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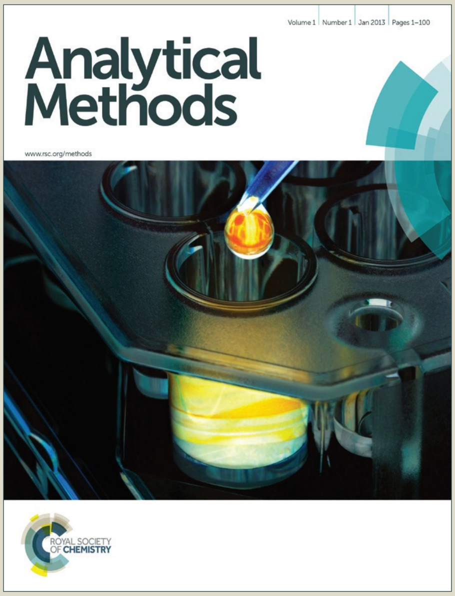

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A rapid single column separation scheme for high-precision Sr-Nd-Pb isotopic analysis in geological samples using thermal ionization mass spectrometry

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Abstract:

Thermal ionization mass spectrometry (TIMS) is considered the most accurate technique for determining Sr-Nd-Pb isotopic ratios in geological samples. However, time-consuming and complex sample separation procedures greatly hinder the instrumental measurement efficiency. In this study, a single-column separation chemistry procedure for Sr-Nd-Pb from single rock dissolution was developed. The chemistry procedure was designed to minimize the number of evaporation steps and considerably shorten separation time, enabling high throughput for TIMS. In contrast to conventional three-column separation procedures (~3 days), this technique was characterized by high efficiency superiority in terms of separation time (~8 hours), a 3-fold enhancement in the separation efficiency. The stability of our procedure was demonstrated by replicated TIMS measurements of $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios for six international silicate rock reference materials, spanning a wide range of bulk compositions. The analytical results obtained for these standards well agreed with published data. The external reproducibility (2 RSD, n = 10) of a BCR-2 standard sample was ± 0.0020 % for $^{87}Sr/^{86}Sr$, ± 0.0023 % for $^{143}Nd/^{144}Nd$, and ± 0.021 % ~ 0.033 % for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios.

Keywords: Sr-Nd-Pb isotope; Single-column separation; Geological samples; Thermal ionization mass spectrometry; Pb double spike

1. Introduction

The $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ isotopic ratios, which show variation by the radioactive decay of long half life isotopes of ^{87}Rb, ^{147}Sm, ^{238}U, ^{235}U and ^{232}Th, respectively. These ratios are routinely used for geochemical and environmental tracing, and for interpreting the evolution of lithosphere, source provenance, atmospheric circulation and transport[1-4]. Thermal ionization source mass spectrometry (TIMS) is regarded as a benchmark analytical technique and is widely used in Earth Sciences because of high accuracy, excellent sensitivity, and low memory. However, to obtain stable and high intensity of ion signals of Sr-Nd-Pb during measurements of TIMS, elements must be separated from sample matrices as clean as possible. Traditionally, for the Sr, Nd and Pb isotope analyses using TIMS, tedious column chemistry includes many evaporation and complex operation steps. The purification of Sr-Nd-Pb prior to mass spectrometric measurement is traditionally accomplished by three-column chromatography after single sample digestion[5,6].

The first step of this process is usually the separation of Pb from other elements using an anion resin column[5-15] such as AG 1 or Dowex 1 resin, or special resin columns, such as Pb Spec resin[16, 17] or Sr Spec resin[18, 19]. The discarded material from the first column is then dried and re-dissolved using HCl or HNO_3. Afterward, Sr and rare earth elements (REEs) are separated from above matrix elements using a second cation exchange resin column, such as a AG 50W or Dowex 50W resin column[20-34]. Finally, Nd is separated from the REEs using a third resin column, such as HDEHP resin column[20, 22-27, 30, 34, 35], HEHEHP resin column[31], and Aminex A27 resin column[25]. With the traditional multi-step chemical procedures, it takes 3 days on completion of column chemistry for a batch of geological samples (~30). Recently, Pin et al.[35] developed a high efficiency separation method that the Sr, Nd, Pb analytes with high purity can be obtained by three different mini resin columns (Sr Spec + TRU Spec + LN Spec). However, the operational steps are still complex, which is similar to the traditional three-column techniques. Before loading sample, three different mini resin columns are pre-cleaned and pre-conditioned using different chemical reagents, respectively. Twice tandem arrangements[35] are performed to obtain good sample purity, which include thrice back-extractions that are back-extraction of Sr and Pb from Sr-Spec resin column, back-extraction of LREEs (light rare earth elements) from TRU-Spec resin column and back-extraction of Nd from LN-Spec resin column, respectively.

Thus, using traditional three-column methods, the operational steps are complex and the separation efficiency is low. In addition, traditional separation procedures might increase contamination risks from cross-operation in column chemistry associated with complex operation steps.

To the best of our knowledge, there is no analytical protocol reported in the literature for concomitant separation of Sr-Nd-Pb isotope systems from a single sample digest using a single-column separation method. Recently, Li[28] and Yang[32, 36] presented a method to precisely determine Nd isotopic ratios from REEs using TIMS or MC-ICP-MS. In this method, the traditional two-step Nd separation method was simplified to a one-step procedure. More importantly, the method allowed Sr-Nd-Pb isotopic ratios can be precisely measured using TIMS or MC-ICP-MS so long as high-purity Sr, Pb, and REEs could be obtained.

The objective of this work is to establish a simplified and rapid analytical procedure, based on optimization of mixed cation resins (AG50W-X12 + Sr Spec), to obtain Sr-Nd-Pb radiogenic isotopic information from the same rock powder aliquot. This new single-column separation routine of Sr-Nd-Pb from a single dissolution enables higher throughput for data acquisition with TIMS, especially by reducing evaporation steps of solutions and reagent consumption. To verify the robustness of the new separation protocol, six 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, nitric acid and hydrofluoric acid) were further purified using Savillex^{TM} DST-1000 sub-boiling distillation system (Minnetonka, USA). Phosphate acid (0.20 M) was purified using chromatographic method of AG50W-X12 resin manufactured by the Bio-Rad company. Ultrapure water with a resistivity (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 Merk company is dispersed in Milli-Q H_2O.

Sr-Nd-Pb standard solutions: A stock solution of 100 ppm Sr, Pb and Nd was gravimetrically prepared to monitor a Triton Plus TIMS instrument using NIST NBS-987, NIST NBS-981 and JNdi-1 reference materials.

Ta and 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 form Oka Ridge National Laboratory, USA. ^{207}Pb-^{204}Pb double spike composition and the spike/sample mixing ratio have been optimally determined by error simulation using the method reported by Galer[37]. 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 strong acid cation resin AG50W-X12 (200-400 mesh particle size) manufactured by Bio-Rad company and the Sr Spec resin produced by Eichrom company were used for chromatographic extraction. The Sr Spec resin was based on a crown ether (4,4$^{'}$(5$^{'}$)-di-tert-butylcyclohexane-18-crown-6) in octanol, sorbed onto an inert chromatographic support (particle diameter: 50-100 μm).

Column: The cation-exchange quartz glass column was 7 cm long with a 5.5 mm i.d. and 6 mL reservoir. The column was packed with a 1.6 mL of Bio-Rad AG50W-X12 resin and 0.40 mL of Sr Spec resin.

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

Labwares: 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 and column chemistry

2.2.1. Sample digestion

To achieve excellent Sr-Nd-Pb blank levels for applications of geological rock samples, all chemistry was performed inside better than Class 100 chemical workstations located inside a suite of Class 1000 over-pressured clean rooms. Approximately 65~70 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 and 0.3 mL of 14 M HNO_3 for 4 days. The dissolved sample solution was then evaporated to dryness and treated overnight with 2 mL of 6 M HCl at ca. 100 ^{o}C. The solution was then dried down at approximately 150 ^{o}C again. Finally, the samples were dissolved with 1.0 mL of 2.5 M HNO_3 on a 100 ^{o}C hotplate overnight. Clear solutions of all sample fractions were obtained and no insoluble fluoride compounds were found in this study.

2.2.2. Column chemistry

The resulting solutions obtained from the former steps are loaded onto the pre-conditioned mixed resin column with 1.6 mL of AG50W-X12 (200-400 mesh) + 0.40 mL of Sr Spec resin (100-200 mesh) for separation of Sr-Nd-Pb from sample matrix. The mixed resin column was pre-washed with 15 mL of 7 M HNO_3, 5 mL of 0.05 M HNO_3, and 5 mL of 2.5 M HNO_3 before sample loading for separation of Sr-Nd-Pb from the sample matrix.

As shown in Table 1 and Fig 1, the column is washed with 23 mL of 2.5 M HNO_3 after rinsing four times with 0.5 mL of 2.5 M HNO_3. The REEs fraction is then stripped with 6 mL of 7 M HNO_3. Afterwards, Sr fraction is then stripped with 5 mL of 0.05 M HNO_3. Finally, the Pb fraction is stripped with 3 mL of 8 M HCl.

2.3 Thermal ionization mass spectrometry

Sr, Nd and Pb isotopic compositions were measured using a Triton Plus instrument (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 with an integration time of 33 s by deflecting the beams using the x-symmetry lens. Single Ta and Re filament geometry was used to obtain Sr^+ and Pb^+ ion beams, respectively. Double Re filament geometry was employed to obtain Nd^+ ion beam. Re and Ta filaments were degassed at 4.5 A for 30 min in vacuum condition before use.

2.3.1 Loading Sr and analysis conditions for TIMS

Approximately 1 μL of 0.20 M H_3PO_4 was first dried on ~1 mm spot in the middle of the Ta filament at 0.8 A. Sr analyte was dissolved with 1 μL of 2.5 M HCl, then loaded on the spot and dried at 0.8 A. Once the sample was dry, the current was then increased further until a dull red glow was achieved for 3~4 s.

^{88}Sr ion beam intensities of 5~7 V are obtained for all samples with 1~5 μg sample loading sizes. Data acquisition was started when the signal intensity of ^{88}Sr had reached ~5 V. The ^{87}Sr signal intensity was corrected for the potential bias caused by the remaining isobaric overlap of ^{87}Rb on ^{87}Sr using an ^{87}Rb/^{85}Rb value of 0.385041[38] before mass fractionation correction. In this study, the ^{85}Rb/^{86}Sr ratios in all actual silicate standard samples were lower than 0.00005, demonstrating negligible isobaric interference from ^{87}Rb. Then, corrected ^{87}Sr/^{86}Sr values were normalized to ^{88}Sr/^{86}Sr = 8.375209 using an exponential law[6, 19, 23, 24, 29, 33-35]. Usually, a single analysis consisted of minimum of 140 ratios (7 blocks of 20 cycles). Typical internal precision of ^{87}Sr/^{86}Sr was better than ± 0.002 % (2 RSE) for most samples after isobaric interference and mass fractionation correction. Replicate analyses of the Sr reference material NBS-987 yielded ^{87}Sr/^{86}Sr values of 0.710251 ± 0.000016 (2 SD; n =5), showing good agreement with published data[6, 19, 23, 24, 29, 33-35].

2.3.2 Loading Nd and analysis conditions for TIMS

Approximately 1 μL of 0.20 M H_3PO_4 was first dried on ~1 mm spot in the middle of the Re filament at 0.8 A. Nd analyte enriched with other REEs was dissolved with 1 μL of 2.5 M HCl, then loaded on the spot and dried at 0.8 A. Once the sample was dry, the current was then increased further until a dull red glow was achieved for 3~4 seconds.

^{146}Nd ion beam intensities of 1~1.5 V are obtained for all samples with 0.5~3 μg sample loading sizes. Data acquisition was started when the signal intensity of ^{146}Nd had reached ~1.2 V. Data were collected for 10~12 blocks with each block containing 15 cycles, which consisted of 4 s of integration time. The typical intensity of ^{147}Sm was about ~0.3 V during the period of data acquisition. Due to the mixed signal of ^{144}(Sm+Nd) in actual samples were acquired, the Sm isobaric interferences on Nd was subtracted and corrected[28]. Prior to Nd normalization using ^{146}Nd/^{144}Nd ratio of 0.7219 the interference-free ^{147}Sm/^{149}Sm ratio was measured to determine Sm mass discrimination (β_{Sm}) using a ^{147}Sm/^{149}Sm ratio of 1.08583. Then, the isobaric correction of ^{144}Sm on ^{144}Nd was calculated using a ^{147}Sm/^{144}Sm ratio of 4.87090. Afterwards, corrected ^{143}Nd/^{144}Nd and ^{145}Nd/^{144}Nd ratios were normalized to ^{146}Nd/^{144}Nd = 0.7219 using an exponential law. For more detailed analytical procedures, see the method reported by Li et al[28].

Most of the data were acquired and yielded an internal precision of ≤ 0.0015 % (2 RSE), which was corrected using our off-line program. Replicate analyses of the JNdi-1 reference material gave a ^{143}Nd/^{144}Nd value of 0.512106 ± 0.000009 (2 SD; n = 5), illustrating good agreement with published data[26-33, 39].

2.3.3 Loading Pb and analysis conditions for TIMS

Each chemically separated Pb sample was split into two batches in a ratio of ca. 1:2, and a ^{204}Pb-^{207}Pb double spike was added to the former batch. About 2 μL of high purity 0.20 M H_3PO_4 was added to the Pb fraction before evaporation to keep the residue in a moist state before loading onto the out-gassed Re filament with 1 μL of silica gel + 1 μL of 0.20 M H_3PO_4. Once the load was completely dry, the filament was heated and kept at dull glow for 3~4 s.

As to Pb determination, each filament was automatically heated to 1150–1200 ^{o}C over 4–5 min (400 mA/min). Data acquisition was started when the signal intensity of ^{208}Pb had reached ~4 V. A typical run consisted of 10–12 blocks, and the 100~120 scan data were collected in a temperature range of 50–150 ^{o}C. The final lead isotopic data reduction was performed off-line using method reported by Woodhead[13]. The NBS-981 Pb standard was diluted with 0.5 M HCl and used as a reference material and to demonstrate analytical reproducibility. With external reproducibility of ≤ 0.032 % (2 RSD) is attainable for NBS-981, e.g., ^{206}Pb/^{204}Pb = 16.932 ± 0.003, ^{207}Pb/^{204}Pb = 15.486 ± 0.003, ^{207}Pb/^{206}Pb = 0.9146 ± 0.0002 and ^{208}Pb/^{204}Pb = 36.678 ± 0.011 (n = 12).

3. Results and discussion

3.1 Separation protocol

The selectivity of the Sr Spec resin for Sr allows an efficient separation of Rb and

Sr. In addition, it is noteworthy that Pb is retained even stronger than Sr on the Sr Spec resin[18, 19]. Previous results of the determination of distribution coefficients clearly show that Pb is easily bounded directly to the Sr Spec resin in the HNO_3 media. The AG50W-X12 resin shows excellent separation character for REEs from geological matrix solution. Hence, optimization of the extraction performance of AG50W-X12 and Sr Spec resin are crucial for our one-column separation procedure. Three key points should be considered:

First, a pretreatment of Sr Spec resin is crucial for TIMS analysis in order to remove or reduce the Pb blank and traces of labile organic compounds which compromise the efficiency of surface ionization, especially for Pb. Semi-transparent jam-like residues in Pb fraction are found in this study. On the one hand, it is difficult to load sample on the filament because the jam-like residues enriched with Pb are very sticky and hardly dissolved using HCl or HNO_3 acids. On the other hand, the intensity of Pb is very low and unstable even for high Pb content samples, presumably as the result of a significant amount of organic components released from the Sr Spec resin. In order to minimize the effect of organic components from the Sr Spec resin, the Sr Spec resins are pretreated using 7 M HNO_3 and 6 M HCl. For example, a few grams (10 mL) of Sr Spec resin were then thoroughly washed with 100 mL of 7 M HNO_3, 100 mL of 6 M HCl and 50 mL of Millipore water in succession on a large quartz column with a porous polyethylene frit at the bottom. Most organic components can be washed during this step. After pre-cleaning the Sr Spec resin, no jam-like residue in the Pb fraction was observed and the stable and strong lead ion beams were obtained in the TIMS measurement. This pre-cleaned Sr Spec resin was then stored in Millipore water in a PFA vial.

Second, the resin setup order is a crucial consideration. As shown in Fig 1, 1.6 mL of AG50W-X12 resin was used as the upper layer of the column and 0.40 mL of Sr Spec resin was used as the bottom layer. At early stages of separation, most of the Rb, Sr, Pb, REEs and matrix elements were fixed on the AG50W-X12 resin. As separation proceeded, matrix elements and Rb were quickly washed out from the AG50W-X12 resin using 2.5 M HNO_3. Given that matrix elements (K, Na, Ca, Mg, Al, Fe, Mn, Ti) and Rb are not absorbed by the Sr Spec resin and quickly pass through the column in medium-concentration HNO_3 (e.g., 2~3 M), potential matrix interference during subsequent REEs-Sr-Pb analyses is avoided. REEs fraction enriched Nd and Sr fraction with high purity were eluted with consecutive volumes of 7 M of HNO_3 and 0.05 M of HNO_3 before collection of Pb. Finally, retained Pb on the Sr Spec resin was eluted completely using 8 M of HCl.

Third, the concentration of HNO_3 acid is crucial as main eluting reagent. By many condition experiments, 2.5 M HNO_3 is the most suitable acid to use for rinsing out matrix elements before collection of Sr, Nd, and Pb. Several concentrations of HNO_3, e.g., 3~4 M, were tested to determine which concentration best rinses out matrix elements. However, the sample purity obtained was unsatisfactory. As such, although matrix elements and Rb can be quickly washed out by high concentrations of HNO_3 (3 M or 4 M), good sample purity of Sr and REEs cannot be achieved.

3.2 Purity, recovery and blank

The experimental measurements required to calibrate the columns (Major and Trace element distribution curve) are performed by using an ICP-MS (Finnigan Element). As shown in Fig 2, all matrix elements (K, Na, Ca, Mg, Al, Fe, Ti), Rb and part of Ba and REEs had been rinsed in fraction1 before collection of Nd fraction. Minor Ba, Sr and most REEs are co-exited with Nd in fraction 2. The yield of Nd is 96.2 % in fraction 2. Additionally, most Sr (~ 81.2 %) with high purity is rinsed in fraction 3 and no Rb is detected in Sr fraction. Most Pb (~ 91.4 %) with high purity is rinsed in fraction 4. The recovery of Sr (~81%) and Pb (~91%) is slightly lower than the previous studies. The loss of part of the Sr and Pb may cause minor bias on the isotopic composition due to isotopic fractionation during the process of chemical separation. Such fractionation for Sr can be corrected by internal ratio (^{88}Sr/^{86}Sr = 8.375209) during mass spectrometry measurement. As to the potential Pb isotope composition bias due to imperfect Pb yield, Baker[11] had ever performed system investigations using different ion exchange resin column to observe those chemical fractionations in different collected fractions. Baker[11] found that the biggest fractionation was ca 200 ppm/amu when the eluted Pb fraction was lower than 10 %. With the increasing of the Pb yield (≥ 85%), these fractionations become very small compared to the analytical reproducibility of Pb isotope[11]. In this study, the yield of Pb is higher than 90 %. Thus, Pb isotopic fractionations from resin column should be very small and no detectable within analytical error in theory.

In spite of good purity can be achieved for Sr, Nd and Pb TIMS analysis.

However, the very minor organic materials derived from the Sr Spec resin during column chemistry could affect the performance of the emitter substance, even if the Sr Spec resin has undergone the pretreatment using 6 M HCl and 7 M HNO_3. Hence, the Sr, Nd and Pb fractions are first evaporated to dryness, and then digested using a 0.3 ml of 14 M HNO_3 in a 180 ^oC hotplate for 2 hours in the closed PFA vials. Finally, the digested Sr-Nd-Pb fractions were dried down at approximately 150 ^oC again prior to TIMS measurements.

Blanks are very critical in any work especially for the determination of low level Sr, Nd and Pb concentrations. Therefore, they must be carefully evaluated. The Sr, Nd and Pb blanks are determined using ^{84}Sr-enriched, ^{150}Nd-enriched and ^{204}Pb-enriched spikes by isotope dilution method, respectively. In this study, the whole procedure blank for Sr, Nd, and Pb is lower than 110 pg, 70 pg and 150 pg, respectively. The ratios of 65~70 mg silicate materials over blank in this study are larger than 3500 for Sr, 2200 for Nd, and 1300 for Pb at least. Thus, the blanks for Sr, Nd and Pb are negligible relative to the amount of analytes contained in a 65~70 mg silicate aliquot. However, due to imperfect blank level, this method is not suitable for those silicate samples with low contents (≤ 2 ppm) of Sr-Nd-Pb.

3.3 Memory effects

In previous investigations, strong Sr and Pb memory effects were observed for the Sr Spec resin. Misawa et al[18] found that an extremely high “carry-over” of Sr (~1.4 ng) from one sample to the next. Likewise, the Pb memory effect is even stronger than that of Sr for the Sr Spec resin. In addition, obvious Pb memory effects (~1.8 ng) are observed for those used AG50W-X12 resin in this study. Therefore, we consider that it is not advisable to recycle it for further Sr and Pb separation.

3.4 Reproducibility and precision of Sr, Nd and Pb isotopic ratios

To evaluate and validate this method, six CRMs from USGS and GSJ were conducted for Sr, Nd and Pb isotopic ratios by a Triton Plus TIMS. These CRMs encompassed samples with a wide range of matrix composition and elemental content. As shown in Tables 3 and 4, the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios for all the analyzed USGS and GSJ reference materials were obtained with an internal precision better than 0.0025 % (2 RSE). As shown in Tables 5, the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ for all the analyzed USGS and GSJ reference materials were obtained with an internal precision better than 0.005 % (2 RSE). In order to check the accuracy of Sr, Nd and Pb isotopic ratios in this study, we plot and compare these data with the published data. As shown in Fig 3 and Fig 4, the Sr, Nd and Pb data presented here show good agreement with previously published data by TIMS and MC-ICP-MS techniques[6, 11, 12, 14, 15, 20-24, 26-35,40-42].

As to $^{143}Nd/^{144}Nd$ 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 according to the previously reported method [28]. As shown in Table 4 and Figure 5, the corrected $^{145}Nd/^{144}Nd$ value is 0.348409 ±

0.000008 (2 SD, n = 30) in actual silicate samples, which agrees well with reported values of 0.348405~0.348419 [28-31, 35, 36]. Both obtained ^{143}Nd/^{144}Nd and ^{145}Nd/^{144}Nd data implied that ^{144}Sm isobaric interference can be accurately subtracted.

The analytical reproducibility for Sr, Nd and Pb was examined using reference materials BCR-2. As shown in Tables 3, 4 and 5, ten replicated measurements of BCR-2 yielded ^{143}Nd/^{144}Nd value of 0.512635 ± 0.000012 (2 SD), ^{87}Sr/^{86}Sr value of 0.705015 ± 0.000014 (2 SD), ^{206}Pb/^{204}Pb value of 18.752 ± 0.004 (2 SD), ^{207}Pb/^{204}Pb value of 15.620 ± 0.005 (2 SD) and ^{208}Pb/^{204}Pb value of 38.715 ± 0.013 (2 SD). BCR-2 analysis data were well consistent with the reported values.[6, 9, 11, 14, 26-33,41] More, the reproducibility of ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd from BCR-2 is approximately 0.002-0.003 %(2 RSD). The reproducibility of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb from BCR-2 is approximately 0.021-0.033 %(2 RSD). In general, data reproducibility and precision are satisfactory and completely fit the demand in geo-science and environmental science.

4. Conclusion

A rapid single-column chemical separation method was developed for measuring ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd, ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb isotope ratios in the same silicate sample digest. Sr, Nd, and Pb were sequentially separated from the same matrix solution using a single column without intervening evaporation. The proposed separation procedure achieves the satisfactory purity and rapid separation of Sr, Nd, and Pb and reduces cross-contamination risk. As such, the proposed procedure offers significant advantages over existing methods in terms of simplicity, separation efficiency and waste reduction. The bottleneck associated with sample preparation prior to thermal ionization mass spectrometric measurements can be significantly reduced with the new chemical separation protocol.

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Figure captions

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

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

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

Fig 4. Comparison of Pb values obtained by the present study and previous data.

Fig 5. Corrected ^{145}Nd/^{144}Nd ratios for silicate rock from USGS and GSJ

Graphic abstract:

Single-column separation scheme in this study compared with the traditional three-step separation procedure

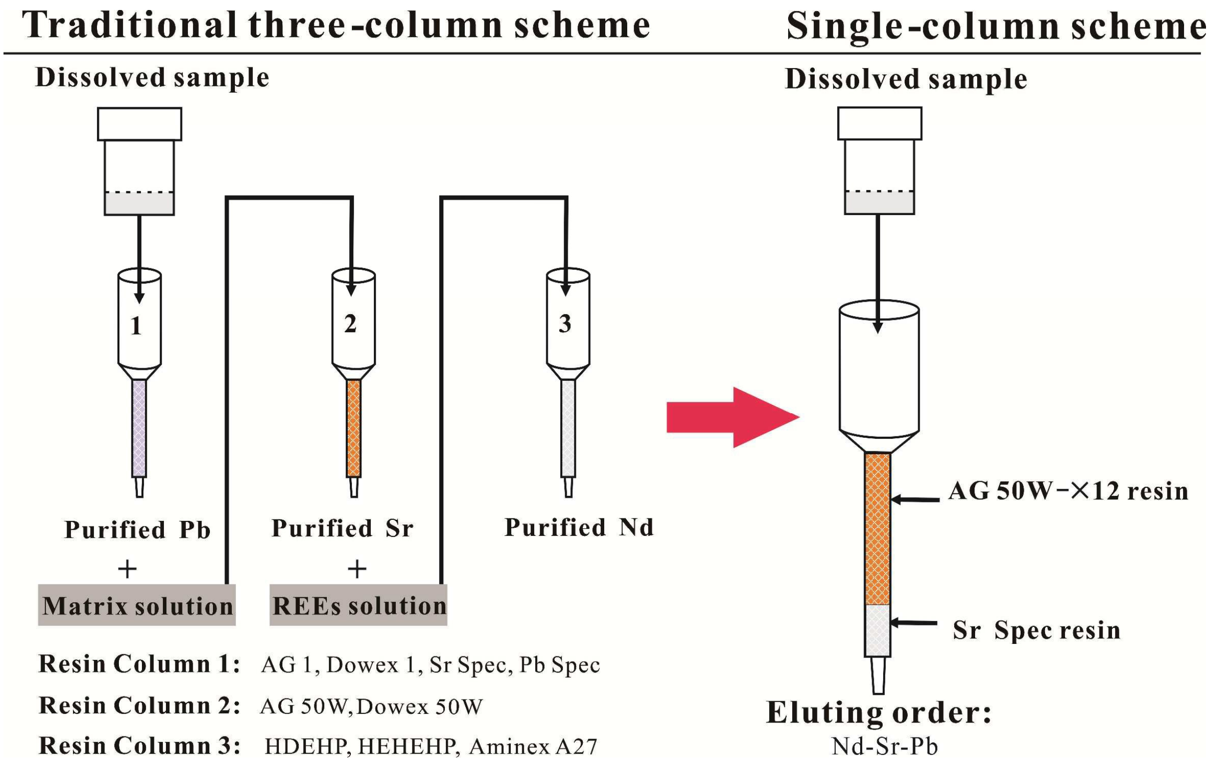

Table 1. Single column Sr-Nd-Pb chemical procedures

Eluting Fraction	Eluting reagent		Eluting volume (mL)	Eluting Fraction
Loading sample	2.5 M	HNO_3	1.0	1
Rinsing	2.5 M	HNO_3	2.0 (0.5×4)	1
Rinsing	2.5 M	HNO_3	23.0	1
Eluting Nd (REEs)	7.0 M	HNO_3	6.0	2
Eluting Sr	0.05M	HNO_3	5.0	3
Eluting Pb	8.0 M	HCl	3.0	4

Table 2. Cup setting of static multi-collector mode in Triton Plus TIMS

Element	L4	L3	L2	L1	CC	H1	H2	H3
Sr			^{84}Sr	^{85}Rb	^{86}Sr	^{87}Sr	^{88}Sr	
Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Sm	^{149}Sm		
Pb					^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb

Table 3. Analytical results of Sr isotopic ratios for CRMs determined by TIMS

CRMs	$^{87}Sr/^{86}Sr$	2 SE	Reported value
BCR-2	0.705019	0.000010	0.705019[6] ; 0.705007[21]
BCR-2	0.705026	0.000009	0.705026[29]; 0.705023[33]
BCR-2	0.705025	0.000011	0.704998[41]
BCR-2	0.705010	0.000012	
BCR-2	0.705015	0.000010	
BCR-2	0.705008	0.000011	
BCR-2	0.705010	0.000011	
BCR-2	0.705019	0.000009	
BCR-2	0.705016	0.000012	
BCR-2	0.705004	0.000011	
Mean ± 2 SD	0.705015 ± 0.000014		0.705015
AGV-2	0.703975	0.000013	0.703987[6]; 0.703989[21]
AGV-2	0.703984	0.000010	0.703978[33]; 0.703985[41]
AGV-2	0.703980	0.000008	
AGV-2	0.703977	0.000010	
Mean	0.703979		0.703985
JR-2	0.705447	0.000012	0.705462[29];0.705482[42]
JR-2	0.705458	0.000012	
JR-2	0.705455	0.000013	
JR-2	0.705448	0.000012	
Mean	0.705452		0.705472
JB-2	0.703691	0.000010	0.703709[23]; 0.703668[24]
JB-2	0.703686	0.000009	0.703675[35];0.703703[42]
JB-2	0.703691	0.000010	
JB-2	0.703697	0.000011	
Mean	0.703691		0.703689
JB-3	0.703426	0.000012	0.703432[23];0.703410[24]
JB-3	0.703432	0.000010	0.703422[35]
JB-3	0.703448	0.000009	
JB-3	0.703435	0.000012	
Mean	0.703435		0.703421

BIR-1	0.703104	0.000010	0.703095[21]; 0.703104[29]
BIR-1	0.703120	0.000011	0.703104[35]; 0.703108[41]
BIR-1	0.703093	0.000012	
BIR-1	0.703102	0.000010	
Mean	0.703105		0.703103

Table 4. Analytical results of Nd isotopic ratios for CRMs determined by TIMS

CRM	^{143}Nd/^{144}Nd	2 SE	Reported Value	^{145}Nd/^{144}Nd	2 SE
BCR-2	0.512629	0.000008	0.512634[6]; 0.512632[26]	0.348406	0.000005
BCR-2	0.512630	0.000006	0.512638[27]; 0.512630[28]	0.348410	0.000003
BCR-2	0.512633	0.000006	0.512636[29]; 0.512638[30]	0.348411	0.000004
BCR-2	0.512626	0.000005	0.512641[31]; 0.512630[32]	0.348405	0.000004
BCR-2	0.512644	0.000008	0.512640[33]	0.348415	0.000005
BCR-2	0.512632	0.000006		0.348408	0.000003
BCR-2	0.512636	0.000010		0.348415	0.000004
BCR-2	0.512641	0.000009		0.348411	0.000005
BCR-2	0.512636	0.000008		0.348412	0.000005
BCR-2	0.512640	0.000010		0.348416	0.000006
Mean ± 2 SD	0.512635 ± 0.000012		0.512636	0.348411 ± 0.000008	
AGV-2	0.512791	0.000005	0.512791[6]; 0.512797[30]	0.348406	0.000004
AGV-2	0.512782	0.000007	0.512811[31];0.512776[32];0.512781[33]	0.348409	0.000005
AGV-2	0.512789	0.000009		0.348411	0.000006
AGV-2	0.512791	0.000007		0.348408	0.000005
Mean	0.512788		0.512791		
JR-2	0.512913	0.000006	0.512910[26]; 0.512917[28]	0.348403	0.000003
JR-2	0.512912	0.000006	0.512911[29]; 0.512919[42]	0.348410	0.000003
JR-2	0.512921	0.000008		0.348409	0.000004
JR-2	0.512926	0.000006		0.348412	0.000004

Mean	0.512918		0.512914		
JB-2	0.513093	0.000006	0.513085[23]; 0.513090[24]; 0.513087[26]	0.348404	0.000003
JB-2	0.513094	0.000007	0.513102[33]; 0.513094[35];0.513097[42]	0.348407	0.000004
JB-2	0.513099	0.000008		0.348410	0.000006
JB-2	0.513097	0.000009		0.348403	0.000006
Mean	0.513096		0.513092		
JB-3	0.513056	0.000008	0.513037[24]; 0.513062[26]; 0.513059[30]	0.348404	0.000004
JB-3	0.513049	0.000008	0.513089[31]; 0.513064[33]; 0.513049[35]	0.348405	0.000004
JB-3	0.513059	0.000009		0.348416	0.000005
JB-3	0.513058	0.000009		0.348407	0.000006
Mean	0.513056		0.513060		
BIR-1	0.513088	0.000009	0.513085[22]; 0.513093[27];0.513084[28]	0.348407	0.000005
BIR-1	0.513085	0.000009	0.513084[30]; 0.513107[31];0.513078[35]	0.348409	0.000006
BIR-1	0.513097	0.000010		0.348403	0.000007
BIR-1	0.513098	0.000008		0.348404	0.000006
Mean	0.513092		0.513089		

Table 5. Comparison of Pb isotopic ratio in this study and reported values

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
BCR-2	18.7512	0.0009	18.753[6];18.750[9]	15.6180	0.0007	15.625[6];15.615[9]	38.7047	0.0018	38.724[6];38.691[9]
BCR-2	18.7526	0.0007	18.765[11];18.760[14]	15.6197	0.0006	15.623[11];15.621[14]	38.7124	0.0016	38.752[11];38.731[14]
BCR-2	18.7512	0.0007		15.6183	0.0006		38.7099	0.0015	
BCR-2	18.7495	0.0005		15.6169	0.0004		38.7078	0.0011	
BCR-2	18.7529	0.0009		15.6221	0.0007		38.7173	0.0018	
BCR-2	18.7543	0.0008		15.6237	0.0007		38.7221	0.0017	
BCR-2	18.7536	0.0008		15.6205	0.0006		38.7164	0.0016	
BCR-2	18.7547	0.0009		15.6217	0.0008		38.7202	0.0019	
BCR-2	18.7490	0.0006		15.6236	0.0005		38.7243	0.0010	
BCR-2	18.7532	0.0006		15.6172	0.0007		38.7135	0.0011	
Mean ± 2 SD	18.752 ± 0.004		18.757	15.620 ± 0.005		15.621	38.715 ± 0.013		38.725
AGV-2	18.8675	0.0006	18.869[6]; 18.864[9]	15.6133	0.0005	15.617[6]; 15.609[9]	38.5246	0.0013	38.544[6]; 38.511[9]
AGV-2	18.8632	0.0008	18.873[11];18.879[14]	15.6266	0.0007	15.621[11];15.618[14]	38.5562	0.0018	38.552[11];38.547[14]
AGV-2	18.8744	0.0007		15.6275	0.0006		38.5674	0.0014	
AGV-2	18.8698	0.0008		15.6126	0.0007		38.5123	0.0015	
Mean	18.869		18.871	15.620		15.616	38.540		38.539
JR-2	18.3435	0.0006	18.345[12]; 18.356[15]	15.5654	0.0005	15.548[12]; 15.560[15]	38.3952	0.0013	38.361[12]; 38.401[15]
JR-2	18.3486	0.0006	18.355[40]	15.5537	0.0005	15.563[40]	38.3795	0.0013	38.413[40]
JR-2	18.3523	0.0005		15.5633	0.0005		38.4037	0.0012	
JR-2	18.3487	0.0006		15.5487	0.0005		38.3731	0.0014	

Mean	18.348		18.352	15.558		15.557	38.388		38.392
JB-2	18.3375	0.0008	18.344[11]; 18.332[12]	15.5550	0.0007	15.562[11]; 15.546[12]	38.2559	0.0017	38.278[11]; 38.224[12]
JB-2	18.3361	0.0007	18.3428[35];18.342[40]	15.5572	0.0007	15.5594[35];15.566[40]	38.2492	0.0018	38.2770[35];38.276[40]
JB-2	18.3481	0.0007		15.5612	0.0006		38.2841	0.0016	
JB-2	18.3419	0.0008		15.5676	0.0007		38.2781	0.0017	
Mean	18.341		18.340	15.560		15.558	38.267		38.264
JB-3	18.2910	0.0008	18.291[8]; 18.284[12]	15.5326	0.0007	15.529[8]; 15.523[12]	38.2331	0.0018	38.230[8]; 38.199[12]
JB-3	18.2865	0.0008	18.2952[35]; 18.291[40]	15.5290	0.0007	15.5356[35]; 15.540[40]	38.2210	0.0018	38.2506[35];38.250[40]
JB-3	18.2949	0.0007		15.5336	0.0006		38.2356	0.0016	
JB-3	18.2873	0.0008		15.5294	0.0007		38.2395	0.0017	
Mean	18.290		18.290	15.531		15.532	38.232		38.233
BIR-1	18.8460	0.0009	18.851[11];18.842[14]	15.6521	0.0008	15.662[11];15.641[14]	38.4724	0.0022	38.501[11];38.449[14]
BIR-1	18.8448	0.0010	18.8533[35]	15.6531	0.0009	15.6585[35]	38.4705	0.0023	38.4968[35]
BIR-1	18.8357	0.0010		15.6563	0.0009		38.4990	0.0021	
BIR-1	18.8361	0.0011		15.6568	0.0010		38.4951	0.0024	
Mean	18.841		18.849	15.655		15.654	38.484		38.482

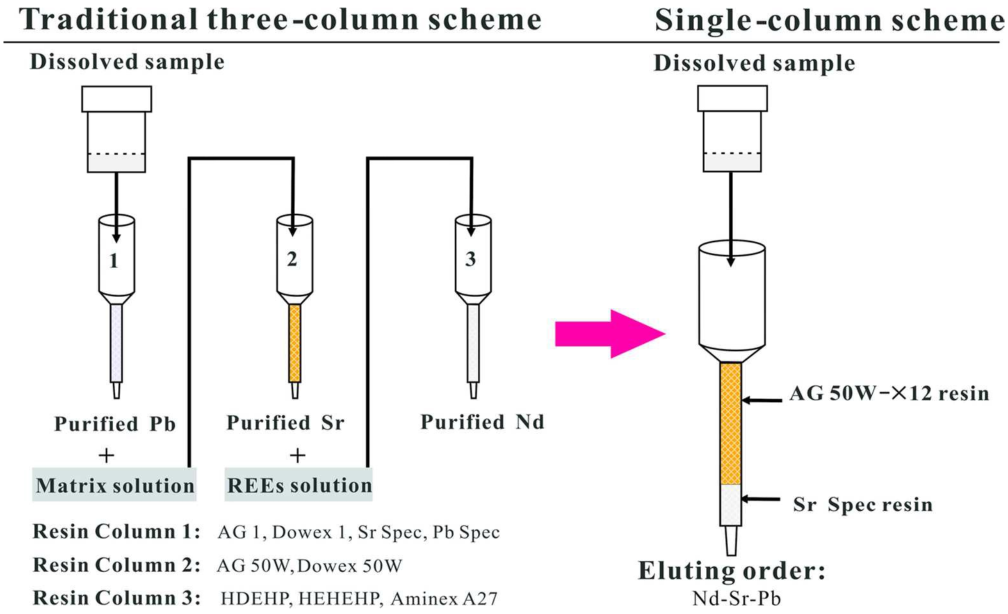

Fig 1
119x72mm (300 x 300 DPI)

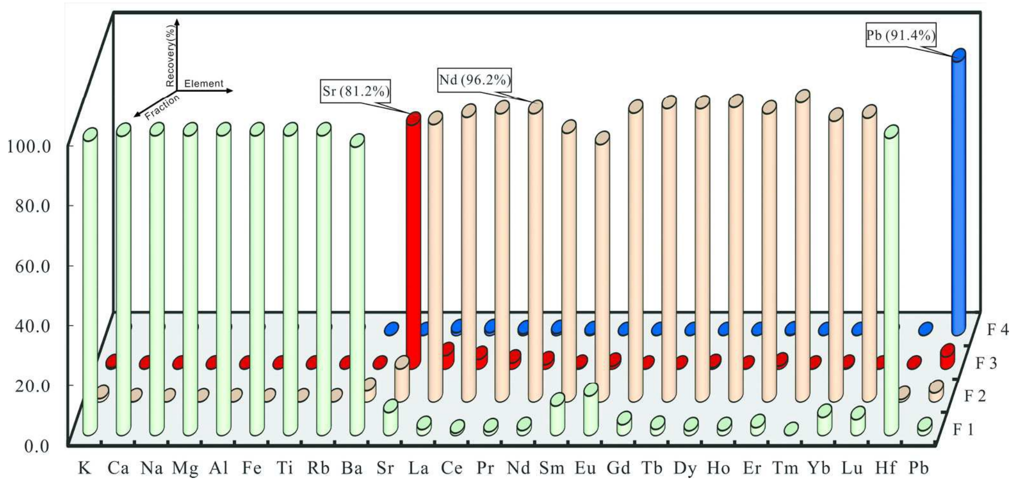

Fig 2
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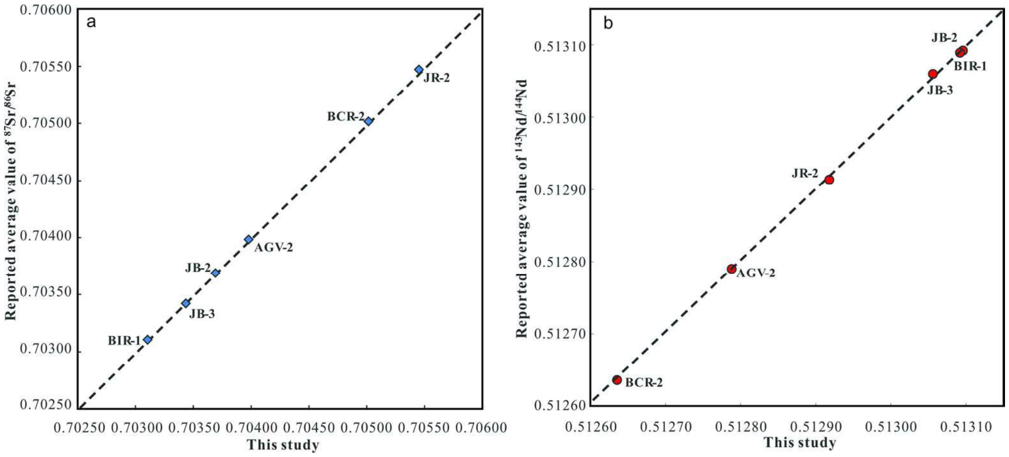

Fig 3
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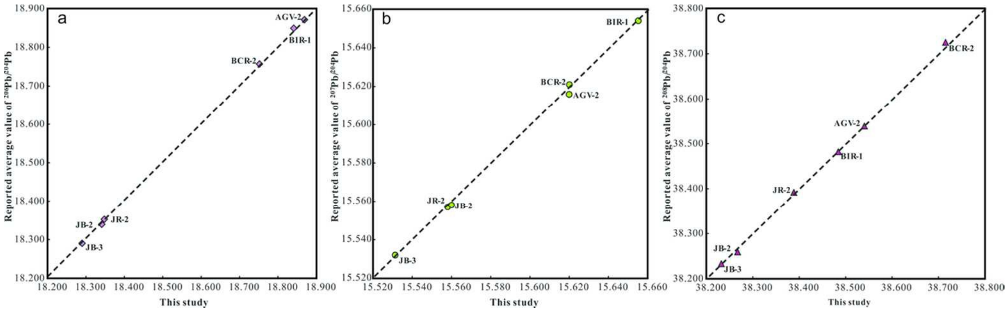

Fig 4
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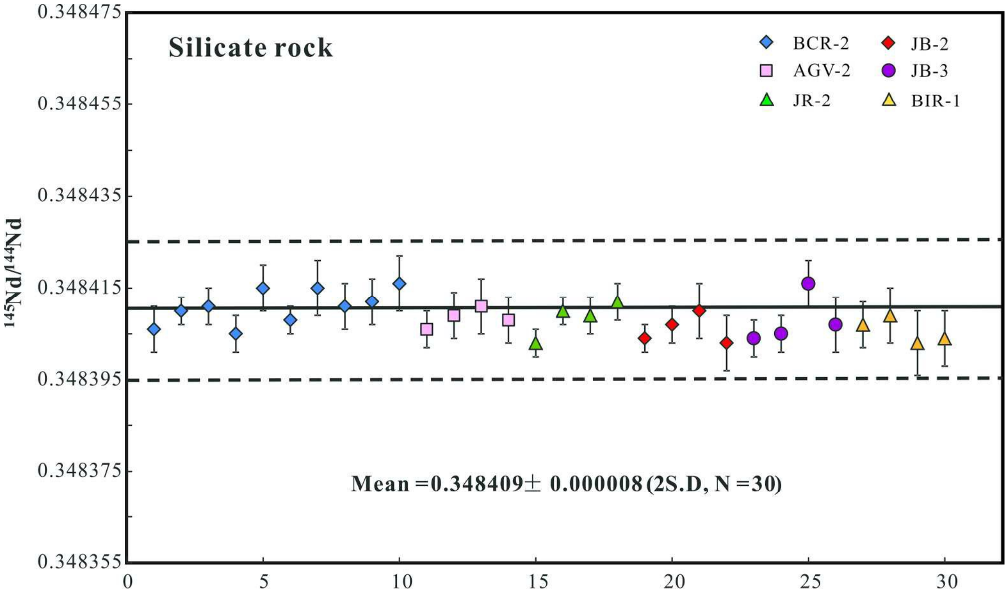

Fig 5
100x58mm (600 x 600 DPI)