Single-step separation scheme and high-precision isotopic ratios analysis of Sr-Nd-Hf in silicate materials

Chao-Feng Li[a]* **Jing-Hui Guo[a]** **Yue-Heng Yang[a]**

Zhu-Yin Chu[a] **Xuan-Ce Wang[b]**

[a]State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

[b]The institute for Geoscience Research (TIGer), Curtin University, GPO Box U1987, Perth, WA6845, Australia

*Corresponding author: Chao-Feng Li

E-mail address: cfli@mail.iggcas.ac.cn

Tel: +86-10-82998583

Abstract:

Thermal ionization mass spectrometry and multiple-collector inductively coupled plasma mass spectrometry are considered “gold standards” for determining the isotope ratios of Sr–Nd and Hf in geological samples because of the extremely high precision and accuracy of these methods. However, the sample throughputs are hindered by time-consuming and tedious chemical procedures. Three-step ion exchange resin separation is traditionally employed to purify Sr-Nd-Hf from matrix elements. In this study, a one-step Sr-Nd-Hf separation scheme is developed to process geological samples. The separation scheme is based on the combined use of conventional AG50W-X12 cation-exchange resin and LN Spec extraction chromatographic material without any intervening evaporation step. The protocol not only prevents cross-contamination during operation using multiple-stage ion exchange resins but also significantly improves the efficiency of sample preparation. The stability of our chemical procedure is demonstrated through replicate measurements of $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, and $^{176}Hf/^{177}Hf$ ratios in six international reference materials of silicate rocks. The analytical results obtained for these standard rocks well agree with the published data. The external reproducibility (2 SD, n = 10) of a BCR-2 standard sample was ±0.000018 for $^{87}Sr/^{86}Sr$, ±0.000010 for $^{143}Nd/^{144}Nd$, and ± 0.000014 for $^{176}Hf/^{177}Hf$.

Keywords: Sr-Nd-Hf isotope ratios; Single-step separation; TIMS; MC-ICP-MS

1. Introduction

$^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ ratios, which show variations by radioactive decay of long half life isotopes of ^{87}Rb, ^{147}Sm and ^{176}Lu, respectively, are routinely used for geochemistry as petro-genetic tracers, yielding information on time-integrated elemental fractionation through processes of melting, crystallization, metasomatism, and contamination.[1] In particular, the combination of radiogenic Sr-Nd-Hf isotope systems has become a more powerful tool for understanding fundamental Earth processes as well as the Earth's evolution. Thus, conducting multi-isotopic analyses (e.g., Sr-Nd-Hf) is critical on the same sample.

Thermal ionization source mass spectrometry (TIMS) and multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) both possess high accuracy, excellent sensitivity, and low memory. The methods are regarded as benchmark techniques for Sr-Nd and Hf isotopic ratio analysis and widely used in Earth science.[2-12] However, to obtain stable and high intensity of ion signals during TIMS and MC-ICP-MS measurements, Sr-Nd-Hf elements must be separated from sample matrices and be as clean as possible. Purification of Sr-Nd-Hf prior to mass spectrometric measurement is traditionally accomplished by using at least three-column chromatography after a single sample digestion.[13-14] The first stage involves the separation of Hf from other elements using an anion resin[15] or a special resin column, such as LN resin[13, 16], U-TEVA resin[12, 14], TEVA[8, 17], or TODGA resin.[10] The discard from the first column is then dried and dissolved using HCl or HNO_3. Subsequently, Sr and rare earth elements (REEs) are separated from the matrix elements using a second cation exchange resin column, such as a AG50W resin column.[2, 5-7, 11, 13, 14, 18, 19] Finally, Nd is separated from the REEs using a third resin column, such as HDEHP resin column,[2, 4-6, 11, 13, 14, 18-20] HEHEHP resin column[7], A25 resin column and A27 resin column.[21] Traditional three-step separation procedures involve tedious pre-cleaning of the column and fraction evaporation. The traditional multi-step chemical procedure takes at least three days to complete and large amounts of reagents upon completion of column chemistry for a batch of geological samples (e.g., 20~30 samples). Thus, the separation efficiency is low for traditional methods and the sample throughput is impeded. In addition, traditional methods increase the probability of contamination from cross-operation in column chemistry associated with complex operation steps.

To the best of our knowledge, no available literature has reported the use of analytical protocols to concomitantly separate Sr-Nd-Hf fractions from a single sample digest using a one-step separation method. Yang[22] and Li[23] recently presented a method to precisely determine Nd isotopic ratios from the REEs using MC-ICP-MS and TIMS. Based on this method, the traditional two-step Nd separation method was simplified to a one-step procedure. More importantly, the method allowed Sr-Nd-Hf isotopic determination using TIMS and MC-ICP-MS so long as high-purity Sr, REE-enriched Nd, and Hf could be achieved. To this end, we present a one-column separation procedure based on optimization of mixed cation resins (AG50W-X12 + LN Spec).

The present study aims to reduce their rather extensive and costly cleaning and separation procedures for resin and columns without negatively affecting the data quality. This one-step separation route of obtaining Sr-Nd-Hf from a single dissolution enables higher throughput for data acquisition by TIMS and MC-ICP-MS. To verify the robustness of the new separation protocol for Sr-Nd-Hf, six certified reference materials (CRMs) of silicate rocks, encompassing a wide range of matrix compositions and analyte concentrations, were analyzed.

2. Experimental

2.1 Reagents, chemicals materials and standards

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

Acids and water: All AR grade acids (hydrochloric acid, nitric acid and hydrofluoric acid) were further purified using Savillex^{TM} DST-1000 sub-boiling distillation system (Minnetonka, USA). Phosphate acid was purified using chromatographic method of AG50W-X12 resin manufactured by the Bio-Rad company. Ultrapure water with a resistivity (18.25 MΩ.cm^{-1}) was obtained from a Milli-Q Element system (Millipore, USA) and used throughout this work for diluting concentrated acids.

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

Resin: Commercially available cation (AG50W-X12, 200-400 mesh size) and LN Spec resin (100-150 μm) were obtained from Bio-Rad company and Eichrom company.

Column: The cation-exchange polypropylene column was 7 cm long and had a 6 mm i.d. and 5 mL reservoir. The column was packed with 1.5 mL of Bio-Rad AG50W-X12 resin and 0.45 mL of LN Spe resin.

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

Labwares: The labware used included 15 and 7.0 mL PFA Teflon vials with screw top lids (Savillex Corporation, USA). The vials were used for sample digestion, solution collection, and evaporation and cleaned prior to use with a degreasing agent followed by sequential washing in AR grade HNO_3, HCl, and ultra-pure H_2O.

2.2 Sample digestion

It was critical to achieve full recovery of Sr-Nd-Hf. Especially for Hf isotopic ratio analysis, a critical point was the common occurrence of Zr + Hf-rich refractory minerals, such as zircon, baddeleyite and garnet, which might host a major proportion of the hafnium contained in the bulk rock. In previous studies, two digestion methods were widely used in digestion geological samples:HF-HNO_3-$HClO_4$ mixture dissolutions based on high-pressure PTFE bomb devices[8, 11, 13, 15] and Lithium metaborate or Na_2O_2 flux melting methods.[10, 12, 24] The flux melting method had the advantages of being rapid and ensuring full sample digestion regardless of mineralogy or composition. However, the procedural blanks were high especially for Nd (~0.37 ng[24], ~1.5 ng[9]). The HF-HNO_3-$HClO_4$ mixture dissolutions based on high-pressure PTFE bomb devices had the advantages of lower blanks. Furthermore, most isotope laboratories had all the necessary equipments and experiences to immediately initiate this method. It has the disadvantages of being slow (2~3 days). Considering the potential blank effect from flux reagents, we adopt the dissolutions of HF-HNO_3-$HClO_4$ mixture in this study.

All chemical preparations were conducted on special class 100 work benches inside a class 1000 clean laboratory. Approximately 50~60 mg of rock powder materials were weighed into a steel-jacketed acid-washed high-pressure PTFE bomb. The samples were dissolved on a hotplate at 190 ^{o}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 11.8 M $HClO_4$ for 5 days. Usually, 2 ~3 days digestions were sufficient for most silicate samples. To obtain perfect sample digestion, we prolonged the digestion time to 5 days in this study. All samples were completely digested in this study. Digested samples were dried on a hotplate overnight at ~ 120 ^{o}C and then reconstituted in 3 mL of 6 M HCl. This solution was again dried at ~ 160 ^{o}C. Finally, the samples were re-dissolved with 1.1 mL of 2.5 M HCl on a 100 ^{o}C hotplate overnight before commencing ion exchange chemistry. Clear solutions of all sample fractions were obtained and no insoluble fluoride compounds were found in this study.

2.3 Column chemistry

The solutions obtained from previous steps were centrifuged at 5000 rpm for 8 min. Then, as shown in Figure 1, 1 mL of the supernatant solution was passed through a two-layered mixed-resin column (70 mm length × 6 mm diameter), with the upper layer containing 1.5 mL of AG50W-X12 (200–400 mesh) resin and bottom layer containing 0.45 mL of LN Spec resin (100–150 μm). Before sample loading for separation of Sr-Nd-Hf from the sample matrix, the mixed resin column was pre-washed with 18 mL of 6 M HCl, 8 mL of 3 M HF, and 4 mL of H_2O in turn.

As shown in Table 1 and Figure 2, after sample loading and rinsing four times with 0.5 mL of 2.5 M HCl, the column was washed with 13.5 mL of 2.5 M HCl. Most matrix elements (K, Ca, Na, Mg, Al, Fe, Mn, Ti) and Rb were removed during this step. Some Sr (~ 27 %) was also washed out in this step. Then, the Sr fraction, containing of ~ 71 % Sr, was stripped with 5.5 mL of 2.5 M HCl. Part of the HREEs (~ 2 % Dy, ~ 5 % Ho, ~ 14 % Er, ~ 23 % Tm, ~ 11 % Yb, ~ 2 % Lu) and ~ 10 % of Ba were then washed out with 3 mL of 2.5 M HCl. Next, the REEs fraction-enriched Sm+Nd (≥ 96%) was then stripped with 8 mL of 6 M HCl. Sr and the REEs fraction-enriched Sm+Nd were dried on a hotplate at 120 ^{o}C to dryness and readied for TIMS analysis. Residual of Ti on the LN Spec resin was completely washed out using 15 mL of 3 M HCl +0.75 % H_2O_2 mixture. Finally, Hf, Zr, Nb, and Ta were extracted from the column with 5 mL of 3.0 M HF. The resulting Hf fraction, containing of ~ 93.4 % Hf, was evaporated on a hotplate at 120^{o}C to dryness, taken up in 0.05 mL of 0.5 M HF + 0.8 mL 2.0 M HNO_3, and then readied for MC-ICP-MS analysis. The complete separation procedure, including pre-cleaning of the column, takes only approximately 9 h for 20 samples or about 70 % less time compared with conventional three-step column chemistry.

2.4 TIMS for Sr and Nd isotopic analysis

The isotopic compositions of Sr and Nd were measured using a Triton Plus TIMS instrument (ThermoFisher) at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS) in Beijing, China. Single and double Re filament geometries were used to obtain Sr^+ and Nd^+ ion beams, respectively. All Sr and Nd data were acquired by static multi-collection. The collector array is illustrated in Table 2.

For Sr isotope ratio measurements, the evaporation filament was heated at 500 mA/min until the ^{88}Sr signal reached ~ 20 mV. The beam was centered and roughly focused, and the evaporation filament was slowly heated to obtain a signal ~ 4 V of ^{88}Sr. Data acquisition was begun when the signal intensity of ^{88}Sr had reached ~ 5 V. A peak-center routine was performed prior to data acquisition, and then the baseline was measured by deflecting the beams using the x-symmetry lens. The measurement run consisted of 8 ~10 blocks of data with 20 cycles per block. The integration time per cycle was 4 s. Before mass fractionation correction, the ^{87}Sr signal intensity was corrected for the potential interference caused by the remaining isobaric overlap of ^{87}Rb on ^{87}Sr using an ^{87}Rb/^{85}Rb value of 0.385041.[25] After column chemistry, the ^{85}Rb/^{86}Sr ratios obtained were $\leq 1 \times 10^{-5}$ in natural silicate sample analysis, showing negligible isobaric interference. Finally, the ^{87}Sr/^{86}Sr ratio data were normalized to

^{88}Sr/^{86}Sr = 8.375209 for mass fractionation correction using exponential law. Most of Sr isotopic data were obtained at an internal precision of ≤ ± 0.000010 (2 SE).

For Nd isotope ratio measurements, the ionization filament was first heated at a rate of 450 mA/min to 4.5 A. The evaporation filament was then heated at 400 mA /min until the ^{146}Nd signal reached 20 mV. Subsequently, the beam was centered and roughly focused, and the evaporation filament was slowly heated to obtain a ~ 1 V intensity of ^{146}Nd. Data acquisition was begun once the intensity of ^{146}Nd had reached ~ 1.2 V. Before the commencement of the analysis, a peak-center routine was run, and then, the baseline was measured. Data were collected for 8~10 blocks with each block containing 20 cycles, which, in turn, consisted of 4 s of integration time. The typical intensity of ^{147}Sm was about ~ 0.4 V during the period of data acquisition. Isobaric interference from ^{144}Sm can be accurately subtracted following our previously reported method.[23] After correction of the isobaric interference, the ^{143}Nd/^{144}Nd ratio data were normalized to ^{146}Nd/^{144}Nd = 0.7219 for mass fractionation correction using exponential law. Most of Nd isotopic data were obtained at an internal precision of ≤ ± 0.000010 (2 SE), which was corrected using our off-line program.[23]

Standards NBS-987 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 = 6), and the JNdi-1 standard gave a mean ^{143}Nd/^{144}Nd of 0.512109 ± 8 (2 SD, n = 6). Both NBS-987 and JNdi-1 standards were good agreement with previous reported values. All measured ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd ratios of silicate samples were normalized to the well-accepted NBS-987 value of

0.710248[11] and JNdi-1 value of 0.512115.[26]

2.5 MC-ICP-MS for Hf isotopic analysis

Hf isotope ratio determinations were carried out using a Thermo Scientific Neptune Plus MC-ICP-MS at the IGGCAS in Beijing, China. Detailed descriptions of this instrument were previously reported.[13, 15] 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 presented in Table 3. A JMC-475 Hf standard solution of 100 ppb was used to evaluate the reproducibility and accuracy of the instrument during analytical sessions. Each run consisted of a baseline measurement and collections of 135~165 cycle that were divided into 9~12 blocks. The integration time of the signals was set to 4 s, and the typical time of one measurement lasted for ~ 15 min. A typical sample size used for most samples except BIR-1 (30~35 ng) was 100~250 ng. 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 one-step 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 data were directly normalized to ^{179}Hf/^{177}Hf = 0.7325 for mass bias correction using exponential law.[13,15] 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 0.282148 ± 9 (2 SD, n = 6), which was slightly lower than that previously reported. Hence, all measured $^{176}Hf/^{177}Hf$ ratios of silicate samples were normalized to the well-accepted JMC-475 value of 0.282160.[17] Last year, 84 analyses of JMC-475 yielded a $^{176}Hf/^{177}Hf$ value of 0.282154 ± 18 (2 SD), which was identical to the recommended the well-accepted JMC-475 value of 0.282160,[17] and within the measurement uncertainties.

3. Results and discussion

3.1 Validation of the method and final results

To assess the analytical reproducibility and feasibility of our procedure for silicate samples, six CRMs were selected to encompass a wide range of matrix compositions, and analyte concentrations were determined. Because the silicate samples used in the present study had high Sr contents (≥ 100 $mg.L^{-1}$), one fifth of the purified Sr fractions and all Nd fractions were loaded on the filament. The sample size of Sr and Nd in TIMS analysis varied significantly, 0.8~3.4 μg for Sr and 0.12~1.6 μg for Nd. For Hf isotope analysis using MC-ICP-MS, the sample consumption was 0.03~0.28 μg. Sample sizes were estimated according to the sample weight, recovery of the chemical procedure, and published Sr, Nd, and Hf concentration data.[27-29]

During Sr and Nd isotope analyses, as shown in Tables 4 and 5, the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios of all analyzed USGS and GSJ reference materials were obtained with an internal precision better than 0.000013 (2 SE). Average values of $^{87}Sr/^{86}Sr$ and

^{143}Nd/^{144}Nd in the present study as well as previous published data are plotted in Figs. 3a and 3b. The ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd data presented in the figures agree well with the previously published data obtained through TIMS or MC-ICP-MS.[2, 4, 7, 9, 11, 13, 18-20, 22, 30-32]

During ^{143}Nd/^{144}Nd ratio determination, the analyzed objects were REEs 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) or not, the ^{145}Nd/^{144}Nd ratio of silicate samples was also measured and corrected following the previously reported method.[23] As shown in Table 5 and Figure 4, the corrected ^{145}Nd/^{144}Nd value is 0.348413 ± 0.000008 (2 SD, n = 20) in actual silicate samples, which agrees well with reported values of 0.348405~0.348419. The obtained data implied that ^{144}Sm isobaric interference can be accurately subtracted.[22, 23, 33-35]

For Hf isotope analysis, as shown in Table 6, the ^{176}Hf/^{177}Hf ratios of most standard samples except BIR-1 were achieved with an internal precision better than 0.000012 (2 SE). The internal precision (0.000016~0.000018, 2 SE) of BIR-1 was worse than 0.000012 because the Hf concentration of BIR-1 was only 0.6 ppm,[27] and 60 mg of BIR-1 materials yielded a small sample size (~ 32 ng) of Hf. The internal precision of BIR-1 could be improved further by digesting larger amounts of material (~ 120 mg). Subsequently, the digested sample could be divided into two aliquots. Each aliquot should be lower than 60 mg and individually separated so that the purified amalgamated Hf could be obtained sufficient sample sizes (≥ 50 ng). The average values of ^{176}Hf/^{177}Hf in this study and previously published data are plotted in

Figure 3c. As shown in Figure 3c and Table 6, the $^{176}Hf/^{177}Hf$ ratios of all CRMs, except JA-3 that was slightly lower than the published data, agreed well with previously published data.[10, 12, 13, 15-17, 36, 37]

The BCR-2 CRM possesses an excellent homogeneousness and is widely used to monitor the quality of the chemical procedure and the instrumental status in most geochemical laboratories. Hence, we employ BCR-2 to verify our chemical procedure. The reproducibility of our procedure was demonstrated by ten different dissolutions of BCR-2 powder materials. As shown in Tables 4, 5, and 6, ten replicate measurements of BCR-2 yielded a $^{87}Sr/^{86}Sr$ value of 0.705010 ±0.000018 (2 SD), a $^{143}Nd/^{144}Nd$ value of 0.512634 ±0.000010 (2 SD), and a $^{176}Hf/^{177}Hf$ value of 0.282885 ±0.000014 (2 SD). The external reproducibility of $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, and $^{176}Hf/^{177}Hf$ ratios of BCR-2 were better than ±0.000018 (2 SD), ±0.000010 (2 SD), and ±0.000014 (2 SD), respectively.

In general, the data reproducibility and precision of the proposed method were satisfactory and completely fitted the demands of geochemistry and petrology. Practical silicate samples further demonstrated the usefulness and feasibility of our method.

3.2 Separation protocol

To avoid isobaric interferences and matrix effects, good chemical separation of Sr-Nd-Hf from the silicate samples is required. Previous studies have revealed that the AG50W cation resin showed an excellent performance in separating Sr and REEs from silicate matrix solutions.[2, 11, 18-20] Similarly, the selectivity of LN spec resin for Hf allows efficient separation of Hf from silicate matrix solutions.[13] Further optimization and setup of both LN Spec and AG50W resins are crucial for our one-step separation procedure. Our proposed procedure features three key points as follows:

First, the order of the resin setup is a crucial consideration. As shown in Figure 1, 1.5 mL and 0.45 mL of AG50W-X12 and LN Spec resins are used as the top and bottom layers, respectively. Reversing the setup order of the AG50W-X12 and LN Spec resins, Ti and Hf will be re-distributed on the AG50W-X12 resin after removal of the matrix elements and collection of Sr and REEs, resulting in failure of separation between Ti and Hf.

Second, 2.5 M HCl is the most suitable acid to rinse out matrix elements before collection of Sr, REEs, and Hf. Several HCl concentrations (e.g., 3~4 M) were tested to determine the concentration that best removes the matrix elements. However, the sample purity obtained was unsatisfactory because yellow residues in both the Sr and REE fractions were observed.

Third, the selection of cross-linking degree of AG50W should be carefully considered. In previous studies, medium cross-linked resin (X8) was preferred because this resin allowed high separation speeds and low experimental costs to purify Sr and REEs. However, for our short column, a more highly cross-linked cation exchange resin (X12, 200–400 mesh) was preferred. The performances of AG50W-X8 and AG50W-X12 were carefully compared prior to the confirmation of the final separation procedure. As the sample loading size increased, the sample purity of Sr and REEs deteriorated significantly if AG50W-X8 resin was used for separation. In particular, when the loading sample size was larger than 35 mg of silicate material, e.g., BCR-2, minor matrix elements tailed into the Sr and REE fractions and strongly suppressed the intensities of Sr and Nd signal during TIMS measurement. The sample loading size would increase to 60 mg and the sample purity of Sr and REEs remained acceptable if a cross-linked (X12) AG50W cation exchange resin was employed.

3.3 Purity, recovery, and blank

To investigate the behavior of matrix and trace elements retained on the column, a basalt standard material (BCR-2) was employed. A 50 mg of BCR-2 was dissolved in 1 mL of 2.5 M HCl. Six successive fractions were collected, and corresponding eluting messages were shown in Table 1 and Figure 2. Distribution curves of the matrix and semi-quantitative trace element analyses were determined using a Thermo Fisher Element-XR ICP-MS instrument.

As shown in Figure 2, most matrix elements (K, Na, Ca, Mg, Al, Fe, Ti), Rb, some Sr (~ 27%), and HREEs were rinsed in fraction 1 before collecting the Sr fraction. Several residual elements in the Sr fraction (fraction 2), Ba, Er, Tm, and Yb, were found. The yield of Sr in fraction 2 was about 71.0 %. Unwanted elements, including some HREEs and small amounts of Ti and Sr, were washed out in fraction 3 using 3 mL of 2.5 M HCl. Most of the REEs and partly of the Yb (~ 11.4 %) were stripped in Nd fraction (fraction 4). Most of the Lu (~ 98 %) and Yb (~ 83 %) were also rinsed out in fraction 4. Generally, few residual elements were observed in the Nd fraction (fraction 4).

Ti must be completely removed from the sample. The use of H_2O_2, which raises the oxidation state of Ti and forms the yellow-tinted peroxytitanyl compound $Ti(O\text{-}O)^{2+}$ and results in a satisfactory separation of Hf and Ti.[38] In the present study, 15 mL of 0.075 % H_2O_2 + 3 M HCl was employed to remove Ti. All of the Ti residues were washed out in fraction 5, and most of the Hf +Zr+Ta mixture was rinsed out in fraction 6. The yield of Hf in fraction 6 was ~ 93.4 %, which was within the range reported by other investigators.[9, 10, 13, 38] In summary, the removal efficiency of major elements (Al, Fe, Ca, Mg, K, Na, Ti) was higher than 99.9 % in the Hf fraction (fraction 6).

Procedural blanks are crucial for accurate Sr-Nd-Hf isotope analysis. Blank values of 170~200, 70~80, and 55~65 pg are obtained for Sr, Nd, and Hf, respectively. For Sr, Nd, and Hf analyses, the blanks are negligible relative to the amount of analytes contained in a 50~60 mg silicate aliquot.

4. Conclusions

A rapid and robust one-step chemical separation procedure was developed for measuring $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, and $^{176}Hf/^{177}Hf$ isotope ratios in the same sample digest. Sr, Nd, and Hf were sequentially separated from the same rock matrix solution using a single column without intervening evaporation. The chemical separation scheme was based on the enhanced elemental selectivity permitted by the combined use of AG50W-X12 cation-exchange and LN Spec resins. This scheme allowed the use of relatively small columns. The proposed separation procedure achieved the satisfactory and rapid separation of Sr, Nd, and Hf and reduced cross-contamination risk, thereby offering significant advantages over existing methods in terms of simplicity, separation efficiency, miniaturization, and waste reduction. The potential fractionation of Sr-Nd-Hf isotopes existed in the chemical resin column could be corrected by using the traditional internal correction methods. The bottleneck associated with sample preparation prior to thermal ionization mass spectrometric measurements can be significantly reduced with the new protocol. An alternative approach to the measurement of these isotope ratios using MC-ICP-MS could be considered. In the present investigation this would involve modifications of the column protocols, especially in the case of Sr.

Acknowledgements

This work was jointly supported by the National Natural Science Foundation of China (grants 41273021 and 41373020) and the State Key Laboratory of Lithospheric Evolution (grant 11301520), Institute of Geology and Geophysics, Chinese Academy of Sciences.

References:

1. J.P. Davidson, D.J. Morgan, B.L.A. Charlier, R. Harlou, J.M. Hora, Annu. Rev. Earth Planet Sci., 2007, 35, 273-311.

2. C. Na, T. Nakano, K. Tazawa, M. Sakagawa, T. Ito, Chem.Geol., (Isotope Geoscience Section)., 1995, 123, 225-237.

3. C. Pin, D. Briot, C. Bassin, E. Poitrasson, Anal. Chim. Acta., 1994, 298, 209-217.

4. C. Pin, J. Francisco, S. Zalduegui, Anal. Chim. Acta., 1997, 339, 79-89.

5. Y. Arakawa, Geochem. J., 1992, 26, 105-109.

6. C. F. Li, F. K. Chen and X. H. Li, Int. J. Mass Spectrom., 2007, 266, 34-41.

7. Z. Y. Chu, F. K. Chen, Y. H. Yang, J. H. Guo, J. Anal. At. Spectrom., 2009, 24, 1534-1544.

8. X.J. Yang, C. Pin, Anal. Chem., 1999, 71, 1706-1711.

9. B. Lefvre, C. Pin, Anal. Chim. Acta., 2005, 543, 209-221.

10. J.N. Connelly, D.G. Ulfbeck, K. Thrane, M. Bizzarro, T. Housh, Chem.Geol., 2006, 233, 126-136.

11. D. Weis, B. Kieffer, C. Maerschalk, J. Barling, J. D. Jong, G. A. Williams, D. Hanano, W. Pretorius, N. Mattielli, J. S. Scoates, A. Goolaerts, R. M. Friedman and J. B. Mahoney, Geochem. Geophys. Geosyst., 2006, DOI: 10.1029/2006GC001283.

12. B. Lefvre, C. Pin, Anal. Chem., 2001, 73, 2453-2460.

13. Y.H. Yang, H.F. Zhang, Z.Y. Chu, L.W. Xie, F.Y. Wu, Int. J. Mass Spectrom.,

2010, 290, 120-126.

14. A. Makishima, E. Nakamura, Geochem. J., 2008, 42, 199-206.

15. Y.H. Yang, F.Y. Wu, S.A. Wilde, L.W. Xie, Int. J. Mass Spectrom., 2011, 299, 47-52.

16. N.C. Chu, R.N. Taylor, V. Chavagnac, R.W. Nesbitt, R.M. Boella, J.A. Milton, C.R. German, G. Bayon, K. Burton, J. Anal. At. Spectrom., 2002, 17, 1567-1574.

17. M. Bizzarro, J.A. Baker, D. Ulfbeck, Geostand. Newslett., 2003, 27, 133-145.

18. Y. Orihashi, J. Maeda, R. Tanaka, R. Zeniya, K. Niida, Geochem. J., 1998, 32, 205-211.

19. T. Miyazaki, K. Shuto, Geochem. J., 1998, 32, 345-350

20. C.F. Li, X.H. Li, Q.L. Li, J.H. Guo, X.H. Li, T. Liu, Anal. Chim. Acta., 2011, 706, 297-305.

21. M. Griselin, J.C.V. Belle, C. Pomies, P.Z. Vroon, M.C.V. Soest, G.R. Davies, Chem. Geol., 2001, 172, 347-359.

22. Y.H. Yang, F.Y. Wu, L.W. Xie, Y.B. Zhang, Anal. Lett., 2010, 43, 142-150.

23. C.F. Li, X.H. Li, Q.L. Li, J.H. Guo, X.H. Li, J. Anal. At. Spectrom., 2011, 26, 2012-2022.

24. I.C. Kleinhanns, K. Kreissig, B.S. Kamber, T. Meisel, T.F. Nagler, J.D. Kramers, Anal. Chem., 2002, 74, 67-73.

25. B.L.A. Charlier, C. Ginibre, D. Morgan, G.M. Nowell, D.G. Pearson, J.P. Davidson, C.J. Ottley, Chem.Geol., 2006, 232, 114-133.

26. T. Tanaka, S. Togashi, H. Kamioka, H. Amakawa, H. Kagami,T. Hamamoto, M.

Yuhara, Y. Orihashi, S. Yoneda, H. Shimizu,T. Kunimaru, K. Takahashi, T. Yanagi, T. Nakano, H. Fujimaki, R. Shinjo, Y. Asahara, M. Tanimizu and C. Dragusanu, Chem.Geol., 2000, 168, 279-281.

27. P. Dulski, Geostand. Newslett., 2001, 25, 87-125.
28. M. Willbold, K.P. Jochum, Chem.Geol., 2005, 29, 63-82.
29. R. L. Korotev, Geostand. Newslett., 1996, 20, 217-245.
30. C.F. Li, X.H. Li, Q.L. Li, J.H. Guo, X.H. Li. L.J. Feng, Z.Y. Chu, Anal. Chem., 2012, 84, 6040-6047.
31. C.F. Li, X.H. Li, Q.L. Li, J.H. Guo, X.H. Li, Y.H. Yang, Anal. Chim. Acta., 2012, 727, 54-60.
32. Y.H. Yang, F.Y. Wu, Z.C. Liu, Z.Y. Chu, L.W. Xie, J.H. Yang, J. Anal. At. Spectrom., 2012, 27, 516-522.
33. B. Luais, P. Telouk and F. Albarede, Geochim. Cosmochim. Acta., 1997, 61, 4847-4854.
34. G. Caro, B. Bourdon, J.L. Birck, S. Moorbath, Geochim.Cosmochim.Acta., 2006, 70,164-191.
35. G. J. Wasserburg, S. B. Jacobsen, D. J. DePaolo, M. T. McCulloch and T. Wen, Geochim. Cosmochim. Acta., 1981, 45, 2311-2323.
36. T. Hanyu, S. Nakai, R. Tatsuta, Geochem. J., 2005, 39, 83-90.
37. Y.H. Lu, A. Makishima, E. Nakamua, J. Anal. At. Spectrom., 2007, 22, 69-76.
38. C. Munker, S. Weyer, E. Scherer, K. Mezger, Geochem. Geophys. Geosyst., 2001, DOI: 2.10.1029/2001GC000183.

Table 1. Single-step chemical procedure for Sr-Nd-Hf separation

Procedure	Eluting reagent	Eluting volume (mL)	Eluting Fraction
Loading sample	2.5M HCl	1.0	1
Rinsing	2.5M HCl	2.0 (0.5 x 4)	1
Rinsing	2.5M HCl	13.5	1
Eluting Sr	2.5M HCl	5.5	2
Rinsing	2.5M HCl	3.0	3
Eluting Nd	6.0M HCl	8.0	4
Rinsing	3.0M HCl + 0.75 % H_2O_2	15.0	5
Eluting Hf	3.0M HF	5.0	6

Table 2.Cup configuration for Sr-Nd 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			
Hf	^{172}Yb	^{173}Yb	^{175}Lu	^{176}Hf	^{177}Hf	^{178}Hf	^{179}Hf	^{180}Hf	^{182}W

Table 3.Typical operating parameters for Hf measurement using Neptune Plus MC-ICP-MS

Neptune Plus MC-ICP-MS	Setting
RF forward power	1300 W
Cooling gas	15.5 L/min
Auxiliary gas	0.7 L/min
Aerosol carrier gas	~ 1.10 L/min (optimized daily)
Extraction	- 2000 V
Focus	- 645 V
Detection system	Nine Faraday collectors
Acceleration voltage	10 kV
Interface cones	Nickel
Spray chamber	Glass cyclonic
Nebulizer type	Micromist PFA nebulizer
Sample uptake rate	50 μL/min
Uptake mode	Free aspiration
Instrument Resolution	~ 400 (Low)
Typical sensitivity on ^{180}Hf	~ 16 V/ppm (10^{11} Ω resistors)
Sampling mode	9~12 blocks of 15 cycles
Integration time	4 sec
Analytical time	~ 660 sec
Baseline	*ca*.1 min on peak in 2% HNO_3

Table 4. Analytical results of ^{87}Sr/^{86}Sr ratios for CRMs determined by Triton Plus TIMS

CRMs	Raw ^{87}Sr/^{86}Sr	Corrected ^{87}Sr/^{86}Sr	2 SE	Reported value	Rb/Sr ratio
BCR-2	0.702128	0.705018	0.000012	0.705019[11]; 0.705023[13]	0.1395[28]
BCR-2	0.705617	0.705002	0.000012	0.705026[31]; 0.704998[32]	
BCR-2	0.708509	0.705004	0.000012		
BCR-2	0.702479	0.705005	0.000009		
BCR-2	0.708523	0.704999	0.000010		
BCR-2	0.703277	0.705018	0.000011		
BCR-2	0.705146	0.705023	0.000010		
BCR-2	0.701334	0.705015	0.000011		
BCR-2	0.702338	0.705002	0.000009		
BCR-2	0.701511	0.705021	0.000010		
Mean ± 2 SD		0.705010	0.000018	0.705017	
W-2	0.707856	0.706983	0.000009	0.706966[13]; 0.706973[31]	0.1010[27]
W-2	0.712276	0.706997	0.000010		
Mean		0.706990		0.706970	
BHVO-2	0.704378	0.703470	0.000011	0.703487[11];0.703479[31]	0.0217[28]
BHVO-2	0.711143	0.703488	0.000010	0.703468[32];	
Mean		0.703479		0.703478	

JA-1	0.703465	0.703543	0.000008	0.703533[2];0.703557[18]	0.044[29]
JA-1	0.706042	0.703529	0.000009	0.703543[19]	
Mean		0.703536		0.703544	
JA-3	0.705905	0.704172	0.000010	0.704160[19]; 0.704177[31]	0.1232[27]
JA-3	0.707787	0.704169	0.000008		
Mean		0.704171		0.704169	
BIR-1	0.705128	0.703117	0.000010	0.703130[31]; 0.703108[32]	0.0033[27]
BIR-1	0.704220	0.703114	0.000011		
Mean		0.703116		0.703119	
NBS-987	0.706769	0.710246	0.000011		
	0.706296	0.710254	0.000010		
	0.708337	0.710244	0.000009		
	0.706772	0.710249	0.000009		
	0.705853	0.710241	0.000010		
	0.707506	0.710238	0.000010		
Mean ±2 SD		0.710245	0.000011		

Table 5. Analytical results of ^{143}Nd/^{144}Nd ratios for CRMs determined using TIMS without Nd and Sm separation

						Reported Values	
CRMs	Raw ^{143}Nd/^{144}(Nd+Sm)	Corrected ^{143}Nd/^{144}Nd	2 SE	^{145}Nd/^{144}Nd	2 SE	^{143}Nd/^{144}Nd	Sm/Nd
BCR-2	0.497824	0.512631	0.000008	0.348413	0.000006	0.512632[6]; 0.512641[7]	0.224[28]
BCR-2	0.501391	0.512640	0.000006	0.348412	0.000004	0.512634[11]; 0.512640[13]	
BCR-2	0.504291	0.512636	0.000006	0.348414	0.000004	0.512630[20]; 0.512638[22]	
BCR-2	0.500965	0.512629	0.000005	0.348414	0.000003	0.512630[23]; 0.512638[30]	
BCR-2	0.471586	0.512642	0.000008	0.348414	0.000005	0.512636[31]	
BCR-2	0.510027	0.512635	0.000005	0.348411	0.000003		
BCR-2	0.495168	0.512633	0.000005	0.348411	0.000003		
BCR-2	0.491770	0.512630	0.000004	0.348411	0.000002		
BCR-2	0.502585	0.512635	0.000005	0.348411	0.000002		
BCR-2	0.501244	0.512627	0.000008	0.348414	0.000004		
Mean ± 2 SD		0.512634	0.000010	0.348413	0.000003	0.512635	
W-2	0.478999	0.512525	0.000010	0.348416	0.000008	0.512510[4]; 0.512537[7]; 0.512516[13]	0.254[27]
W-2	0.488623	0.512521	0.000012	0.348415	0.000008	0.512511[22]; 0.512528[30]	
Mean		0.512523		0.348416		0.512520	
BHVO-2	0.463961	0.512971	0.000006	0.348409	0.000005	0.512989[6]; 0.512951[7];0.512981[11]	0.247[28]
BHVO-2	0.494408	0.512981	0.000008	0.348409	0.000005	0.512984[22]; 0.512985[23];0.512983[30]	
Mean		0.512976		0.348409		0.512979	

JA-1	0.489061	0.513080	0.000012	0.348406	0.000009	0.513066[2]; 0.513107[9]	0.343[29]
JA-1	0.490259	0.513094	0.000010	0.348406	0.000009	0.513078[18]; 0.513092[19]	
Mean		0.513087		0.348406		0.513086	
JA-3	0.487184	0.512841	0.000012	0.348413	0.000008	0.512835[6]; 0.512859[19]	0.248[27]
JA-3	0.495082	0.512851	0.000012	0.348414	0.000010	0.512840[23]; 0.512859[30]	
Mean		0.512846		0.348414		0.512848	
BIR-1	0.425078	0.513106	0.000012	0.348425	0.000008	0.513107[7]; 0.513108[9]	0.460[27]
BIR-1	0.463980	0.513095	0.000014	0.348417	0.000010	0.513093[20]; 0.513084[23]	
Mean		0.513101		0.348421		0.513098	
JNdi-1	0.512576	0.512110	0.000008				
	0.512662	0.512117	0.000007				
	0.511807	0.512107	0.000008				
	0.511720	0.512106	0.000008				
	0.512935	0.512109	0.000009				
	0.512539	0.512107	0.000007				
Mean ± 2 SD		0.512109	0.000008				

Table 6. Analytical results of ^{176}Hf/^{177}Hf ratios for CRMs determined by Neptune Plus MC-ICP-MS

CRMs	Raw ^{176}Hf/^{177}Hf	Corrected ^{176}Hf/^{177}Hf	2 SE	Reported Value	Lu/Hf	Yb/Hf
BCR-2	0.279622	0.282883	0.000006	0.282869[10]; 0.282884[12]; 0.282877[13]	0.106[28]	0.709[28]
BCR-2	0.279592	0.282877	0.000006	0.282859[16]; 0.282875[17]; 0.282895[36]		
BCR-2	0.279581	0.282879	0.000006			
BCR-2	0.279608	0.282895	0.000006			
BCR-2	0.279576	0.282880	0.000008			
BCR-2	0.279608	0.282884	0.000010			
BCR-2	0.279606	0.282895	0.000006			
BCR-2	0.279621	0.282888	0.000010			
BCR-2	0.279623	0.282877	0.000010			
BCR-2	0.279599	0.282888	0.000012			
Mean ± 2 SD		0.282885	0.000014	0.282875		
W-2	0.279652	0.282742	0.000008	0.282715[12]; 0.282724[13]	0.133[27]	0.871[27]
W-2	0.279623	0.282723	0.000008	0.282715[15]		
Mean		0.282733		0.282718		
BHVO-2	0.279880	0.283101	0.000012	0.283094[15]; 0.283116[17]	0.061[28]	0.454[28]
BHVO-2	0.279874	0.283097	0.000013			
Mean		0.283099		0.283105		
JA-1	0.279941	0.283269	0.000012	0.283250[9]; 0.283258[12]	0.169[29]	1.14[29]

JA-1	0.279911	0.283247	0.000013	0.283292[36]; 0.283264[37]		
Mean		0.283258		0.283266		
JA-3	0.279773	0.283046	0.000010	0.283084[36]; 0.283063[37]	0.461[27]	0.566[27]
JA-3	0.279778	0.283057	0.000008			
Mean		0.283052		0.283074		
BIR-1	0.280145	0.283292	0.000016	0.283247[9]; 0.283291[12]	0.417[27]	2.73[27]
BIR-1	0.280138	0.283283	0.000018	0.283277[17]; 0.283265[36]		
Mean		0.283288		0.283270		
JMC-475	0.278803	0.282154	0.000008			
	0.278901	0.282151	0.000008			
	0.278815	0.282145	0.000008			
	0.278804	0.282143	0.000007			
	0.278808	0.282144	0.000006			
	0.278874	0.282148	0.000006			
Mean ± 2 SD		0.282148	0.000009			

Figure captions

Fig 1. Single-step separation scheme in this study compared with the traditional three-step separation procedure.

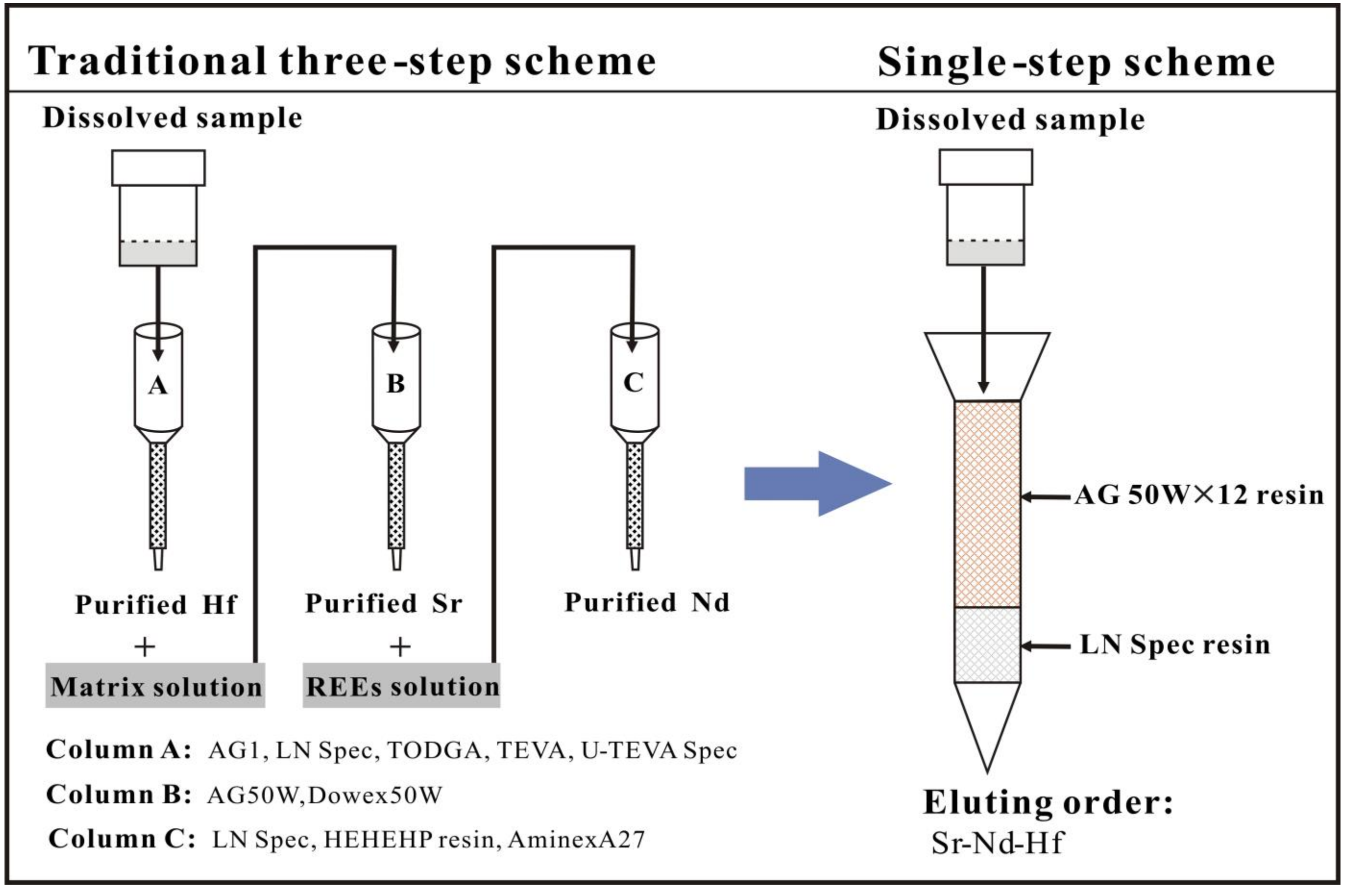

Fig 2. Distribution curve of all eluted fractions of BCR-2 in the mixed AG50W-12 + LN Spec resin column.

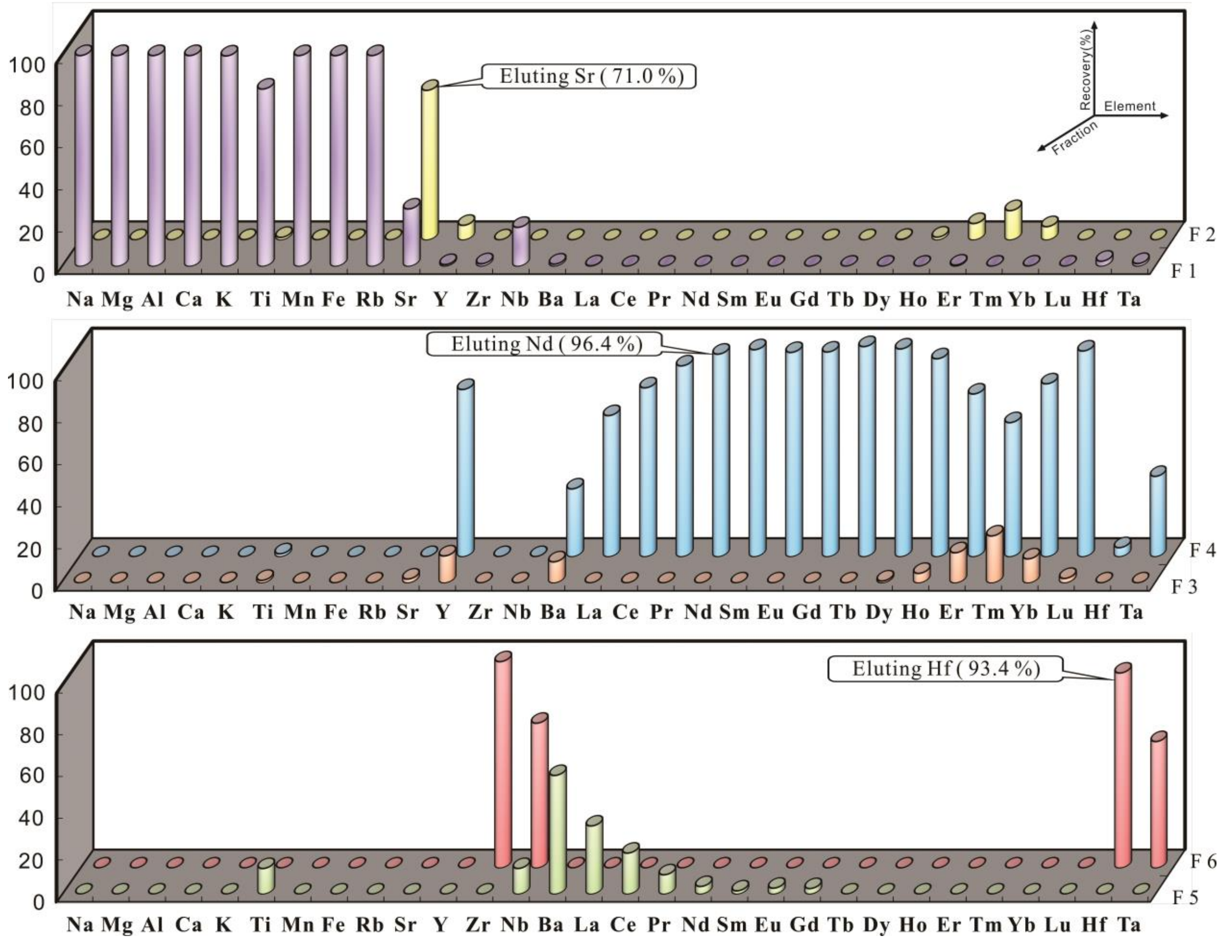

Fig 3. Comparison of Sr-Nd-Hf values obtained by the present study and previous data.

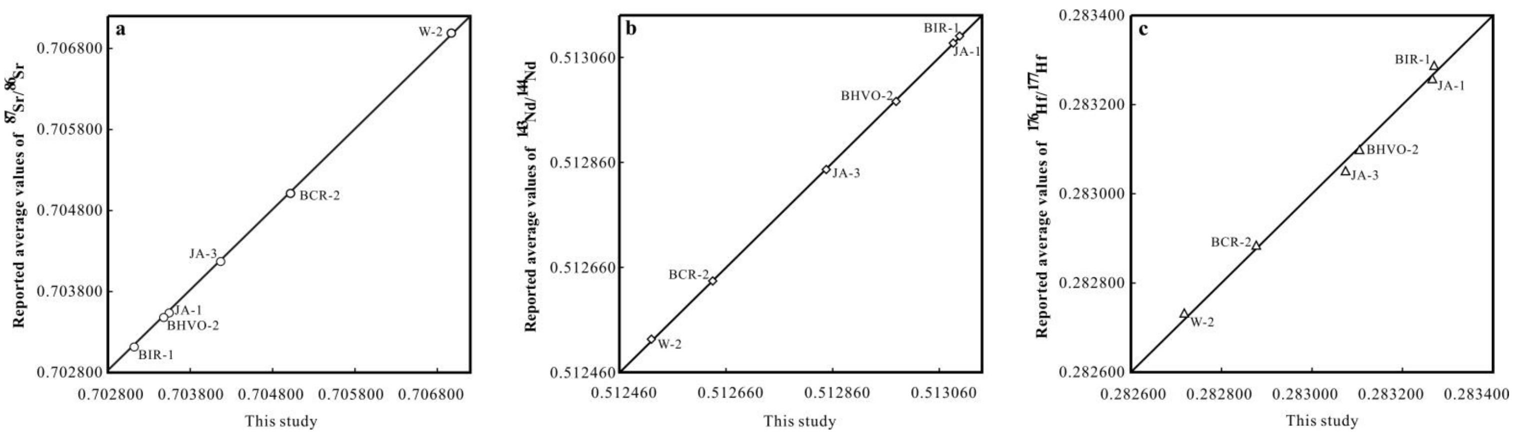

Fig 4. Corrected $^{145}Nd/^{144}Nd$ ratios for silicate rock from USGS and GSJ.