-called S-Option) was used in order to achieve a higher sensitivity. At a subsequent stage of this work, another ICP-QMS (Agilent 7500, Agilent Technologies, Massy, France) was used for blank measurements and for determining the amount of Pb recovered following column separation. A Triton TI (Thermo Scientific, Bremen, Germany) thermal ionisation mass spectrometer (GIS Laboratory, Nîmes University) was used, in the static multicollection mode, for isotope ratio measurements of Sr and Nd. Lead isotope analyses were made in Clermont-Ferrand by using a Neptune Plus (Thermo Scientific, Bremen, Germany) multi-collector ICP-MS.

2.3. Chemical Procedure

2.3.1. Sample digestion：About 100 mg to 250 mg (depending on the amount of Sr, Pb, and Nd present in the sample) of powder is weighted, wetted with 1 mL of 7M HNO_3, then dissolved with 1 to 2 mL of 29M HF at 110°C. The solution is evaporated to dryness, then, treated several times with a mixture of 6M HCl and conc. HNO_3. After evaporation the residue is treated again with conc. HNO_3, in order to convert the sample to nitrates. Then, the solid residue is taken up with 2 mL of 1M HNO_3, and centrifuged, in order to check for the presence of solid residues, especially sparingly soluble fluorides. Any whitish gelatinous compound observed at that stage is treated with a few hundred µL of a 1M HNO_3 solution saturated in boric acid. This generally ensures a nearly complete dissolution, and the resulting solution is combined with the bulk sample solution. Finally, 100 to 200 mg (depending on the quantity of iron in the sample) of ascorbic acid ($C_6H_8O_6$) is added as a reducing agent to decrease the amount of Fe(III). After allowing *ca.* 10 minutes for the dissolution and reducing action of ascorbic acid, the initially colourless sample solution becomes pale yellow and is ready for the column work.

2.3.2. Separation of the analytes: The sample solution is loaded in several small aliquots onto the Sr and TRU columns arranged in tandem (Fig. 1a). Each column is previously preconditioned with 0.1 mL of 1M HNO_3 containing 50 mg mL^{-1} of ascorbic acid (that is, 0.28 M). After complete draining of the sample solution, the two superposed columns are rinsed twice with 0.5 mL of the same mixed acid solution. Following this extraction step, achieving the sorption of Sr plus Pb onto the Sr resin, and the LREE onto the TRU resin, respectively, the two columns are decoupled and further processed separately (Fig. 1b):

(a) The Sr column is first washed with 2 x 1 mL of 7M HNO_3 to get rid of unwanted elements (especially Ba which is appreciably extracted by the Sr resin from nitric acid medium), then with 0.5 mL of 2M HNO_3. The Sr fraction is then collected with 2 x 1 mL of 0.05 M HNO_3. Finally, 2 x 1 mL of 3M HCl are passed through the column, before collection of the Pb fraction with 2 x 1 mL of 6M HCl.

(b) The decoupled TRU column is washed with 0.25 mL of 1M HNO_3 containing 50 mg mL^{-1} of ascorbic acid. Then, four fractions of 0.5 mL of 1M HNO_3 are passed through the column to ensure the removal of all unwanted elements. At this stage, only the LREE (+

Th and U) are still retained on the TRU resin. In preparation to the next elution step, 100 µL of HNO_3 0.05M, followed by 100 µL HCl 0.05M, are passed through the column.

(c) The Ln column is then placed beneath the tip of the TRU column in order to transfer directly the LREE from the TRU to the Ln column (Fig. 1c). This is done by using 3 x 0.5 mL of 0.05 M HCl, a medium which achieves the back-extraction (stripping) of the LREE from the TRU resin, while affording the sorption of these elements by the HDEHP-based Ln resin. The Ln column is then rinsed twice with 0.1 mL of 0.05M HCl. Then, the lanthanides are eluted sequentially by using 0.25M HCl, with 2.7 mL (containing La, Ce and part of Pr) discarded, before collection of a Nd fraction (still containing some Ce and much Pr, but entirely free of Sm) with 2 mL of 0.25 M HCl (Fig. 1d). If required, a Sm fraction can be obtained with a further addition of 1.5 mL of 0.75M HCl. The separation protocol is outlined in Table 1.

The Sr and Nd fractions, stripped from the columns with very dilute acids, are collected into single use, pre-cleaned (with cold, dilute HCl) polystyrene vials with a conical bottom, gently evaporated to dryness (at *ca.* 55°C), and ready for mass spectrometric measurements. The Pb fraction, back-extracted (stripped) with strong HCl, is collected into PFA vials, and evaporated to dryness. Before isotope ratio measurements, it is further treated with conc. HNO_3, in order to oxidize any organic agent leached from the Sr Spec EXC material, which might hamper Pb recovery when taking up the sample with dilute nitric acid for MC-ICP-MS measurements. The amount of Pb recovered is determined at this stage by analysing an aliquot of the solution by ICP-QMS, thereby permitting to add the Tl internal standard solution in an appropriate proportion [11-12], and achieve an optimal final dilution of Pb with 0.05M HNO_3 prior to isotope ratio measurements by MC-ICP-MS.

2.4. Mass spectrometry

2.4.1. Strontium: The isotope analysis is made with a Triton thermal ionization mass spectrometer operated in static mode, by using a relay matrix (the so-called “virtual amplifier”) connecting the various Faraday cups to different amplifiers aiming to cancel any gain difference left after the initial, pre-measurement gain cross calibration. The separated Sr is dissolved with dilute nitric acid, then, an aliquot containing a few hundreds of ng is loaded onto a 0.76 mm wide, 25 µm thick W filament (H. Cross Company, Moonachie, NJ, USA). Prior to sample loading in a small (ca. 0.2 µL) drop of 3M H_3PO_4, the filament is outgassed, then covered in its central part with a solution of “Ta activator” [8], and briefly heated *in vacuo* to eliminate the volatile components and produce a thin, homogeneous layer of Ta oxide [9]. ^{88}Sr ion beams obtained at about 1450°C ranged from 7 to 16 10^{-11} A. The time dependent fractionation of ^{87}Sr/^{86}Sr ratios during the analyses was corrected by normalisation to the constant ratio ^{86}Sr/^{88}Sr = 0.1194, using an exponential law. It is believed that, as far as Sr isotope measurements are concerned, MC-ICP-MS does not offer any distinct advantage compared to TIMS in terms of sample usage, precision and accuracy. For this reason, we did not analyse our samples by this technique.

2.4.2. Neodymium: Neodymium was measured as the metal species by static multi-collection TIMS (Triton TI), by using 300 to 500 ng of Nd dissolved in dilute HCl and loaded in a droplet of 1M H_3PO_4 on the outgassed evaporation filament of a double Re filament assembly (99.98% grade, 0.76 mm width, 25 µm thickness, obtained from the H. Cross Company, Moonachie, NJ, USA). Ion beams (^{144}Nd$^+$) ranging from 4 to 15 10^{-11} A (but occasionally as high as 25 10^{-11} A) were achieved, depending on the amount of Nd loaded and geometry of the double filament assembly, which was not tightly controlled at the time of these analyses.

The ^{143}Nd/^{144}Nd and ^{145}Nd/^{144}Nd ratios were corrected for time-dependent mass fractionation by normalisation to ^{146}Nd/^{144}Nd=0.7219, with an exponential law.

Aliquots of the same samples (*ca.* 200 ng each) were also analysed with a MC-ICP-MS (Neptune Plus). The collector array was set as reported in Table 2. A PFA concentric nebuliser (Elemental Scientific Inc., Omaha, NE) operated at an uptake flow rate of ~100 µL min^{-1} was used, in combination with a cyclonic spray chamber at room temperature. The Nd ion beam obtained under these conditions was typically ~ 6.5 10^{-10}A/ppm (corresponding to a signal of 65 V/ppm with the 10^{11} Ω resistors used in this work).

2.4.3 Lead: Isotope analyses were made with a Neptune Plus MC-ICP-MS, in static mode, by using the cup configuration listed in Table 2. Since Pb has only one isotope free of radiogenic component (^{204}Pb), no constant isotope ratio is available for internal normalization, as is conveniently the case for Sr and Nd. This is a basic limitation to the precision and accuracy achievable by TIMS. But, as first shown by Longerich et al. [10] with a quadrupole-based instrument, ICP-MS offers the unique possibility to correct for mass dependent instrumental bias by using the constant ratio of another element of neighbouring mass, added as an isotopic internal standard: Tl in the case of Pb isotope ratio determinations**.** Following Walder et al. [11], this simple strategy has become the standard method to correct for mass bias high precision isotope ratio measured by using double focusing MC-ICP-MS, although the method is not free of drawbacks linked - among other potential pitfalls - to the fairly complex solution chemistry of thallium.[12, 13] Accordingly, the samples are spiked with a solution of the NIST SRM 997 Tl standard [with a recommended ^{203}Tl/^{205}Tl ratio of 2.3871 +/- 0.0010 [14]] in order to obtain a final solution containing ~100 ppb of Pb and 20 ppb of Tl. Because of the relatively large amount of Pb available, a conventional PFA concentric nebuliser (with an uptake rate of ~100 µL min^{-1}), coupled to a cyclonic spray chamber operated at room temperature, was used. Total ion beams of 7.6 10^{-11} A for 100 ppb Pb solutions (*i.e.,* a sensitivity of 76 V/ppm) were achieved under these conditions. Raw intensities measured at mass 204 were corrected for ^{204}Hg (from Ar gas supply) spectral overlap based on the intensity of ^{202}Hg and a ^{202}Hg/^{204}Hg ratio of 4.36.[15]

The NIST SRM 981 common lead standard, measured every two samples, did not reveal any significant instrumental drift during the typically 12-hour long sessions. The reproducibility (or external precision) estimated from the replicate measurements of the SRM 981 (N=30, 2 x 12 hours sessions) standard was 73, 71, 94, 27 and 17 ppm (2 RSD x 10^{6}) for the ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb, ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb ratios, respectively. After correcting for instrumental mass bias using the Tl-normalisation procedure) and an exponential function, the data were re-normalized to the values recommended by Galer and Abouchami [16] for the NIST SRM 981 standard, namely: ^{206}Pb/^{204}Pb=16.9405 +/- 0.0015; ^{207}Pb/^{204}Pb=15.4963 +/- 0.0016, and ^{208}Pb/^{204}Pb=36.7219 +/- 0.0044. These values were determined with a triple spike technique with normalisation to a value of ^{208}Pb/^{206}Pb=1.00016 for the NIST “Equal Atom” lead standard, SRM 982.

3. Results and discussion

3.1. Chemical yields

3.1.1. Strontium: Based on fundamental data published by Horwitz et al. [17] and earlier studies, applying Sr Spec to the extraction of Sr from geological samples [18, 19], it is known that the extraction efficiency of Sr is better in relatively strong (3-5M) nitric acid medium and that the separation of the Ba-Sr pair is optimal in 7 M HNO_3. It is important to separate Sr from Ba because this easily ionisable element might compete with Sr on the TIMS filament and cause serious suppression of the Sr signal. However, while quite appropriate when using Sr Spec alone, loading the sample in 3M HNO_3 [18] is not permitted if a TRU column is to be used in tandem with the Sr column in view of an isolation of LREE. This is because Fe and Ti, two major elements in silicate rocks (particularly in mafic samples) are extracted significantly, leading to a large decrease (50 % or even more) of chemical yields of the LREE. Sample loading in 2M HNO_3 [19] may achieve an acceptable trade-off only for those samples which contain limited amounts of iron, such as felsic silicate rocks. When processing Fe-Ti rich rocks, an earlier approach removed these two elements prior to TRU Spec chemistry by using a short cation-exchange column in HCl medium [20]; but this involves an evaporation step prior to the TRU Spec resin separation step. Misawa et al. [21] described a miniaturized separation scheme for the REE and Sr based on extraction chromatography using the RE Spec and Sr Spec resins; but two stages with an intervening evaporation to dryness were necessary to isolate the REE from matrix elements. Likewise, the procedure of Makishima et al. [22] separates Sr and Pb on a first column of Sr Spec resin, but a relatively convoluted scheme involving a cation exchange column and a drying and redissolution step was used prior to the final separation of Nd on a Ln Spec column.

In this work, the iron-titanium interference on the extraction of the LREE by the TRU Spec resin was overcome by using less concentrated, specifically 1M, nitric acid for the extraction step. In this medium, the distribution coefficients of Fe(III) and Ti are 5 and 7, respectively, much lower than those in stronger acid, while the distribution coefficients of the LREE (from La to Sm) are at their maximum, between 90 and 175 [23]. Nevertheless, even in this case, the very large amount of Fe(III) present in solutions prepared from basaltic rocks (typically containing 10-15 wt% Fe_2O_3 in the solid sample) impairs the extraction of the LREE. However, using a relatively dilute solution of nitric acid allows the use of ascorbic acid as a reducing agent to convert most of Fe(III) to the Fe(II) species [as can be done in hydrochloric acid medium [24]] which is not appreciably extracted by the TRU resin.

A 1M HNO_3-ascorbic acid mixture (with about 100 mg $C_6H_8O_6$ per 100 mg of basaltic sample) proved to conveniently circumvent the Fe(III) interference, while keeping the extraction of Ti to a relatively small extent. This approach alleviates the need for a preliminary separation of iron and a subsequent evaporation step, as used in previous works [20-22].

However, as a consequence of using dilute nitric acid, the extraction efficiency of strontium by the Sr Spec resin is reduced significantly, as indicated by capacity factors of *ca.* 30 in 1M HNO_3, against 50-90 in 3-7M HNO_3 [17]. Nevertheless, under these conditions, the column may extract ~10 µg Sr, which is more than enough for isotopic analyses by TIMS, keeping in mind that this technique allows high precision measurements of ^{87}Sr/^{86}Sr ratios to be made on sample loads of a few hundred ng, or less. In all cases, the Ba/Sr ratio in the Sr fraction was reduced to less than 1%.

3.1.2. Lead: The crown ether used as the extracting agent in the Sr Spec resin exhibits a very high affinity for Pb [17]. This property was already exploited in many studies, either for separating lead [25-28], or for the concomitant isolation of Pb and Sr [29-31], or Ba, Sr, and Pb [32]. In agreement with these previous reports, chemical recoveries of ~ 95% were achieved in this work. This compares favourably with the chemical yields typical for the separation methods based on anion-exchange in hydrobromic and/or hydrochloric acid medium. Indeed, the high selectivity of anion-exchange in HBr medium is mitigated by the fact that repeated leaching steps with dilute HBr of the fluorides left after sample digestion are necessary in order to extract Pb before column work. Besides the fact that this leaching procedure does not extract efficiently other elements of potential radiogenic isotope interest such as Sr and the REE, it may lead to relatively poor Pb recoveries due to occlusion in the solid residue, resulting in low amounts of lead loaded onto the column, and variable and often far from quantitative yields.[12]

It is noteworthy that Pb is extracted very efficiently by Sr Spec even in the presence of a large excess of Sr, and Ba, the two other elements having a strong affinity for the resin, as exemplified by sample BE-N with Ba/Pb ~255 and Sr/Pb ~345 [33]. In this case, 100 mg were processed, corresponding to *ca.* 135 µg Sr and *ca.* 100 µg Ba. While the column was grossly overloaded with Sr and Ba in this case, Pb extraction was almost quantitative, thereby demonstrating that the presence of large amounts of Sr and Ba does not significantly compromise the chemical yield of Pb. This is an interesting feature because silicate samples typically contain much more Sr and Ba than Pb. Finally, it is emphasized that the nearly quantitative recovery makes the potential issue of isotopic fractionation during column separation irrelevant, as already pointed out by Gale [26] and Smet *et al.* [30]. This is a distinct advantage over conventional separation methods based on anion-exchange chromatography which have been reported to induce large isotopic fractionation of lead when relatively poor (as low as 50%) chemical yields are achieved [34].

3.1.3. Neodymium: The TRU Spec column operated in 1M HNO_3 with ascorbic acid in order to circumvent the interference of Fe(III) allowed us to recover more than 90% of Nd and Sm. This chemical yield is identical to that achieved when an earlier cation-exchange separation step was used to get rid of iron prior to extraction chromatographic isolation of the LREE from other matrix elements such as Al, Ca, Ba, *etc*[20]. Therefore, 1M HNO_3 containing ascorbic acid as a reducing agent makes the single-stage separation of the LREE from matrix elements possible even for iron-rich samples. In addition, the use of TRU Spec and Ln Spec columns in series [20] allows the analyst to cancel an evaporation step and thus recover a Nd fraction ready for isotopic analysis without any intervening action.

3.2. Procedural blanks

Column blanks measured on already used resin, thus including any memory effect from previous rock samples, are listed in Table 3. It can be seen that, with careful column cleaning, fairly low contamination levels can be obtained for the short, Sr Spec and TRU Spec columns: namely, in the 15-70 pg range for Sr, 2-5 pg for Pb on Sr Spec, and 2-10 pg for Nd on TRU Spec. Reducing memory effects of the longer Ln Spec column to a very low level proved to be far from straightforward. Columns blanks of 40-50 pg ranges (but occasionally as high as 150 pg) are obtained routinely. However, much lower blank levels (<10 pg) can only be achieved through time-consuming, extended cleaning steps with alternating 6M HCl and 0.25M HCl.

Total procedural blanks were only marginally higher than the contamination introduced by the separation procedure: <100 pg for Sr, <10 pg for Pb, and < 50 pg for Nd. Bearing in mind that the amounts of analytes processed were 10 µg Sr, 50-1000 ng Pb, and 0.5-3.5 µg Nd, respectively, the contribution of analytical contamination to the separated analytes was negligible. It is noticed that, for Sr and Pb, the ascorbic acid used in this study (standard analytical grade reagent) is a significant contributor to the separation blank, with ca. 5 pg of each element for 100 mg of $C_6H_8O_6$ used. If low level samples are to be analysed, this problem might be circumvented by adding ascorbic acid after completion of the first separation step on the Sr Spec column. Indeed, the reducing role of ascorbic acid is only needed during the second separation step (TRU Spec). Alternatively, the ascorbic acid could be purified by dissolving solid $C_6H_8O_6$ in H_2O and passing the solution on a cation-exchange column.

3.3. Isotope ratios measured on international rock standards

In order to evaluate the potential of our procedures, including the ability of the new separation scheme to handle iron-rich samples, a set of basaltic standard reference materials have been analysed in triplicate for the radiogenic isotope ratios of Sr (^{87}Sr/^{86}Sr), Nd (^{143}Nd/^{144}Nd) and Pb (^{206,207,208} Pb/^{204}Pb): namely, BIR-1 (from the U.S. Geological Survey, USGS), B-THO (an Icelandic standard broadly equivalent to BIR-1), BHVO-1 (USGS), JB-2, JB-3 (both from the Geological Survey of Japan, GSJ), PM-S and WS-E (from International Working Group, IWG [35]). In addition, the reference sample BE-N (from Association Nationale de la Recherche Technique, France, ANRT [33]) and the USGS BHVO-2 standard (delivered as a substitute to the older, now exhausted batch BHVO-1 basalt) have also been included in the samples analysed for lead, because earlier studies by Baker et al. [36] and Smet et al. [30] suggested that these reference materials were isotopically heterogeneous for lead. As stated earlier, BE-N was also used to investigate the chemical yield of Pb in the presence of a large excess of Ba and Sr, the two other elements strongly extracted by the Sr Spec resin. In the subsequent sections, all the analytical uncertainties are quoted at the 95% confidence level: specifically, 2 x standard error (2 SE) for within-run precisions, 2 x standard deviation (2 SD) for the uncertainty (or external precision) of the mean value calculated from replicate measurements. These external precisions, reflecting the overall reproducibility of the determinations (including sample preparation and any powder heterogeneity at the *ca.* 100 mg sampling scale) are also expressed in terms of relative standard deviation, given in ppm (2 RSD x 10^6), or in per mil in cases of highly scattered results.

3.3.1 Strontium

The ^{87}Sr/^{86}Sr ratios measured by TIMS are listed in Table 4, along with their individual within-run precision (2 SE). The mean of the three determinations on different powder aliquots is also given, with its uncertainty expressed in absolute (2 SD) and relative (2 RSD in ppm) terms. It can be seen that good internal precisions comprised between +/- 0.000004 and +/-0.000006 were achieved in every cases, showing that the purity of Sr fractions was quite adequate for good quality mass spectrometric measurements by TIMS. The external reproducibilities are more variable, ranging from *ca.* 2-3 ppm in WS-E and B-THO to 17-19 ppm in JB-2 and BHVO-1. There is no relationship with Sr contents, therefore suggesting that this relatively wide range of external precision might possibly reflect somewhat different degree of powder homogeneity at the 100-200 mg sampling scale. However, it is noticed that the reproducibility of mass spectrometric measurements alone, evaluated from 8 replicate measurements of the NIST SRM 987 isotopic standard measured during the whole period of these analyses was 17 ppm. Overall, these results demonstrate that the chemical separation and mass spectrometric procedures evaluated in this work show a very good degree of reproducibility for Sr.

3.3.2 Neodymium

The ^{143}Nd/^{144}Nd (variable in nature due to radioactive decay of ^{147}Sm) and ^{145}Nd/^{144}Nd (constant) isotope ratios measured by TIMS are listed in Table 4. For all samples but BIR-1 and B-THO, for which the Nd fractions were entirely consumed, the separated Nd left after TIMS analyses was also measured by MC-ICP-MS for the sake of comparison of the two mass spectrometric approaches, and the results are also given in Table 4. The within-run (internal) precisions of individual measurements and the mean of the different determinations with their standard deviation (external reproducibility) show that a very good reproducibility, in the 4-9 ppm range for ^{143}Nd/^{144}Nd, and 3-12 ppm for ^{145}Nd/^{144}Nd isotope ratios, was achieved during the TIMS measurements [with more scatter for B-THO: 18 ppm (2 RSD) for ^{143}Nd/^{144}Nd]. The external precision of measurements by MC-ICP-MS (ranging from 12 to 32 ppm) are worse by a factor of 3-5, but it is noteworthy that when adjusted to a common value of the JNdi-1 isotopic reference standard, the average values of ^{143}Nd/^{144}Nd isotope ratios determined by both methods agree fairly well. Based on this comparison, also highlighted in Fig. 2, it is concluded that although MC-ICP-MS cannot compete with TIMS in terms of ultimate within-run precision and external reproducibility, it is nonetheless able to provide in a straightforward manner accurate Nd isotope data with a precision suitable for many geological applications. This is obtained at a significantly reduced cost, at least in terms of analyst effort (no need for preparing and loading filaments, as required for TIMS) and machine time, since the overall sample throughput of MC-ICP-MS is about three times higher than that of TIMS.

The accuracy of our Sr and Nd isotope ratio measurements can be assessed by a comparison with data obtained in other laboratories for the same basaltic standards (albeit on different batches of powder) by using different chemical separation methods. This comparison is depicted in Figs. 2 and 3. It can be observed that our results plot in the central part of the fields defined by published data compiled on the GeoRem website [37], suggesting that the chemical separation and mass spectrometric procedures described in this study do not introduce any significant systematic bias.

3.3.3 Lead

The MC-ICP-MS results are listed in Table 5 and depicted in Figs. 4 and 5, together with their analytical uncertainties. For most samples studied, the three replicate measurements show very little scatter for all isotope ratios and are in good agreement with the average values compiled from published data. However, for PM-S and to a lesser degree BHVO-2, one measurement departs significantly from the two others (Fig. 4). Our measurements for BE-N (suspected to be isotopically heterogeneous) show a very good reproducibility, supporting the inference that our batch of powder is homogeneous. However, for the $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, our data are clearly less radiogenic than published values. This confirms earlier findings [30, 36] concerning this sample. Indeed, BE-N was prepared from a relatively old (*ca.* 30 Ma) nephelinite, possibly altered as suggested by its fairly high CO_2 concentration of 0.74% [33], which would require leaching procedures to remove spurious, radiogenic lead components hosted, for example, by carbonate secondary phases. A similar remark can be made for PM-S, prepared from a Late Caledonian microgabbro [35], which might have developed relatively large isotopic differences among its constituting minerals since about 400 Ma ago. BHVO-2 differs quite significantly from its earlier generation BHVO-1, by exhibiting less radiogenic, and more scattered isotope ratios, as already noticed by Baker et al.[36]. Apart from these three geostandards, our analyses are both internally consistent and in fair agreement with published data (Fig. 5). This supports the conclusion that the chemical and mass spectrometric procedures used in this work can provide results that are both precise and accurate. Our data further suggest that, amongst the reference materials investigated here, JB-2 and JB-3 appear to be the most suitable basaltic geostandards for Pb isotope analysis, as indicated by the reproducibility better than 100 ppm [36].

3.4. Practical advantages of the method

A clear advantage of the chemical protocol described in this work is the short overall duration of the column separation step which can be completed in about 6 hours only. Sr, Pb, and Nd ready for isotope ratio measurements are therefore obtained in a single working day.

This is because using the columns in tandem configuration alleviates the need for evaporation steps and lengthy waiting periods. Besides the shortened separation time, this reduces to nil the risk of analyte loss during re-dissolutions of fractions evaporated to dryness following an earlier separation step.

Also, our method involves low acid consumption, and Sr and Nd are recovered in fairly dilute solutions of nitric and hydrochloric acid, respectively, which can be evaporated to dryness in disposable polystyrene cups without production of copious volumes of harmful gases. In contrast, Pb requires a relatively strong HCl solution for its back-extraction, but a rather small volume allows a nearly quantitative recovery to be achieved.

Finally, a thorough cleaning procedure of already used resin allows the columns to be re-used without significant memory effect, making the method rather cost-effective.

4. Conclusions

The procedure described in this work permits the rapid separation of three elements of great interest in radiogenic isotope studies of terrestrial or extra-terrestrial materials. Following sample decomposition by standard acid dissolution methods, Sr, Pb, and Nd fractions are isolated by using three small extraction chromatographic columns in series, during a *ca.* 6-hour analytical session. The target elements show a recovery of >90% (Pb, Nd), or are obtained in adequate amount (~10 µg Sr), and with low procedural blanks. The purity of fractions separated in this way is suitable for direct, high precision isotope ratio measurements by TIMS and/or MC-ICP-MS. The overall capabilities of the method are evaluated by the repeated analyses of reference materials of basaltic composition. The results demonstrate that ^{87}Sr/^{86}Sr (TIMS), ^{143}Nd/^{144}Nd (TIMS and MC-ICP-MS) and $^{208,\,207,\,206}$Pb/^{204}Pb (MC-ICP-MS) ratios can be determined with good internal precision and a high degree of reproducibility. The accuracy can be judged from the comparison of the values measured in this work with a compilation of data measured in other laboratories.

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Figure captions

Fig. 1. Elution scheme, depicting the three successive steps of the separation procedure: (a) extraction (sorption) step of Sr and Pb, and LREE on microcolumns used in tandem of Sr Spec and TRU Spec resin, respectively; (b) back-extraction (stripping) of Sr and Pb from the Sr Spec column; (c) back-extraction (stripping) of the LREE from the TRU Spec column with concomitant extraction of the coupled Ln Spec column, followed by (d) sequential elution (from La to Sm) of the LREE from the Ln Spec column. Average flow rates : ~ 75 µL min^{-1} for Sr Spec and TRU Spec columns ; ~ 45 µL min^{-1} for the Ln Spec column.

Fig. 2. ^{143}Nd/^{144}Nd isotope ratios measured in this work by TIMS (filled circles) and by MC-ICP-MS (open circles) for a set of basaltic geostandards, compared with literature data[40].

Fig. 3. ^{143}Nd/^{144}Nd vs ^{87}sr/^{86}Sr plot of the results obtained in this work, compared with published data [40]).

Fig. 4. ^{206}Pb/^{204}Pb isotope ratios measured in this work by MC-ICP-MS (filled circles) for a set of basaltic geostandards, compared with literature data [40].

Fig. 5. ^{207}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb (a) and ^{208}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb diagrams showing the results obtained in this work and literature data [40] (shaded field).

Table 1. Outline of the separation scheme enabling the concomitant isolation of Sr, Pb, and Nd by extraction chromatography without intervening evaporations.

Column pre-cleaning (3 cycles) and pre-conditioning

	Reagents	**Volume (mL)**
Sr Spec (83 mg)	6M HCl	10
	0.05M HNO_3	10
	1M HNO_3 - $C_6H_8O_6$	0.1
TRU Spec (83 mg)	0.1M HCl - 0.29M HF	4
	0.05M HNO_3	10
	1M HNO_3 - $C_6H_8O_6$	0.1
Ln Spec (300 mg)	6M HCl	10
	0.25M HCl	4
	0.05M HCl	0.1

Sr Spec and TRU Spec columns in tandem

Sample loading	1M HNO_3 - $C_6H_8O_6$	2 x 1
Beaker and pipette tip cleaning	1M HNO_3 - $C_6H_8O_6$	2 x 0.5

Columns decoupling, and further elution

Sr Spec		
Elution of Ba	7M HNO_3	2
Elution of Sr	0.05M HNO_3	2
Elution of Pb	6M HCl	2
TRU Spec		
Elution of unwanted elements	1M HNO_3	2 x 1
	0.05M HNO_3	0.1
	0.05M HCl	0.1

TRU Spec and Ln Spec columns in tandem

LREE back-extraction / loading	0.05M HCl	3 x 0.5

Ln Spec after column decoupling

Rinse	0.05M HCl	2 x 0.1
Elution of La-Ce-Pr	0.25M HCl	2.7
Elution of Nd	0.25M HCl	2
Elution of Sm	0.75M HCl	1.5

Table 2. Instrument settings and data acquisition parameters for isotope ratio measurements of Nd and Pb by MC-ICP-MS (Neptune Plus, Thermo Fisher Scientific).

RF power	1200W
Cool gas flow	15 L min^{-1}
Auxiliary gas	0.75 L.min^{-1}
Sample gas	1.1 L.min^{-1}*
Standard Sample cone	Ni, aperture diameter 1.1 mm
H Skimmer cone	Ni, aperture diameter 0.7 mm
Sample uptake	100 µL.min^{-1}
Integration time	8.4 s
Number of cycles	40 per block
Number of blocks	2

*optimised daily for maximum ^{144}Nd$^+$ or ^{208}Pb$^+$ sensitivity

Nd cup configuration on Neptune (MC-ICP-MS) and Triton (TIMS)

L2	L1	C	H1	H2	H3	H4
^{143}Nd$^+$	^{144}Nd$^+$	^{145}Nd$^+$	^{146}Nd$^+$	^{147}Sm$^+$	^{148}Nd$^+$	^{150}Nd$^+$

Pb cup configuration on Neptune MC-ICP-MS

L3	L2	L1	C	H1	H2	H3
^{202}Hg$^+$	^{203}Tl$^+$	^{204}Pb$^+$(^{204}Hg$^+$)	^{205}Tl$^+$	^{206}Pb$^+$	^{207}Pb$^+$	^{208}Pb$^+$

Table 3. Column and total procedural blanks measured by ICP-QMS for the elements of interest (given in pg). The relatively high Nd column blank C4 is considered as doubtful, because it is not associated to a correspondingly elevated value for Sm. This might possibly be explained as the result of a late-stage, post-column contamination of the Nd fraction. Blanks of the acids used in the chemical procedure are also indicated (in pg/g).

Column blanks (pg)	C1	C2	C3	C4	C5	C6	**Mean ± 1 S.D.**
Sr Spec columns							
Sr	15	42	28	72	35	23	**36 ± 20**
Pb	3.3	4.1	3.7	2.2	2.1	4.7	**3.4 ± 1.0**
TRU Spec columns							
Nd	3.0	4.5	2.2	10	3.5	1.6	**4.1 ± 3.0**
Sm	1.3	1.6	0.6	0.3	1.4	0.7	**1.0 ± 0.5**
Ln Spec columns Nd							
Regular cleaning	120	45	30	20	23	44	**47 ± 37**
Regular cleaning	50	30	60	32	32	60	**44 ± 14**
Doubly cleaned	3	4	6	5	3	4	**4.2 ± 1.2**
Doubly cleaned	11	6	5	7	3	9	**6.8 ± 2.9**

Total procedural blanks (pg)	TPB#1	TPB#2	TPB#3	TPB#4	TPB#5	TPB#6	
Sr	37	9	78	30	30	64	**41 ± 25**
Pb	9.5	5.1	9.6	8.2	7.2	3.2	**7.1 ± 2.5**

Reagent blanks (pg/g)	14M HNO_3	6M HCl	29M HF	Ascorbic acid
Sr	1.6	2.9	3.2	51
Nd	0.3	0.2	0.6	1.3
Pb	1.4	0.3	1.4	49

Table 4. Isotope ratios of Nd (measured both by TIMS and MC-ICP-MS, except for standards BIR-1 and B-THO) and Sr (measured by TIMS) on three different sample dissolutions. The results of individual analyses are listed, with their within-run (internal) precisions. The mean of the triplicate determinations is indicated, with its uncertainty quoted at the 95% confidence level, as twice the standard deviation of the replicates, expressed both in absolute and in relative (ppm) terms. The results obtained for the Nd isotope standard JNdi-1[41] are also given.

Sample	Instrument	$^{143}Nd/^{144}Nd$	2 S.E	$^{145}Nd/^{144}Nd$	2 S.E	Sample	Instrument	$^{87}Sr/^{86}Sr$	2 S.E
BHVO1-A	TIMS	0.512977	0.000003	0.348404	0.000002	BHVO1-A	TIMS	0.703479	0.000004
BHVO1-B	TIMS	0.512974	0.000003	0.348403	0.000002	BHVO1-B	TIMS	0.703472	0.000005
BHVO1-C	TIMS	0.512975	0.000004	0.348403	0.000002	BHVO1-C	TIMS	0.703485	0.000005
BHVO1-A	MC-ICPMS	0.512976	0.000006	0.348400	0.000003				
BHVO1-B	MC-ICPMS	0.512976	0.000006	0.348403	0.000003	**BHVO-1 mean ± 2 S.D.**	**TIMS**	**0.703479 ± 13**	
BHVO1-C	MC-ICPMS	0.512968	0.000005	0.348403	0.000002	**ppm 2 R.S.D.**		**18**	
BHVO-1 mean ± 2 S.D.	**TIMS**	**0.512975 ± 3**		**0.348403 ± 1**					
ppm 2 R.S.D.		**6.0**		**3.3**					
BHVO-1 mean ± 2 S.D.	**MC-ICPMS**	**0.512973 ± 10**		**0.348402 ± 4**					
ppm 2 R.S.D.		**19**		**11**					
BHVO-1 mean ± 2 S.D.	**All**	**0.512974 ± 7**		**0.348403 ± 3**					
ppm 2 R.S.D.		**13**		**8.3**					
BIR-1 A	TIMS	0.513074	0.000006	0.348406	0.000004	BIR-1 A	TIMS	0.703107	0.000006
BIR-1 B	TIMS	0.513080	0.000003	0.348404	0.000002	BIR-1 B	TIMS	0.703102	0.000004
BIR-1 C	TIMS	0.513077	0.000003	0.348401	0.000002	BIR-1 C	TIMS	0.703104	0.000004
BIR-1 C dupl. 1	TIMS	0.513079	0.000003	0.348403	0.000002				
BIR-1 C dupl. 2	TIMS	0.513079	0.000003	0.348404	0.000002	**BIR-1 mean ± 2 S.D.**	**TIMS**	**0.703104 ± 5**	
						ppm 2 R.S.D.		**7.2**	
BIR-1 mean ± 2 S.D.	**TIMS**	**0.513078 ± 5**		**0.3484036 ± 4**					
ppm 2 R.S.D.		**9.3**		**10**					
B-THO A	TIMS	0.513081	0.000004	0.348406	0.000003	B-THO A	TIMS	0.703086	0.000004
B-THO B	TIMS	0.513079	0.000005	0.348404	0.000003	B-THO B	TIMS	0.703087	0.000004
B-THO C	TIMS	0.513088	0.000004	0.348401	0.000003	B-THO C	TIMS	0.703088	0.000004
B-THO mean ± 2 S.D.	**TIMS**	**0.513083 ± 9**		**0.348404 ± 5**		**B-THO mean ± 2 S.D.**	**TIMS**	**0.703087 ± 2**	
ppm 2 R.S.D.		**18**		**14**		**ppm 2 R.S.D.**		**2.8**	
JB2-A	TIMS	0.513093	0.000005	0.348403	0.000002	JB2-A	TIMS	0.703682	0.000004
JB2-B	TIMS	0.513095	0.000002	0.348406	0.000002	JB2-B	TIMS	0.703670	0.000004
JB2-C	TIMS	0.513093	0.000006	0.348402	0.000004	JB2-C	TIMS	0.703674	0.000004
JB2-A	MC-ICPMS	0.513095	0.000007	0.348403	0.000004				
JB2-B	MC-ICPMS	0.513088	0.000006	0.348401	0.000003	**JB2 mean ± 2 S.D.**	**TIMS**	**0.703675 ± 12**	
JB2-C	MC-ICPMS	0.513092	0.000006	0.348403	0.000003	**ppm 2 R.S.D.**		**17**	
JB2 mean ± 2 S.D.	**TIMS**	**0.513094 ± 2**		**0.348404 ± 4**					
ppm 2 R.S.D.		**4.5**		**12**					
JB2 mean ± 2 S.D.	**MC-ICPMS**	**0.513092 ± 8**		**0.348402 ± 2**					
ppm 2 R.S.D.		**15**		**5.9**					
JB2 mean ± 2 S.D.	**All**	**0.513093 ± 5**		**0.348403 ± 3**					
ppm 2 R.S.D.		**10**		**9.5**					
JB3-A	TIMS	0.513047	0.000001	0.348402	0.000001	JB3-A	TIMS	0.703422	0.000004
JB3-B	TIMS	0.513050	0.000003	0.348403	0.000002	JB3-B	TIMS	0.703417	0.000004
JB3-C	TIMS	0.513050	0.000003	0.348404	0.000003	JB3-C	TIMS	0.703426	0.000005
JB3-A	MC-ICPMS	0.513054	0.000005	0.348401	0.000003				
JB3-B	MC-ICPMS	0.513042	0.000005	0.348401	0.000002	**JB3 mean ± 2 S.D.**	**TIMS**	**0.703422 ± 9**	
JB3-C	MC-ICPMS	0.513038	0.000005	0.348402	0.000002	**ppm 2 R.S.D.**		**13**	
JB3 mean ± 2 S.D.	**TIMS**	**0.513049 ± 3**		**0.348403 ± 2**					
ppm 2 R.S.D.		**6.8**		**5.7**					
JB3 mean ± 2 S.D.	**MC-ICPMS**	**0.513044 ± 17**		**0.348402 ± 2**					
ppm 2 R.S.D.		**33**		**4.5**					
JB3 mean ± 2 S.D.	**All**	**0.513047 ± 12**		**0.348402 ± 2**					
ppm 2 R.S.D.		**23**		**6.4**					
PMS-A	TIMS	0.512594	0.000002	0.348403	0.000002	PMS-A	TIMS	0.704615	0.000004
PMS-B	TIMS	0.512596	0.000003	0.348402	0.000002	PMS-B	TIMS	0.704607	0.000004
PMS-C	TIMS	0.512597	0.000002	0.348404	0.000001	PMS-C	TIMS	0.704614	0.000004
PMS-A	MC-ICPMS	0.512600	0.000008	0.348405	0.000003				
PMS-B	MC-ICPMS	0.512594	0.000007	0.348398	0.000004	**PMS mean ± 2 S.D.**	**TIMS**	**0.704612 ± 9**	
PMS-C	MC-ICPMS	0.512584	0.000008	0.348394	0.000004	**ppm 2 R.S.D.**		**12**	
PMS mean ± 2 S.D.	**TIMS**	**0.512596 ± 3**		**0.348403 ± 2**					
ppm 2 R.S.D.		**6.0**		**5.7**					
PMS mean ± 2 S.D.	**MC-ICPMS**	**0.512593 ± 16**		**0.348399 ± 11**					
ppm 2 R.S.D.		**31**		**30**					
PMS mean ± 2 S.D.	**All**	**0.512594 ± 11**		**0.348401 ± 8**					
ppm 2 R.S.D.		**21**		**23**					
WS-E A	TIMS	0.512465	0.000004	0.348403	0.000002	WS-E A	TIMS	0.706599	0.000004
WS-E A dupl. 1	TIMS	0.512469	0.000003	0.348404	0.000001	WS-E B	TIMS	0.706598	0.000004
WS-E A dupl. 2	TIMS	0.512468	0.000002	0.348404	0.000001	WSE-C	TIMS	0.706599	0.000006
WS-E B	TIMS	0.512470	0.000002	0.348404	0.000001				
WSE-C	TIMS	0.512466	0.000001	0.348403	0.000001	**WSE mean ± 2 S.D.**	**TIMS**	**0.706599 ± 1**	
WSE-C dupl.	TIMS	0.512467	0.000001	0.348404	0.000001	**ppm 2 R.S.D.**		**1.6**	
WSE-A	MC-ICPMS	0.512463	0.000006	0.348401	0.000003				
WSE-A dupl.	MC-ICPMS	0.512466	0.000006	0.348402	0.000003				
WSE-B	MC-ICPMS	0.512471	0.000006	0.348399	0.000003				
WSE-C	MC-ICPMS	0.512467	0.000005	0.348400	0.000003				
WSE mean ± 2 S.D.	**TIMS**	**0.512468 ± 4**		**0.348404 ± 1**					
ppm 2 R.S.D.		**7.3**		**3.0**					
WSE mean ± 2 S.D.	**MC-ICPMS**	**0.512467 ± 6**		**0.348401 ± 2**					
ppm 2 R.S.D.		**12**		**5.9**					
WSE mean ± 2 S.D.	**All**	**0.512467 ± 5**		**0.348402 ± 4**					
ppm 2 R.S.D.		**9.0**		**10**					

Table 4. (continued)

Sample	Instrument	^{143}Nd/^{144}Nd	2 S.E	^{145}Nd/^{144}Nd	2 S.E	Sample	Instrument	^{87}Sr/^{86}Sr	2 S.E
JNdi-1	TIMS	0.512102	0.000002	0.348402	0.000001	SRM 987	TIMS	0.710247	0.000006
JNdi-1	TIMS	0.512104	0.000002	0.348403	0.000001	SRM 987	TIMS	0.710234	0.000006
JNdi-1	TIMS	0.512103	0.000003	0.348402	0.000004	SRM 987	TIMS	0.710235	0.000005
						SRM 987	TIMS	0.710241	0.000004
JNdi-1 mean ± 2 S.D.	**TIMS**	**0.512103 ± 2**		**0.348402 ± 1**		SRM 987	TIMS	0.710239	0.000006
ppm 2 R.S.D.		**3.9**		**3.3**		SRM 987	TIMS	0.710238	0.000004
						SRM 987	TIMS	0.710244	0.000004
JNdi-1	MC-ICPMS	0.512089	0.000007	0.348415	0.000004	SRM 987	TIMS	0.710252	0.000004
JNdi-1	MC-ICPMS	0.512097	0.000007	0.348416	0.000004				
JNdi-1	MC-ICPMS	0.512101	0.000007	0.348415	0.000004	**NBS 987 mean ± 2 S.D.**	**TIMS**	**0.710241 ± 12**	
JNdi-1	MC-ICPMS	0.512091	0.000008	0.348412	0.000004	**ppm 2 R.S.D.**		**17**	
JNdi-1	MC-ICPMS	0.512091	0.000007	0.348414	0.000004				
JNdi-1	MC-ICPMS	0.512092	0.000008	0.348412	0.000004				
JNdi-1	MC-ICPMS	0.512096	0.000007	0.348416	0.000005				
JNdi-1	MC-ICPMS	0.512099	0.000008	0.348416	0.000004				
JNdi-1	MC-ICPMS	0.512096	0.000007	0.348417	0.000005				
JNdi-1	MC-ICPMS	0.512099	0.000009	0.348414	0.000005				
JNdi-1	MC-ICPMS	0.512096	0.000007	0.348416	0.000004				
JNdi-1 mean ± 2 S.D.	**MC-ICPMS**	**0.512095 ± 8**		**0.348415 ± 3**					
ppm 2 R.S.D.		**15**		**10**					

Table 5. Pb isotope data for international standard reference materials. Pb isotope ratios measured by MC-ICP-MS by using the Tl-normalisation method for correcting for instrumental mass bias, followed by a second normalisation to the values of NIST SRM 981 reported by Galer and Abouchami.[16]

Sample	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{208}Pb/^{206}Pb	^{207}Pb/^{206}Pb
BHVO1--A	18.6907	15.5720	38.3454	2.05160	0.83316
BHVO1--B	18.7009	15.5702	38.3592	2.05119	0.83260
BHVO1--C	18.6825	15.5714	38.3511	2.05276	0.83349
BHVO-1 mean ± 2 S.D.	**18.691 ± 18**	**15.571 ± 2**	**38.352 ± 14**	**2.0518 ± 16**	**0.8331 ± 9**
ppm 2 R.S.D.	**985**	**123**	**362**	**794**	**1086**
BHVO-2 A	18.6126	15.5413	38.2240	2.05374	0.83499
BHVO-2 B	18.6507	15.5322	38.2370	2.05017	0.83280
BHVO-2 C	18.6505	15.5426	38.2491	2.05086	0.83337
BHVO-2 mean ± 2 S.D.	**18.638 ± 44**	**15.539 ± 11**	**38.237 ± 25**	**2.0516 ± 38**	**0.8337 ± 23**
‰ 2 R.S.D.	**2.4**	**0.73**	**0.66**	**1.8**	**2.7**
BIR-1a--A	18.8521	15.6583	38.4963	2.04203	0.83060
BIR-1a--B	18.8536	15.6583	38.4967	2.04184	0.83051
BIR-1a--C	18.8541	15.6589	38.4974	2.04186	0.83053
BIR-1a mean ± 2 S.D.	**18.8533 ± 21**	**15.6585 ± 7**	**38.4968 ± 11**	**2.0419 ± 2**	**0.8305 ± 1**
ppm 2 R.S.D.	**112**	**45**	**28**	**99**	**111**
JB2-A	18.3428	15.5584	38.2751	2.08664	0.84820
JB2-B	18.3432	15.5602	38.2794	2.08687	0.84829
JB2-C	18.3425	15.5596	38.2766	2.08677	0.84829
JB2 mean ± 2 S.D.	**18.3428 ± 8**	**15.5594 ± 18**	**38.2770 ± 44**	**2.0868 ± 2**	**0.8483 ± 1**
ppm 2 R.S.D.	**42**	**117**	**115**	**113**	**128**
JB3--A	18.2952	15.5352	38.2500	2.09072	0.84915
JB3--B	18.2955	15.5362	38.2512	2.09075	0.84918
JB3--C	18.2949	15.5354	38.2506	2.09079	0.84918
JB3 mean ± 2 S.D.	**18.2952 ± 6**	**15.5356 ± 10**	**38.2506 ± 12**	**2.0908 ± 1**	**0.84917 ± 1**
ppm 2 R.S.D.	**33**	**66**	**33**	**32**	**32**
PMS--A	18.1283	15.5684	37.7810	2.08413	0.85880
PMS--B	18.0729	15.5493	37.7849	2.09071	0.86039
PMS--C	17.6792	15.5424	37.4013	2.11552	0.87913
PM-S mean ± 2 S.D.	**17.96 ± 49**	**15.553 ± 27**	**37.66 ± 44**	**2.097 ± 33**	**0.866 ± 23**
‰ 2 R.S.D.	**27**	**1.7**	**12**	**16**	**26**
WSE--A	18.2871	15.5918	38.1412	2.08569	0.85261
WSE--B	18.2773	15.5936	38.0990	2.08451	0.85318
WSE--C	18.2745	15.5897	38.1218	2.08605	0.85309
WSE--A dupli	18.2863	15.5908	38.1388	2.08566	0.85260
WSE--B dupli	18.2768	15.5931	38.0977	2.08449	0.85317
WSE--C dupli	18.2755	15.5908	38.1243	2.08609	0.85310
WS-E mean ± 2 S.D.	**18.280 ± 11**	**15.592 ± 3**	**38.120 ± 37**	**2.0854 ± 15**	**0.8530 ± 6**
ppm 2 R.S.D.	**614**	**191**	**985**	**700**	**646**
BEN--A	19.1651	15.6043	38.9841	2.03411	0.81420
BEN--A'	19.1751	15.6074	38.9978	2.03379	0.81394
BEN--B	19.1717	15.6058	38.9916	2.03385	0.81401
BEN--B'	19.1778	15.6051	38.9968	2.03341	0.81371
BEN mean ± 2 S.D.	**19.172 ± 11**	**15.606 ± 3**	**38.993 ± 13**	**2.0338 ± 6**	**0.8140 ± 4**
ppm 2 R.S.D.	**574**	**165**	**322**	**284**	**502**

Fig. 1

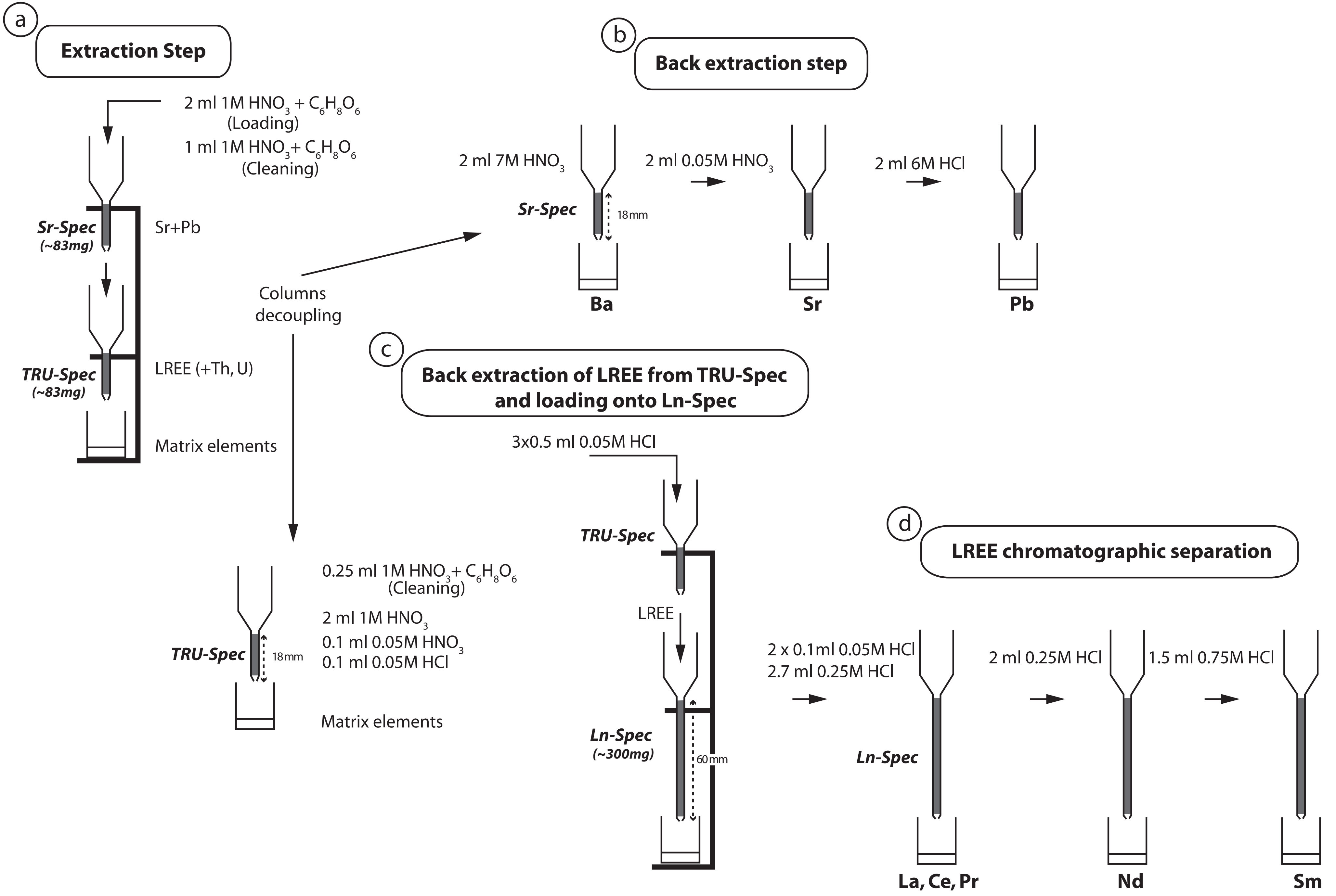

a
Extraction Step
2 ml 1M HNO$_3$ + C$_6$H$_8$O$_6$ (Loading)
1 ml 1M HNO$_3$+ C$_6$H$_8$O$_6$ (Cleaning)
Sr-Spec (~83mg)
Sr+Pb
TRU-Spec (~83mg)
LREE (+Th, U)
Matrix elements
Columns decoupling
b
Back extraction step
2 ml 7M HNO$_3$
Sr-Spec
18mm
2 ml 0.05M HNO$_3$
2 ml 6M HCl
Ba
Sr
Pb
TRU-Spec
18mm
0.25 ml 1M HNO$_3$+ C$_6$H$_8$O$_6$ (Cleaning)
2 ml 1M HNO$_3$
0.1 ml 0.05M HNO$_3$
0.1 ml 0.05M HCl
Matrix elements
c
Back extraction of LREE from TRU-Spec and loading onto Ln-Spec
3x0.5 ml 0.05M HCl
TRU-Spec
LREE
Ln-Spec (~300mg)
60mm
d
LREE chromatographic separation
2 x 0.1ml 0.05M HCl
2.7 ml 0.25M HCl
Ln-Spec
2 ml 0.25M HCl
1.5 ml 0.75M HCl
La, Ce, Pr
Nd
Sm

Fig. 2

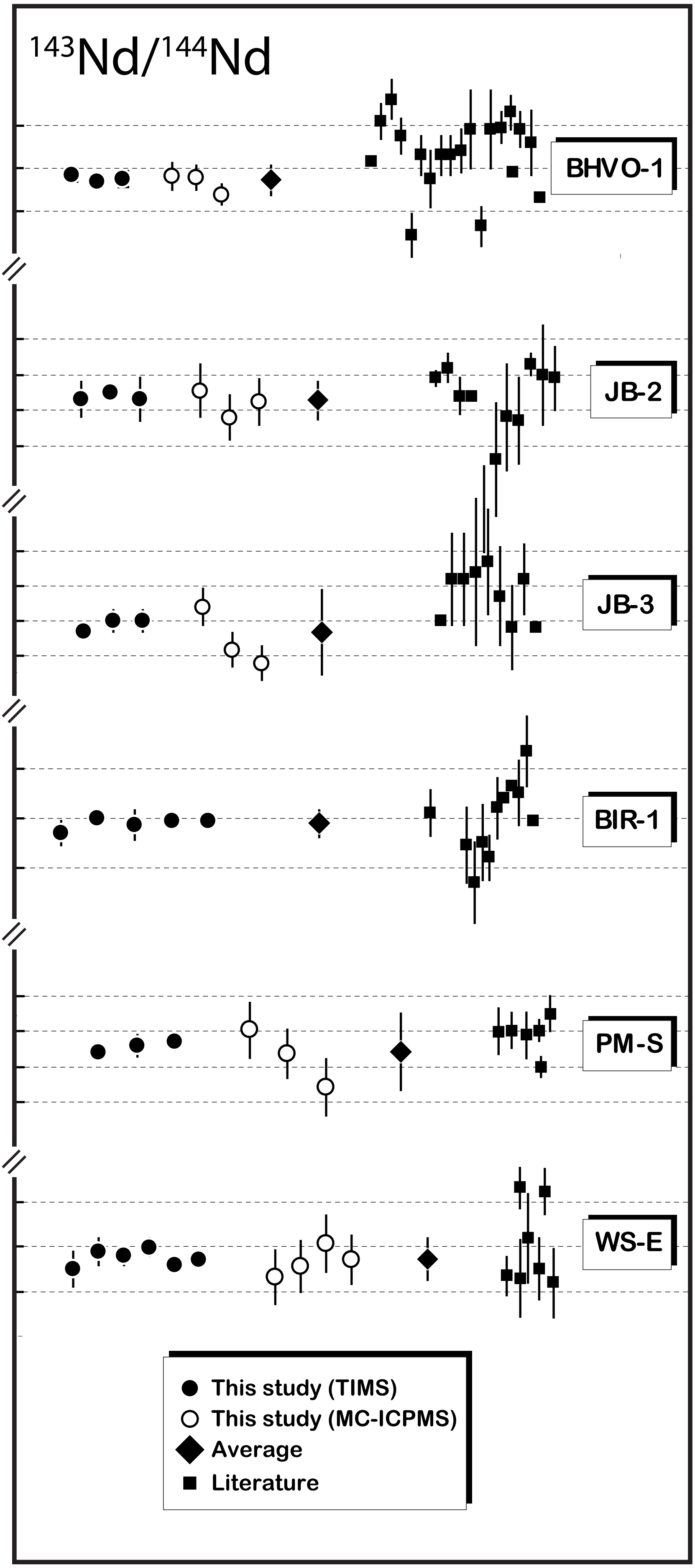
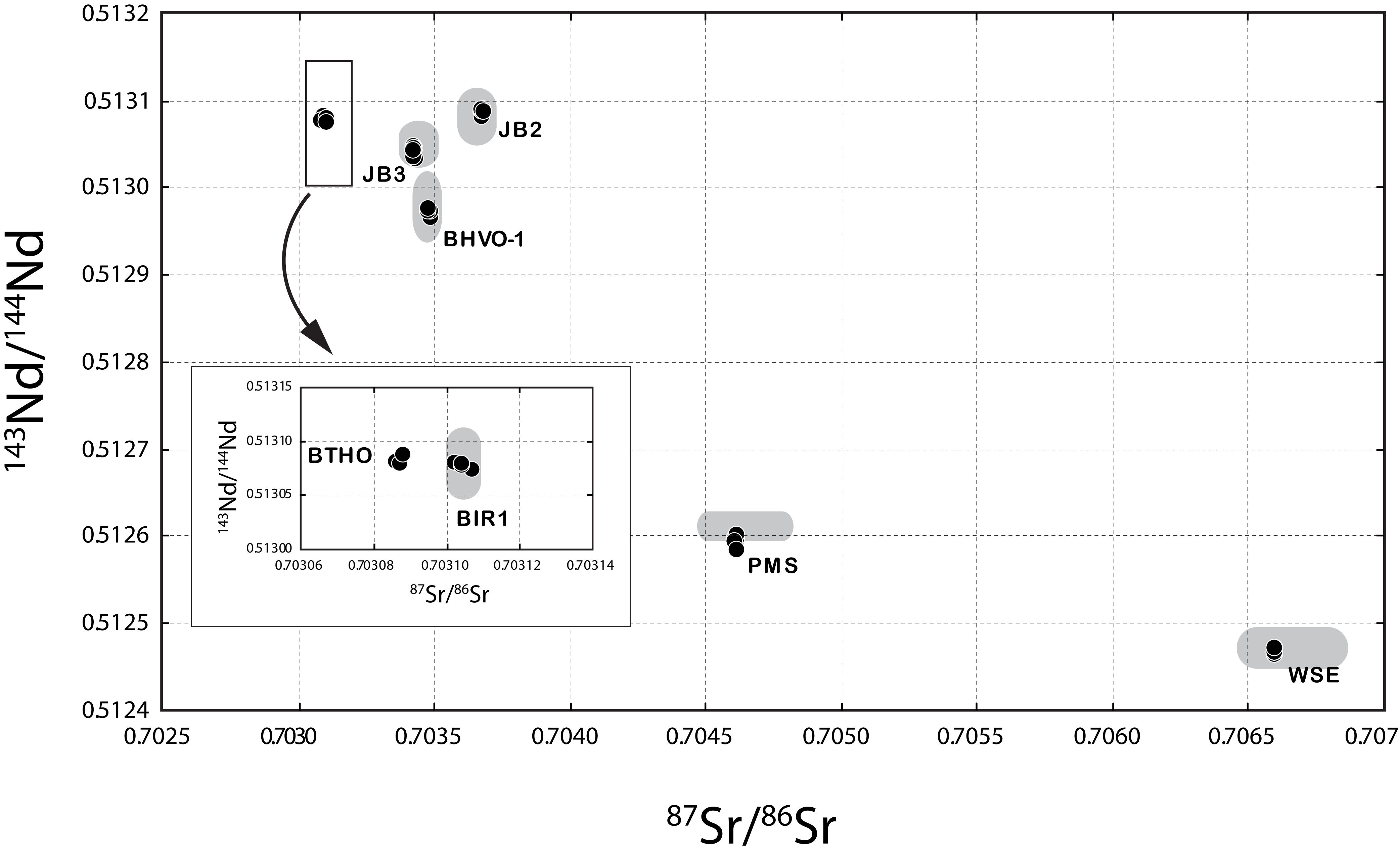

$^{143}Nd/^{144}Nd$
051300
051298
051296
BHVO-1
051311
051310
051309
051308
JB-2
051307
051306
051305
051304
JB-3
051310
051308
051306
BIR-1
051261
051260
051259
051258
PM-S
051248
051247
051246
WS-E
● This study (TIMS)
○ This study (MC-ICPMS)
◆ Average
■ Literature

Fig. 3


0.5132
0.5131
0.5130
0.5129
0.5128
0.5127
0.5126
0.5125
0.5124
^{143}Nd/^{144}Nd
0.7025
0.7030
0.7035
0.7040
0.7045
0.7050
0.7055
0.7060
0.7065
0.7070
^{87}Sr/^{86}Sr
JB2
JB3
BHVO-1
PMS
WSE
BTHO
BIR1
0.51315
0.51310
0.51305
0.51300
0.70306
0.70308
0.70310
0.70312
0.70314

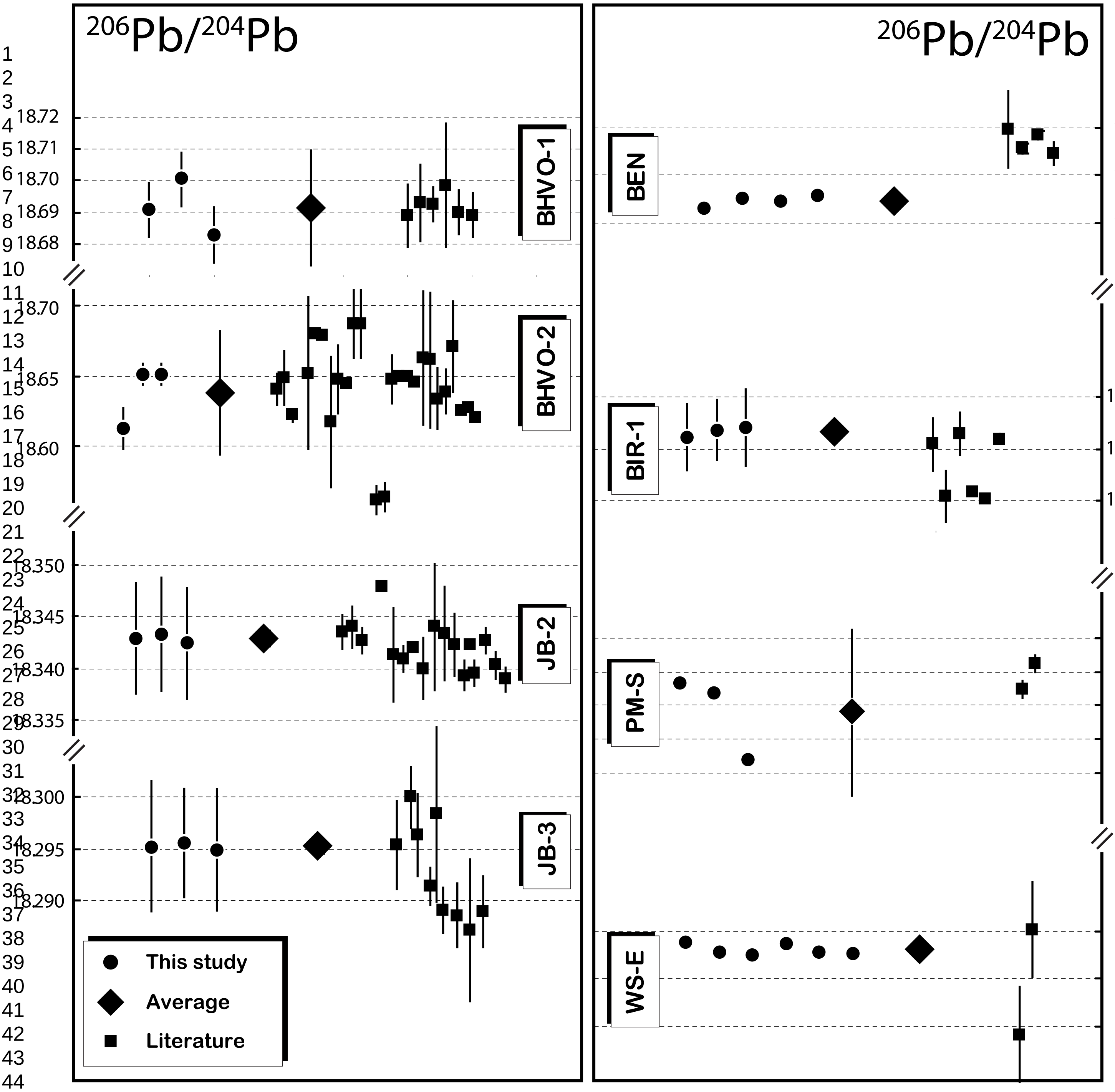
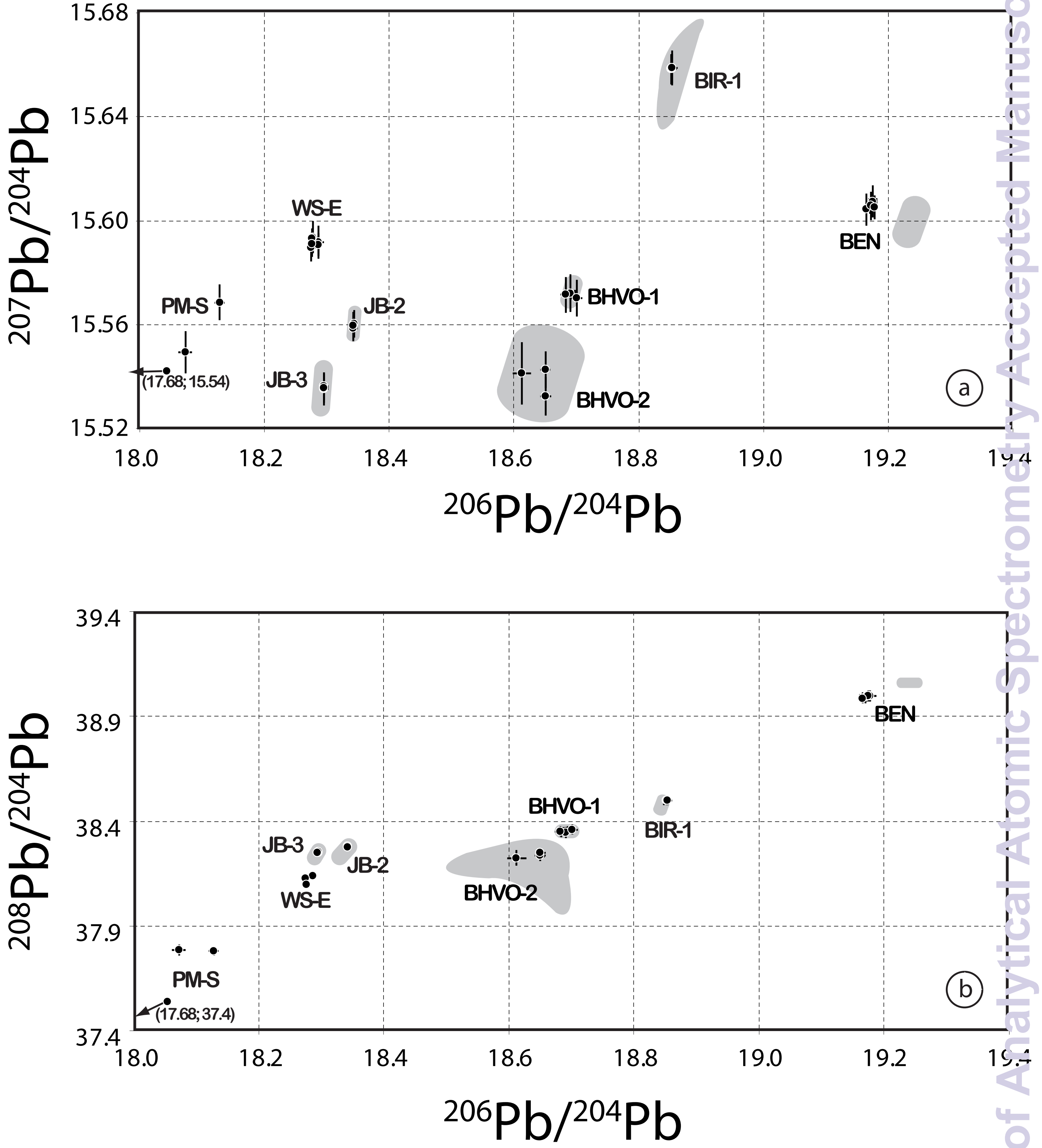

$^{206}Pb/^{204}Pb$
18.72
18.71
18.70
18.69
18.68
BHVO-1
18.70
18.65
18.60
BHVO-2
18.350
18.345
18.340
18.335
JB-2
18.300
18.295
18.290
JB-3
This study
Average
Literature
$^{206}Pb/^{204}Pb$
BEN
BIR-1
18.86
18.85
18.84
PM-S
WS-E

Fig. 4

Fig. 5


15.68
15.64
15.60
15.56
15.52
$^{207}Pb/^{204}Pb$
18.0
18.2
18.4
18.6
18.8
19.0
19.2
19.4
$^{206}Pb/^{204}Pb$
BIR-1
WS-E
BEN
PM-S
JB-2
BHVO-1
JB-3
(17.68; 15.54)
BHVO-2
a
39.4
38.9
38.4
37.9
37.4
$^{208}Pb/^{204}Pb$
18.0
18.2
18.4
18.6
18.8
19.0
19.2
19.4
$^{206}Pb/^{204}Pb$
BEN
BHVO-1
BIR-1
JB-3
JB-2
WS-E
BHVO-2
PM-S
(17.68; 37.4)
b