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Rapid separation scheme of Sr, Nd, Pb, and Hf from a single rock digest using a tandem chromatography column prior to isotope ratio measurements by mass spectrometry

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Abstract:

A straightforward tandem column separation procedure is presented for separation of Sr, Nd, Pb, and Hf from silicate materials. It allows rapid purification, without any intervening evaporation, of these four elements of great interest in Earth science and cosmochemistry. After sample loading, the upper Sr Spec column adsorbs Sr and Pb, while the lower TODGA Spec column adsorbs Hf and Nd. Strontium-lead and hafnium-neodymium elements are then back-extracted from the Sr Spec and TODGA Spec columns, respectively. The whole separation procedure, including column setup, cleaning, and pre-conditioning, takes approximately eight hours for separating a batch of 25 samples. The proposed procedure offers significant improvement in separation efficiency of these often-used four elements, compared with conventional four columns methods. Fractions of Sr, Nd and Pb are then measured by TIMS and the Hf fraction is determined by MC-ICP-MS. The stability of this procedure was demonstrated by replicate measurements of ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd, ^{176}Hf/^{177}Hf, ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb isotope ratios of eight international silicate rock reference materials, spanning a wide range of bulk compositions. The analytical results obtained in this study agree well with published data. The external reproducibility (2 RSD, n = 8) of standard BCR-2 was ± 0.0026 % for ^{87}Sr/^{86}Sr, ± 0.0020 % for ^{143}Nd/^{144}Nd, ± 0.0049 % for ^{176}Hf/^{177}Hf, and ± 0.026 % ~ 0.034 % for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb isotope ratios.

Keywords: Sr-Nd-Pb-Hf isotope; Tandem column separation; Geological samples; TIMS; MC-ICP-MS

1. Introduction

The combination of Sr, Nd, Pb, and Hf isotope systems provide a powerful tool to investigate differentiation and evolution of the silicate Earth and other terrestrial planets.[1-3] This is because the abundances of ^{87}Sr, ^{143}Nd, ^{206}Pb, ^{207}Pb, ^{208}Pb and ^{177}Hf, vary in natural samples as a consequence of the long-lived radioactive decay of their respective parent isotopes ^{87}Rb, ^{147}Sm, ^{238}U, ^{235}U, ^{232}Th and ^{176}Lu. As a result, ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd, ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb and ^{176}Hf/^{177}Hf ratios in a geological sample reflect the time-integrated parent-daughter isotope ratios of its source.[4-6] Therefore, it is crucial to extract Sr, Nd, Pb, Hf multi-isotopic messages from the same sample aliquot.

Thermal ionization mass spectrometry (TIMS) and multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) give excellent accuracy and precision regarding Sr, Nd, Pb and Hf isotopic measurements.[4-46] Commonly, using TIMS or MC-ICP-MS, external precision of ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd, ^{176}Hf/^{177}Hf isotope ratios are 0.002%~0.004% (2 RSD), and external precision of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb isotope ratios are 0.02%~0.03% (2 RSD). However, sample preparations for such high precision isotope measurements are time consuming. This is because high precision determination of Sr, Nd, Pb, and Hf isotope ratios in geological samples using TIMS or MC-ICP-MS requires a high degree of sample purification to avoid potential matrix effects as well as poly-atomic and isobaric interferences. Therefore, it is important to develop an integrated separation scheme that enables the analyst to obtain sufficiently pure fractions of Sr, Nd, Pb, and Hf from single sample dissolutions in a straightforward manner. Purification of Sr-Nd-Pb-Hf is traditionally accomplished by using a four-column chromatography after a single sample digestion. Traditionally, the first column involves the separation of Pb from other elements using an anion resin such as AG 1 or Dowex 1 resin[24, 26, 28-31], or a special resin column, such as Pb Spec[23] or Sr Spec resin[4-6, 25, 27]. The discard containing most of the Sr-Nd-Hf and matrix element fractions from the first column is then dried and dissolved using HCl or HNO_3. Subsequently, Hf is separated from the matrix solution enriched in Sr, Nd, and Hf using a second resin column, such as anion resin column[44] or a special resin column, such as LN resin[12, 35, 42], U-TEVA resin[8, 34, 38, 41], TEVA[33, 36, 37] or TODGA resin[40, 43, 46]. The matrix solution enriched in Sr and Nd from the second column is also collected. Then, Sr and rare earth elements (REEs) enriched in Nd are separated from the matrix elements using a third cation exchange resin (AG50W) column[11-16] or a tandem resin column scheme(Sr Spec + TRU Spec)[19]. Finally, Nd is separated from other REEs using a fourth resin column, such as LN(HDEHP) Spec resin[7-12, 16], HEHEHP resin[21], or Aminex A27 resin column[15]. Traditional four-step separation procedures involve tedious pre-cleaning of the columns and fraction evaporation and take at least four working days to complete Sr-Nd-Pb-Hf sample preparation for a batch of geological samples (e.g., 20~30 samples). Thus, the separation efficiency of traditional methods is low and sample throughput is impeded. In addition, traditional methods increase the probability of contamination from cross-operation in column chemistry associated with the complex operations.

Recently, Yang[17] and Li[18] presented methods to precisely determine $^{143}Nd/^{144}Nd$

isotopic ratios without separation from other REEs using MC-ICP-MS and TIMS. Their methods allowed Sr-Nd-Pb-Hf isotopic determination using TIMS and MC-ICP-MS so well as high-purity Sr, Pb, Hf and REEs-enriched in Nd could be achieved. Based on this method, rapid chemical procedures in our previous investigations were developed to separate Sr-Nd-Pb[5] or Sr-Nd-Hf[6] from a single sample digest. However, analytical protocol to concomitantly separate Sr-Nd-Pb-Hf fractions from a single sample digest has not been documented. More recent, Pourmand[46] presents a rapid separation scheme for Sr-Nd-Hf purification using Sr and TODGA Spec resin. The method[46] gives a clue to afford a possibility of separation Sr-Nd-Pb-Hf from a single sample digest. In this study, we report a rapid tandem column separation procedure for all four elements based on optimization of Sr Spec and TODGA Spec resins.

This new method reduces the rather extensive and costly cleaning and separation procedures of resin and columns without negatively affecting the data quality. This method of obtaining Sr-Nd-Pb-Hf from a single dissolution thus provides the most rapid and efficient separation. This method also avoids potentially sample heterogeneity when the samples are scarce at a given sampling scale. To verify the robustness of this tandem column separation protocol for Sr-Nd-Pb-Hf, eight certified reference materials (CRMs) of silicate rocks, encompassing a wide range of matrix compositions and analyte concentrations, were analyzed.

2. Experimental

2.1 Chemicals and chromatographic materials

Reagents: All AR grade acids (hydrochloric acid, phosphoric acid, nitric acid, hydrofluoric acid, boric acid and perchloric acid) were further purified using a Savillex^{TM} DST-1000 sub-boiling distillation system. Ultrapure water with a resistivity of 18.2 MΩ.cm^{-1} was obtained from a Milli-Q Element system (Millipore, USA) and used throughout this work for diluting concentrated acids. The silica-gel obtained from Merck company was dispersed in Milli-Q H_2O.

Sr-Nd-Pb-Hf standard solutions: A stock solution of 100 ppm Sr, Nd and Pb was gravimetrically prepared to monitor the stability of the Triton Plus instrument using NIST NBS-987, JNdi-1 and NIST NBS-981 reference materials. A JMC 475 Hf international standard solution of 100 ppb was used to monitor the stability of the Neptune Plus instrument.

Re ribbons: 0.035 mm thick, 0.77 mm wide and 99.98% pure, H. Cross Company.

Pb double spike: Instrumental fractionation is the major limiting factor precluding accurate determination of lead isotopic ratios by TIMS. To correct accurately for effects of the Pb mass fractionation, ^{204}Pb-enriched and ^{207}Pb-enriched spikes were obtained from Oka Ridge National Laboratory, USA. The ^{207}Pb-^{204}Pb double spike composition and the spike/sample mixing ratio were optimally determined by error simulation using the method reported by Galer[45]. The ^{207}Pb-^{204}Pb double spike solution was diluted with 0.5 M HNO_3 to 1 ppm and calibrated using NIST NBS-981.

Resin: The Sr Spec and TODGA Spec resins produced by Eichrom Technologies were used for chromatographic extraction. The Sr Spec resin and was based on a crown ether di-tert-butylcyclohexane-18-crown-6 in octanol,[19, 27] at sorbed onto an inert chromatographic support (particle diameter: 100-150 μm). The TODGA Spec resin (particle diameter: 100-150 μm) was based on a synthesized tridentate ligand known as N, N, N`N` tetraoctyl-1, 5-diglycolamide.[43]

Column: The Sr Spec cation-exchange quartz glass column was 7 cm long with a 5 mm i.d. and 6 mL reservoir, packed with 0.4 mL of Sr Spec resin. The TODGA Spec cation-exchange polypropylene column was 7 cm long with a 5 mm i.d. and 5 mL reservoir, packed with 0.8 mL of TODGA Spec resin.

Rock standard samples: Rock powders of CRMs were obtained from the United States Geological Survey (USGS) and the Geological Survey of Japan (GSJ). These CRMs included USGS BCR-2 (basalt), BHVO-2(basalt), BIR-1(basalt) and AGV-2(andesite) GSJ JG-1a (granite), JA-3 (andesite), JB-2 (basalt) and JB-3 (basalt).

Labware: The labware used included 15 and 7 mL PFA Teflon vials with screw top lids (Savillex Corporation, USA). These vials were used for sample digestion, solution collection, and evaporation. These vials were cleaned prior to use with a degreasing agent followed by sequential washing with AR grade HNO_3, HCl, and ultra-pure Milli-Q H_2O.

2.2. Sample digestion

To achieve excellent Sr-Nd-Pb-Hf blank levels, all chemistry was performed inside better than Class 100 chemical workstations located inside a suite of Class 1000 over-pressured clean rooms. Approximately 120~130 mg of rock powder materials were weighed into a steel-jacketed acid-washed high-pressure PTFE bombs.[6] The samples were dissolved on a hotplate at 190 °C using an acid mixture of 3 mL of 29 M HF, 0.3 mL of 14 M HNO_3 and 0.3 mL of $HClO_4$ for 4 days. The dissolved sample solution was then evaporated to dryness and treated overnight with 2 mL of 6 M HCl and 1mL of saturated (~0.46 M) H_3BO_3 solution at ca. 120 °C on a hotplate. After the H_3BO_3 dissolution step, the fluoride gels formed during decomposition of mafic and ultra-mafic rocks were completely dissolved. 1mL of 6M HCl was then added to the residues and evaporated to dryness. When cool, the residues were dissolved in 1.0 mL of 3.5 M HNO_3 + 0.23 M H_3BO_3 mixture. The capsule was then sealed and placed on a 120 °C hot plate overnight prior to chemical separation.

2.2. Column chemistry

Each sample solution was loaded into the Sr Spec resin and TODGA Spec resin columns arranged in tandem (Fig 1 and Table 1). Before sample loading, the tandem column was pre-washed in turn with 10 mL of 7 M HNO_3, 5 mL of H_2O, and 5 mL of 3.5 M HNO_3+0.23 M H_3BO_3 mixture. As shown in Table 1, after complete draining of the sample solution(1 mL), tandem Sr and TODGA Spec columns were rinsed four times with 0.5 mL of 3.5 M HNO_3. At this stage, most Rb, K, Na, Al, Ti, Fe, Mg (>98%) and Ba (>98%) passed through both the Sr and TODGA Spec columns. Sr and Pb were strongly retained into the Sr Spec column, and the REEs enriched in Nd and Hf were strongly retained into the TODGA Spec column. The TODGA Spec column absorbed significant matrix element (Ca), whereas only minor matrix elements (Ba and Fe) and minor Rb were retained into the Sr Spec column. Then, the two columns were decoupled and further processed separately (Table 1 and Fig. 1).

Firstly, Sr and Pb fraction was stripped from the Sr Spec column. The Sr Spec column was washed with 3 mL of 3.5 M HNO_3. Minor matrix elements and all Rb were removed during this step. Minor Sr (~ 8.1 %) was also washed out in this step. Then, the Sr fraction, containing ~ 89.8 % of Sr, was stripped with 5.5 mL of 0.05 M HNO_3. Finally, most Pb (~93.4 %) fraction was then stripped with 2 mL of 8 M HCl.

Secondly, we stripped Hf and Nd fraction from the TODGA Spec column. Minor residual matrix (≤2 %) elements (Mg, Na, Fe, Ti, K, Al) and significant amounts of Ca (~33 %) were removed with 20 mL of 3.5 M HNO_3. Then, the remaining Ca (~39 %) was completely washed with 10 mL of 12 M HCl. The Hf fraction, containing ~ 97.3 % of Hf, is stripped with 25 mL of 3.5 M HNO_3 + 1 M HF mixture. Finally, the LREEs containing the Nd fraction (~98.2 %) was stripped with 10 mL of 0.4 M HCl. All Yb, Lu and other HREEs were washed out with 10 mL of 0.04 M HCl.

To eliminate potential interference from minor organic materials in the Sr Spec and TODGA Spec columns that affect the TIMS measurements,[5, 27] the Sr fraction, the LREEs fraction-enriched in Nd, the Hf fraction, and the Pb fraction were first evaporated to dryness, and then digested using 0.3 ml of 14 M HNO_3 on a 180°C hotplate for 1.5 hours in closed PFA vials. Finally, the digested Sr-Nd-Pb fractions were dried at approximately 150°C again prior to TIMS measurements. The Hf fraction was evaporated to dryness on a hotplate at 120°C, taken up in 0.1 mL of 0.5 M HF + 0.8 mL of 3.5 M HNO_3, and then was ready for MC-ICP-MS analysis. The complete separation procedure, including pre-cleaning of the columns, took approximately 8 hours for 25 samples or approximately 75 % less time compared with conventional four-step column chemistry.

2.3 Thermal ionization mass spectrometry for Sr, Nd and Pb isotopic analysis

Sr, Nd and Pb isotopic compositions were measured using a Triton Plus (ThermoFisher) at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS) in Beijing. All Sr, Nd and Pb data were acquired by static multi-collection with the collector array illustrated in Table 2. To eliminate all gain calibration errors, amplifier gains were calibrated at the start of each day. Before the commencement of the analysis, a peak-center routine was run, and then, the baseline was measured. Single Re filament geometry was used to obtain Sr^+ and Pb^+ ion beams. Double Re filament geometry was employed to obtain the Nd^+ ion beam. Each run consisted of 140~180 cycles that were divided into 7~9 blocks. Detail sample loading and TIMS measurement conditions for Sr, Nd and Pb isotope ratios were reported in our previous investigations.[5,6] The $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios were normalized using $^{88}Sr/^{86}Sr = 8.375209$ and $^{146}Nd/^{144}Nd = 0.7219$ for mass bias correction using the exponential law. Standards NBS-987, NBS-981 and JNdi-1 were analyzed during the sample measurement period to monitor instrument status. The NBS-987 standard gave a mean $^{87}Sr/^{86}Sr$ of 0.710245 ± 11(2 SD, n = 5), and the JNdi-1 standard gave a mean $^{143}Nd/^{144}Nd$ of 0.512109 ± 8 (2 SD, n = 5). The NBS-981 standard gave a mean $^{206}Pb/^{204}Pb$ of 16.934 ± 0.003, $^{207}Pb/^{204}Pb$ of 15.484 ± 0.003, $^{207}Pb/^{206}Pb$ of 0.9144 ±

0.0002 and $^{208}Pb/^{204}Pb$ of 36.682 ± 0.011 (n = 5). All NBS-987, NBS981, and JNdi-1 standards were in good agreement with previously reported values[4-7, 11-14, 16-22, 24-32] within error.

2.4 MC-ICP-MS for Hf isotopic analysis

Hf isotopic ratios were measured using a Thermo Scientific Neptune Plus MC-ICP-MS at the IGGCAS. Analyses were performed in the static mode and cup configurations were shown in Table 2. Typical operating parameters for Hf measurement using Neptune Plus were reported by Yang et al.[12, 44] Each run consisted of a baseline measurement and collections of 96~108 cycles that were divided into 8~9 blocks. The integration time was 4 s, and the typical time of one measurement was ~ 11 min. Isobaric interferences of ^{176}Yb and ^{176}Lu on ^{176}Hf were monitored by ^{172}Yb, ^{173}Yb, and ^{175}Lu. The effects of these interferences were corrected on-line using the following values for the stable ratios: $^{176}Yb/^{173}Yb = 0.79323$ and $^{176}Lu/^{175}Lu = 0.026528$. After column chemistry, Lu/Hf and Yb/Hf ratios were generally $\leq 1\times10^{-5}$ in natural silicate samples, showing no significant difference in ratios before and after interference correction. After subtraction of the isobaric interferences, the $^{176}Hf/^{177}Hf$ ratio was normalized to $^{179}Hf/^{177}Hf = 0.7325$ for mass bias correction using the exponential law. To examine the accuracy of Hf measurement by MC-ICP-MS, samples presented here were interspersed with analyses of the JMC-475 Hf standard. In this study, 100 ppb of JMC-475 yielded a value of 0.282149 ± 14 (2 SD, n = 4), which was slightly lower than the recommended the well-accepted JMC-475 value of

0.282160. Hence, all measured ^{176}Hf/^{177}Hf ratios of silicate samples were normalized to the well-accepted JMC-475 value of 0.282160.[9, 12, 36, 41, 44]

3. Results and discussion

3.1 Separation protocol using tandem columns

To avoid matrix and isobaric interference effects, efficient chemical separation of Sr, Nd, Pb, and Hf from silicate samples is required. Previous studies[25, 27] have revealed that the Sr Spec resin is an excellent resin for separating Sr and Pb from rock matrix solution. In relatively strong concentrations (≥ 3M) of HNO_3 acid, [4, 19, 27] Sr and Pb are retained in Sr Spec resin and few matrix elements are retained. Similarly, the selectivity of TODGA spec resin[40, 43] allows the efficient separation of Hf, LREEs, and HREEs from complex rock matrixes using HNO_3 or HCl. In different concentrations of HNO_3 or HCl acid, Ca, Fe, Ti, LREEs, HREEs, and Hf are variably retained in TODGA Spec resin.[43] Hence, it is possible to separate Sr, Nd, Pb, and Hf fractions from silicate matrix solution in sequence using the tandem columns separation procedure, as long as further optimization of both Sr Spec and TODGA Spec resins is undertaken as described below.

To obtain strong absorption of Hf in TODGA Spec resin, TODGA Spec resin is commonly preconditioned[40] using a mixture of HNO_3 + H_3BO_3. To obtain the best yield of Sr and Pb, previous investigations have documented that the Sr and Pb can be strongly retained in Sr Spec resin in pure HNO_3 acid media rather than the mixture of HNO_3 + H_3BO_3. Thus, the question whether or not the Sr and Pb can be also strongly retained in the Sr Spec resin in the mixture of $HNO_3 + H_3BO_3$ media is unclear. To directly address this issue, 100 mg of BCR-2 in 1 mL of mixture of 3.5M HNO_3 + 0.23M H_3BO_3 was loaded into the Sr Spec resin column and all fractions from the loading sample and the washing columns were collected. Before back-extracted Sr and Pb factions, only ~10 % of Sr and ~7 % of Pb were lost. Thus, in contrast to pure HNO_3 acid media, the yield of Sr using a mixture of 3.5M HNO_3 + 0.23M H_3BO_3 loading seems slightly low. Considering conventional silicate sample digestion size (≥ 100 mg), it is easy to obtain a sufficient sample size (≥ 50 ng) of Sr and Pb for TIMS measurements. Hence, a slightly low yield of Sr is acceptable for TIMS measurements.

The order of the resin setup is a crucial consideration. It is similar to the scheme presented by Pourmand[46] which is devised to purify Sr-Nd-Hf. Pourmand[46] employs a special vacuum box equipped with a pneumatic pressure regulator to perform Sr-Nd-Hf chemical separation and give a quick eluting speed. In our case, it is no need to prepare a special vacuum box because the eluting speed in our column with a 5mm internal diameter is quick and all operations are convenient. As shown in Figure 1, our columns containing 0.40 mL of Sr Spec and 0.80 mL of TODGA Spec resins were used as the top and bottom layers, respectively. By reversing the setup order of the Sr Spec and TODGA Spec resins, Pb passed through the TODGA Spec resin and was retained into the Sr Spec resin column. However, Sr and Ca are first absorbed on the TODGA Spec resin. In order to wash out Sr from the TODGA Spec rein, at least, 10 mL of high concentration (≥ 10 M) of HNO_3 should be employed.

Then, Sr is retained into the Sr Spec resin. However, some matrix elements (Ca, Fe) are also gradually washed out from TODGA Spec resin and absorbed into the Sr Spec resin. In order to obtain high purity Sr and Pb, more HNO_3 acid should be used to eliminate these matrix element effects. Hence, an imperfect column setup will result in a long chemical procedure for Sr and Pb separation and rising procedure blanks of Sr and Pb.

The concentration of HNO_3 is crucial as the main eluting reagent. Strong HNO_3 acid is necessary to strongly retain Sr-Pb on the Sr Spec resin, and Hf-Nd on the TODGA Spec resin. Hence, using strong HNO_3 acid as the loading and rinsing reagent is crucial to obtain a high yield of Sr, Nd, Pb and Hf. However, strong HNO_3 acid hamper the rinsing of Ti and Fe from the TODGA Spec resin due to the fact that the distribution coefficient (K_d) value of Ti and Fe is significant elevated with increasing concentration of HNO_3.[43] Hence, to quickly wash out Ti and Fe from TODGA Spec resin, several HNO_3 concentrations (e.g., 3~5 M) were tested to check which concentration of HNO_3 acid shows the best performance to remove the matrix elements. After many experimental analyses, we found that moderately strong concentration (3.5 M) of HNO_3 is most suitable to quickly remove Fe and Ti before back-extraction of Nd and Hf from TODGA Spec resin.

In addition, a mixture of HF +HNO_3 acid was employed as eluting reagent in previous investigations[40, 43] to get a satisfactory yield of Hf and back-extract Hf quickly. These studies recommend weak HF (0.2~0.5 M) acid as the eluting reagent for stripping Hf from TODGA Spec resin. However, our study shows that a large eluting volume is required to achieve a high yield of Hf when using weak HF (0.2~0.5M) acid. To give a quick eluting Hf, Pourmand[46] employ a hot mixture solution (1M HNO_3 + 0.2M HF) as eluting reagent. In spite of good yield of Hf is obtained, the mixture solution must be preheated to 70°C and eluting Hf step should be performed in ambient temperature of 90°C. Hence, it is inconvenient and unfriendly for most users who need pre-heat eluting reagent and keep a good temperature control for eluting solution (70°C) and ambient (90°C) in a special vacuum box. Hence, it is necessary to search the most suitable eluting reagent for Hf from TODGA resin. The effect of variation proportion of HNO_3 versus HF in the mixture, such as 3.5M HNO_3 + 0.3 M HF, 3.5M HNO_3 + 0.5 M HF, 3.5M HNO_3 + 1 M HF, 4.5M HNO_3+ 0.5 M HF and 4.5M HNO_3 + 1 M HF, on the yield of Hf and back-extraction of Hf were further examined. This study showed that the 3.5M HNO_3+ 1 M HF mixture is the optimal eluting reagent to obtain a satisfactory yield and purity of Hf. Thus, the concentration of HF acid in the mixture of HNO_3+HF should be higher than 1M otherwise it is difficult to elute Hf quickly.

3.2 Purity, recovery, blank and memory effect

To investigate the behavior of matrix and trace elements retained in the tandem columns, a basalt standard (BCR-2) was employed. A 100 mg aliquot of BCR-2 was dissolved and loaded onto the tandem columns. Strontium, Pb, Hf and Nd fractions were collected following the procedure described in Table 1. Semi-quantitative trace element analyses were performed using a Thermo Fisher Element-XR ICP-MS. Strontium, Pb and Hf fractions showed very high sample purity. Lanthanum, Ce, Pr, Sm were also co-existed in Nd fraction. In spite of the ^{144}Sm isobaric interference exists in TIMS analysis, it is easy to correct using our previously reported method.[18]

In summary, the yield of Sr, Nd, Pb and Hf fractions was good at 89.8 %, 98.2 %, 93.4 %, and 97.3 %, respectively. Procedural blanks are crucial for accurate Sr-Nd-Pb-Hf isotope analysis. In this study, blank values of 30~40, 50~60, 110~130, and 55~65 pg were obtained for Sr, Nd, Pb, and Hf, respectively. Bearing in mind that amounts of analytes processed were 1.3~7.9 μg for Sr, 0.3~3.4 μg for Nd, 0.15~3.1 μg for Pb, 0.08~0.6 μg for Hf, respectively, the contribution of analytical contamination to the separated analytes was negligible. Previous studies show significant memory effect when re-using Sr Spec resin.[5, 25] To eliminate the "memory effect" and obtain the lowest blank, fresh Sr and TODGA Spec resins are recommended to use especially for samples with low concentration of Sr, Nd, Pb, Hf.

3.3 Validation of the method and final results

To examine the analytical reproducibility and feasibility of our procedure for silicate samples, eight CRMs were selected to encompass a wide range of matrix compositions, and analyte concentrations were determined. During Sr, Nd and Hf isotope analyses, as shown in Table 3, the ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf ratios of all analyzed USGS and GSJ reference materials were obtained with an internal precision better than 0.005 % (2 RSE), most internal precision was better than 0.003 % (2 RSE) . For Pb isotope analysis, as shown in Table 4, ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios of all analyzed USGS and GSJ reference materials were obtained with an internal precision better than 0.01 % (2 RSE). Average values of $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{176}Hf/^{177}Hf$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ in the present study agreed well with previously published data[4-7, 10-14, 16, 18, 20-22, 24-26, 28-32, 35, 36, 39-41, 44] obtained using TIMS or MC-ICP-MS. Currently the reference value of the $^{176}Hf/^{177}Hf$ ratio of JG-1a is not available. In this study, we provide the first the high precision $^{176}Hf/^{177}Hf$ value for JG-1a.

During $^{143}Nd/^{144}Nd$ ratio determination, the analyte was a LREEs mixture instead of high-purity Nd. Thus, to further examine whether ^{144}Sm can be accurately subtracted from mixed signals of 144($^{144}Sm+^{144}Nd$), the $^{145}Nd/^{144}Nd$ ratio of silicate samples was also measured and corrected following the previously reported method[18]. As shown in Table 3 and Fig 2, the corrected $^{145}Nd/^{144}Nd$ value is 0.348406 ± 0.000006 (2 SD, n = 22) in actual silicate samples, which agrees well with reported values of 0.348405 ± 0.000015.[4-6, 11, 17, 18, 20, 22] The obtained data imply that the ^{144}Sm isobaric interference can be accurately subtracted.

The BCR-2 CRM has an excellent homogeneity and is widely used to monitor the quality of chemical procedures and the instrumental status in many geochemical laboratories. Hence, in this study, we employed BCR-2 to verify the stability of the procedure. The reproducibility was demonstrated by eight different dissolutions of BCR-2 powder materials. As shown in Table 3, eight replicate measurements of BCR-2 yielded a $^{87}Sr/^{86}Sr$ value of 0.705004 ± 0.000018 (2 SD), a $^{143}Nd/^{144}Nd$ value of 0.512630 ± 0.000010 (2 SD), and a $^{176}Hf/^{177}Hf$ value of 0.282871 ± 0.000014 (2 SD). Strontium, Nd and Hf isotope data of BCR-2 were thus consistent with reported values.[5, 6, 11, 12, 17, 18, 20-22, 34-36, 40] The external reproducibility of the $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, and $^{176}Hf/^{177}Hf$ ratios of BCR-2 were better than ± 0.0026 % (2 RSD), ± 0.0020 % (2 RSD), and ± 0.0049 % (2 RSD), respectively. As shown in Table 4, eight replicate measurements of BCR-2 yielded $^{206}Pb/^{204}Pb$ value of 18.758 ± 0.006 (2 SD), $^{207}Pb/^{204}Pb$ value of 15.624 ± 0.004 (2 SD) and $^{208}Pb/^{204}Pb$ value of 38.721 ± 0.013 (2 SD). Pb isotope data of BCR-2 were consistent with the reported values.[5, 11, 26, 29, 31] The external reproducibility of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ from BCR-2 was 0.027~0.034 % (2 RSD).

Overall, the data reproducibility and precision of the proposed method is satisfactory and completely fills the demands of geochemistry and petrology.

4. Conclusions

A rapid and robust tandem chemical separation procedure was developed for measuring $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{176}Hf/^{177}Hf$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ isotope ratios in the same sample digest. Sr, Pb, and Nd, Hf were sequentially separated from the same rock matrix solution using tandem columns packed with Sr Spec resin and TODGA Spec resin without the need for intervening evaporation. The chemical separation scheme is based on the enhanced elemental selectivity permitted by the Sr Spec and TODGA Spec resins. The proposed separation procedure achieved both the satisfactory and rapid separation of Sr, Pb, Nd, and Hf and reduced cross-contamination, thereby offering significant advantages over existing methods in terms of simplicity, separation efficiency and waste reduction. High separation performance was examined by analysing a series of reference silicate rock samples. The bottleneck associated with sample preparation prior to TIMS and MC-ICP-MS measurements can be significantly reduced using the new protocol.

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Figure captions

Fig 1. Tandem column separation scheme in this study compared with the traditional four columns separation procedure

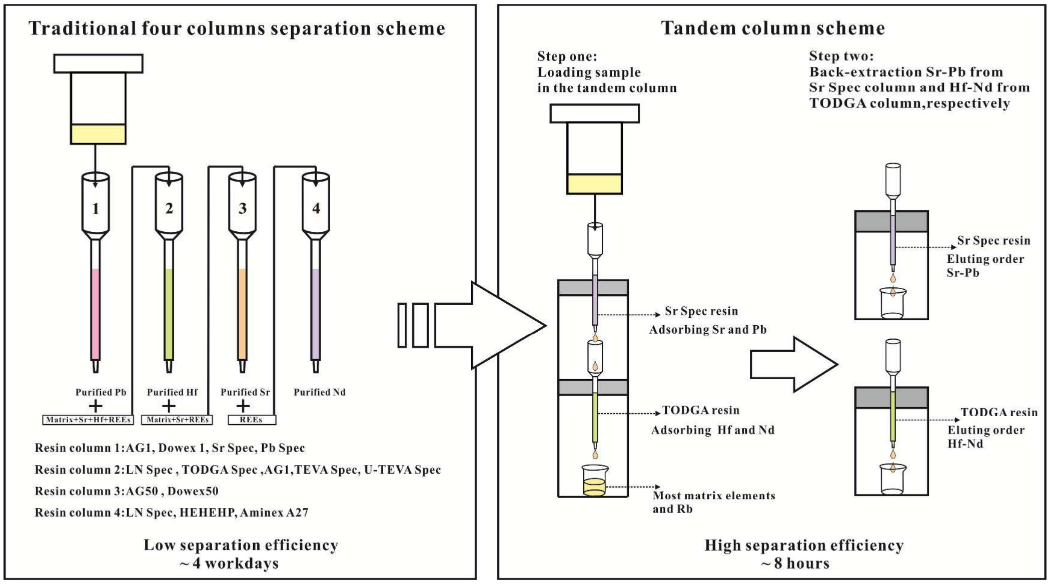

Fig 2. Corrected ^{145}Nd/^{144}Nd ratios for silicate rock from USGS and GSJ.

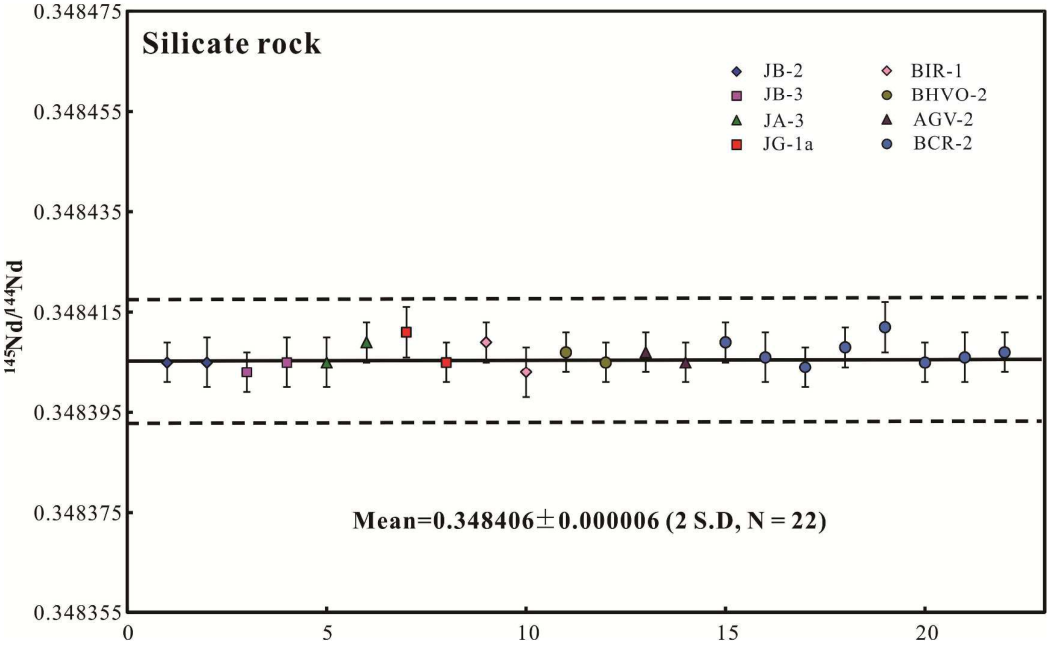

Table 1. The separation scheme enabling the successive isolation of Sr, Pb, and Nd, Hf by tandem extraction chromatography without intervening evaporations.

Procedure	Reagents	Eluting Volume(mL)
Tandem column pre-cleaning and sample loading		
Cleaning column	7M HNO_3	10
Cleaning column	Millipore water	5
Pre-conditioning column	3.5M HNO_3 +0.23M H_3BO_3	5
Sample loading	3.5M HNO_3 +0.23M H_3BO_3	1
Rinsing matrix	3.5M HNO_3	2(0.5×4)
Decoupling Sr and Pb from the Sr Spec resin column		
Rinsing matrix	3.5M HNO_3	3
Eluing Sr	0.05M HNO_3	5.5
Eluing Pb	8M HCl	2
Decoupling Nd and Hf from the TODGA Spec resin column		
Rinsing matrix	3.5M HNO_3	20
Rinsing matrix	12M HNO_3	10
Eluing Hf	3.5M HNO_3 +1M HF	25
Eluing LREEs enriched Nd	0.4M HCl	10
Rinsing Lu,Yb and other HREEs	0.04M HCl	10

Comment: The yield of Sr, Pb, Hf, and Nd is approximately 89.8 %, 93.4 %, 97.3 %, and 98.2 %, respectively.

Table 2.Cup configuration for Sr-Nd-Pb isotope analysis using Triton plus TIMS and for Hf isotope analysis using Neptune plus MC-ICP-MS

Element	L4	L3	L2	L1	CC	H1	H2	H3	H4
Sr			^{84}Sr	^{85}Rb	^{86}Sr	^{87}Sr	^{88}Sr		
Nd	^{143}Nd	^{144}Nd+^{144}Sm	^{145}Nd	^{146}Nd	^{147}Sm	^{149}Sm			
Pb					^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb	
Hf	^{172}Yb	^{173}Yb	^{175}Lu	^{176}Hf	^{177}Hf	^{178}Hf	^{179}Hf	^{180}Hf	^{182}W

Table 3. Comparison of Sr, Nd, and Hf isotopic ratios in this study with reported values for CRMs

CRMs	$^{87}Sr/^{86}Sr$ (±2 SE)	Refs values	$^{145}Nd/^{144}Nd$ (±2 SE)	$^{143}Nd/^{144}Nd$ (±2 SE)	Refs values	$^{176}Hf/^{177}Hf$ (±2 SE)	Refs value
BIR-1	0.703112(8)	0.703104[4]; 0.703105[5]	0.348409(4)	0.513099(7)	0.513078[4]; 0.513092[5]	0.283263 (14)	0.283288[6]; 0.283268[34]
BIR-1	0.703090(12)	0.703116[6]; 0.703104[22]	0.348403(5)	0.513092 (8)	0.513101[6]; 0.513107[21]	0.283275 (14)	0.283277[36]; 0.283265[39]
Mean	0.703101	0.703107	0.348406	0.513096	0.513095	0.283269	0.283275
JB-2	0.703678(10)	0.703675[4];0.703691[5]	0.348405(4)	0.513098(6)	0.513094[4]; 0.513096[5]	0.283258 (8)	0.283246[12];0.283287[39]
JB-2	0.703670(9)	0.703671[12]; 0.703668[14]	0.348405(5)	0.513100 (6)	0.513102[12]; 0.513090[14]	0.283238 (12)	0.283244[41]
Mean	0.703674	0.703676	0.348405	0.513099	0.513096	0.283248	0.283259
JB-3	0.703420(11)	0.703422[4];0.703435[5]	0.348403(4)	0.513056(6)	0.513049[4];0.513056[5]	0.283242 (10)	0.283223[9];0.283222[12]
JB-3	0.703421(9)	0.703396[12];0.703432[13]	0.348405(5)	0.513058 (6)	0.513064[12];0.513056[13]	0.283248 (8)	0.283249[39]; 0.283223[41]
Mean	0.703421	0.703421	0.348404	0.513057	0.513056	0.283245	0.283229
JA-3	0.704170(10)	0.704171[5]; 0.704160[14]	0.348405(5)	0.512850(5)	0.512846[6];0.512859[14]	0.283082 (10)	0.283052[6]; 0.283084[39]
JA-3	0.704157(6)	0.704177[22]	0.348409(4)	0.512860 (6)	0.512859[20];0.512852[22]	0.283088 (8)	0.283063[41]; 0.283067[42]
Mean	0.704164	0.704169	0.348407	0.512855	0.512854	0.283085	0.283067
JG-1a	0.710951(10)	0.710981[13]; 0.710970[14]	0.348411(5)	0.512376(7)	0.512365[13]; 0.512383[14]	0.282741 (10)	No data
JG-1a	0.710975(11)		0.348405(4)	0.512384 (6)	0.512374[18]	0.282736 (8)	
Mean	0.710963	0.704175	0.348408	0.512380	0.512374	0.282739	
BHVO-2	0.703466(11)	0.703479[5];0.703487[11]	0.348407(4)	0.512979(6)	0.512984[11];0.512983[20]	0.283110 (8)	0.283096[7]; 0.283116[36]

BHVO-2	0.703470(8)	0.703479[22]	0.348405(4)	0.512987(5)	0.512988[22]; 0.512978[17]	0.283106 (8)	0.283105[42]; 0.283094[44]
Mean	0.703468	0.703482	0.348406	0.512983	0.512983	0.283108	0.283103
AGV-2	0.703977(12)	0.703979[5]; 0.703981[11]	0.348403(4)	0.512794(7)	0.512788[5]; 0.512791[11]	0.282984 (8)	0.282966[12],0.282961[42]
AGV-2	0.703965(12)	0.703978[12]	0.348405(4)	0.512789(6)	0.512781[12]; 0.512797[20]	0.282976 (8)	
Mean	0.703971	0.703979	0.348404	0.512792	0.512789	0.282980	0.282964
BCR-2	0.704997 (11)	0.705015[5]; 0.705010[6]	0.348409(4)	0.512633(6)	0.512635[5]; 0.512634[6]	0.282877 (10)	0.282885[6]; 0.282877[12]
BCR-2	0.704999(12)	0.705018[11]; 0.705023[12]	0.348406(5)	0.512633(6)	0.512637[11]; 0.512640[12]	0.282880 (10)	0.282884[34]; 0.282859[35]
BCR-2	0.705010(11)	0.705026[22]	0.348404(4)	0.512630(6)	0.512638[17]; 0.512636[18]	0.282876 (10)	0.282875[36]; 0.282869[40]
BCR-2	0.705004(10)		0.348408(4)	0.512627(6)	0.512638[20]; 0.512641[21]	0.282873 (12)	
BCR-2	0.705000(11)		0.348412(5)	0.512630(7)	0.512636[22]	0.282862 (12)	
BCR-2	0.705005(10)		0.348405(4)	0.512634(6)		0.282870 (13)	
BCR-2	0.705023(11)		0.348406(5)	0.512622(6)		0.282863 (10)	
BCR-2	0.704995(13)		0.348407(4)	0.512629(5)		0.282865 (14)	
Mean ± 2 SD	0.705004(18)	0.705018	0.348407(5)	0.512630(10)	0.512637	0.282871 (14)	0.282875

Table 4. Comparison of Pb isotopic ratios in this study with reported values for CRMs

CRMs	^{206}Pb/^{204}Pb (±2 SE)	Reported values	^{207}Pb/^{204}Pb (±2 SE)	Reported values	^{208}Pb/^{204}Pb (±2 SE)	Reported values
BIR-1	18.8566(6)	18.8533[4]; 18.841[5]	15.6484(6)	15.6585[4]; 15.655[5]	38.4901(17)	38.4968[4]; 38.484[5]
BIR-1	18.8586(5)	18.842[29]; 18.851[31]	15.6534(4)	15.641[29]; 15.662[31]	38.5040(12)	38.449[29]; 38.501[31]
Mean	18.8576	18.847	15.6509	15.654	38.4970	38.483
JB-2	18.3478(5)	18.3428[4]; 18.341[5]	15.5469(4)	15.5594[4]; 15.560[5]	38.2669(11)	38.2770[4]; 38.267[5]
JB-2	18.3495(6)	18.3436[30];18.3416[32]	15.5513(6)	15.5624[30];15.5658[32]	38.2726(16)	38.2786[30]; 38.276[32]
Mean	18.3487	18.342	15.5491	15.562	38.2698	38.275
JB-3	18.2993(7)	18.2952[4]; 18.290[5]	15.5259(6)	15.5356[4]; 15.531[5]	38.2442(16)	38.2506[4]; 38.232[5]
JB-3	18.3001(4)	18.2958[30]; 18.2910[32]	15.5257(4)	15.5389[30]; 15.5403[32]	38.2440(9)	38.2540[30]; 38.250[32]
Mean	18.2997	18.293	15.5258	15.536	38.2441	38.247
JA-3	18.3359(5)	18.3290[30]; 18.3263[32]	15.5585(5)	15.5701[30]; 15.5719[32]	38.4257(15)	38.4282[30]; 38.428[32]
JA-3	18.3355(4)		15.5561(4)		38.4170(10)	
Mean	18.3357	18.328	15.5573	15.571	38.4213	38.428
JG-1a	18.6223(3)	18.6177[30]; 18.6442[32]	15.6140(3)	15.6265[30]; 15.6257[32]	38.7793(7)	38.7425[30]; 38.761[32]
JG-1a	18.6240(4)		15.6123(3)		38.7421(8)	
Mean	18.6231	18.631	15.6131	15.626	38.7607	38.752
BHVO-2	18.6765(6)	18.638[4]; 18.6474[11]	15.5249(6)	15.539[4]; 15.5334[11]	38.2513(18)	38.237[4]; 38.2367[11]
BHVO-2	18.6278(6)	18.641[26]; 18.649[31]	15.5589(6)	15.538[26]; 15.540[31]	38.2751(22)	38.228[26]; 38.249[31]

Mean	18.6522	18.644	15.5419	15.538	38.2632	38.238
AGV-2	18.8781(4)	18.869[5]; 18.8474[11]	15.6116(3)	15.620[5]; 15.6173[11]	38.5497(8)	38.540[5]; 38.5443[11]
AGV-2	18.8784(4)	18.879[29]; 18.873[31]	15.6111(4)	15.618[29]; 15.617[31]	38.5477(9)	38.547[29]; 38.552[31]
Mean	18.8783	18.867	15.6114	15.618	38.5487	38.546
BCR-2	18.7546(4)	18.752[5];18.7529[11]	15.6247(3)	15.620[5];15.6249[11]	38.7207(8)	38.715[5];38.7237[11]
BCR-2	18.7587(3)	18.750[26]; 18.760[29]	15.6225(2)	15.615[26]; 15.621[29]	38.7204(6)	38.691[26]; 38.731[29]
BCR-2	18.7568(4)	18.765[31]	15.6241(3)	15.628[31]	38.7160(9)	38.752[31]
BCR-2	18.7631(3)		15.6234(2)		38.7200(6)	
BCR-2	18.7613(4)		15.6241(3)		38.7261(7)	
BCR-2	18.7587(4)		15.6244(3)		38.7332(7)	
BCR-2	18.7549(3)		15.6207(3)		38.7109(8)	
BCR-2	18.7595(4)		15.6266(3)		38.7228(8)	
Mean ± 2 SD	18.758(6)	18.760	15.624(4)	15.622	38.721(13)	38.723