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Rubidium purification *via* a single chemical column and its isotope measurement on geological standard materials by MC-ICP-MS

Zhuoying Zhang,^{ab} Jinlong Ma,^{ID}*^a Le Zhang,^a Ying Liu^a and Gangjian Wei^{ID}^a

A chromatographic procedure for Rb, K, Ba and Sr one-by-one separation from geological materials has been developed by using a single column with packing Sr-spec resin, followed by high-precision Rb isotope measurement by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The main matrix elements (Ti, Al, Mg, Fe, Mn, Na and Ca) were removed with 4.4 mL of 3 M HNO₃ first; Rb and K were then sequentially eluted in different volumes with the same acid. After that, Ba was eluted with 8 M HNO₃, and finally Sr was eluted with Milli-Q water. This procedure enables us to collect pure Rb, K, Ba and Sr one by one in a single column with recovery close to 100%. The purified Rb was measured by using a standard-sample bracketing method *via* MC-ICP-MS. The short-term precision for $\delta^{87}\text{Rb}$ was better than $\pm 0.03\text{‰}$ (2SD, for 15 hours), and the long-term (more than 12 months) external precision was better than $\pm 0.06\text{‰}$ (2SD) based on repeated analysis of Rb standard solution NIST SRM 984. Matrix effects on Rb isotope measurement by MC-ICP-MS were tested by doping pure Rb standard with various amounts of matrix elements and were found to be insignificant when Na/Rb < 2, Ca/Rb < 4 and K/Rb < 25. We measured a set of geological reference standards by this method and found significant Rb isotopic variation. Our study suggests that Rb isotope geochemistry may be a promising tracer of various cosmochemical and geological processes.

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Introduction

Rubidium is a volatile, lithophile, incompatible, alkaline element that is widely distributed as a trace element in major reservoirs. It has two natural isotopes, ⁸⁵Rb and ⁸⁷Rb. Among them, ⁸⁷Rb is a radioactive isotope and decays to ⁸⁷Sr with a long half-life ($T_{1/2} = 4.88 \times 10^{10}$ y).¹ Nonetheless, the Rb isotope ratio ($^{85}\text{Rb}/^{87}\text{Rb} = 2.593$)^{2,3} is considered to remain constant in definite geological periods because of its long half life and heavy mass, which in theory should not lead to large mass-dependent Rb isotope fractionation. However, recent studies have found significant mass-dependent fractionation for Sr and Nd isotopes,^{4–8} which have similar or even smaller relative mass when compared to Rb isotopes. Therefore, Rb isotope fractionation may indeed occur during geological processes. Thus it is necessary to evaluate whether Rb isotopes fractionate in nature, which has important implications for Rb–Sr geochronology and using Rb and Sr isotopes as tracers of many geological processes.^{9,10}

Even today, the study of Rb isotope geochemistry is in its infancy because of two obstacles preventing high-precision Rb

isotopic analysis. One is that Rb is hard to effectively separate from the matrix by using conventional cation exchange resins, especially from K, which is confirmed to affect the high-precision Rb isotope measurement.^{11–13} Even if great progress has been made by using Cs–Rb resin in recent studies, it is still difficult to back-extract Rb.¹⁴ The other one is the poor precision (around $\pm 1\%$) obtained when using thermal ion mass spectrometry (TIMS).¹⁵ Recent developments in MC-ICP-MS have significantly improved the precision to 0.02–0.05% (2SD, standard deviation) for $^{87}\text{Rb}/^{85}\text{Rb}$ in a single measurement session, corresponding to an error of 0.2–0.5‰ for $\delta^{87}\text{Rb}$.^{11,12} However, this precision is not enough to identify Rb isotope fractionation during terrestrial geological processes. In an updated study, a better precision with a long-term reproducibility of $\pm 0.08\text{‰}$ (2SD) for $\delta^{87}\text{Rb}$ was achieved using MC-ICP-MS in SSB mode. This method, however, involved complicated procedures of Rb purification to reduce matrix interference in Rb isotope measurement.¹³ Therefore, a new technique is needed to simplify and improve Rb separation and MC-ICP-MS analysis.

Here, we developed a novel and convenient method to purify Rb from the matrix by using Sr-spec resin *via* a single column procedure. At the same time, K, Ba and Sr can also be obtained sequentially. By following this procedure, we analyzed Rb isotopes for a set of geological reference materials using MC-ICP-MS by using a sample-standard bracketing (SSB) method. We found significant Rb isotopic variation during different

^aState Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China. E-mail: jlma@gig.ac.cn; Fax: +86-020-85290116; Tel: +86-020-85290116

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

geological processes, and Rb isotope geochemistry may become a promising new tool in the geochemistry toolbox.

Experimental

Reagents and materials

Milli-Q water was prepared using a Milli-pore system (USA), yielding a resistivity of 18.2 M Ω cm. Hydrofluoric acid (HF) was purified from BVIII grade reagents (electronic grade) using a Savillex DST-1000 system (USA), while nitric acid (HNO₃) was double-distilled from a GR grade reagent with the same system. These concentrated acids were diluted with Milli-Q water to appropriate concentrations for chemical treatment.

Eichrom-Sr-spec resin (50–100 mesh, Eichrom Technologies, USA) was chosen for separation and purification of Rb, K, Ba, and Sr from the matrix elements.

Sample preparation

Here we selected a series of geological reference materials, ranging in composition from basalts to granites.

All experiments were carried out in a class 100 clean hood at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS). According to the Rb concentration, about 30–100 mg samples were weighed into pre-cleaned 7 mL PFA Savillex® beakers. The rock samples were digested in an acid mixture of HF–HNO₃ with a volume ratio of 2 : 1 in the capped beakers and put on a hotplate at a temperature of 120 °C for 7 days. After that, they were evaporated to dryness. Then, 2 mL of concentrated HNO₃ were added into the beakers and dried again, and the above steps repeated twice. Then 2 mL of 1 : 1 HNO₃ were added and the beakers were capped again and kept on a hotplate overnight. Finally, the samples were dried again, re-dissolved with 3 M HNO₃, and heated for at least 4 hours for chromatography treatment on Sr-spec resin.

Column chemistry

1.5 g of Sr-spec resin (50–100 mesh) was packed in a polypropylene column with a diameter of 0.5 cm and a length of 12.7 cm. The resin was subsequently washed with 12 mL of 3 M HNO₃ and 18 mL of Milli-Q water, and conditioned with 12 mL of 3 M HNO₃. Then 100 μ L of the prepared solution was extracted and loaded onto the resin. Before collecting Rb, the resin was washed with 4.4 mL of 3 M HNO₃ to remove most major and trace elements, such as Ca, Na, Al, Fe, Mn, Ti, P and REE elements. Rb was collected with 7.5 mL of 3 M HNO₃. Then another 15 mL of 3 M HNO₃ were added onto the resin to recover K. After this step, 5.5 mL of 8 M HNO₃ were added onto the resin, and then Ba was recovered with another 18 mL of 8 M HNO₃. Finally Sr was collected using Milli-Q water as the eluent after cutting Ba. All the eluted solutions were dried and Rb was re-dissolved in 2% HNO₃ for isotope measurement. The detailed chemical separation procedures are listed in Table 1.

In order to verify the applicability of this column procedure to different geological materials, the leaching curves of four different USGS rock references with various Rb contents, from

Table 1 Chemical separation procedure for Sr-spec resin

Step	Operation
Step 1	Resin washing and conditioning 3 M HNO ₃ 4 mL Milli-Q water 3 mL \times 2 Repeating the above steps three times 3 M HNO ₃ 4 mL \times 3
Step 2	Loading the sample (0.1 mL)
Step 3	Washing 3 M HNO ₃ 0.4 mL 3 M HNO ₃ 0.5 mL \times 2 3 M HNO ₃ 3 mL
Step 4	Collecting Rb 3 M HNO ₃ 7.5 mL
Step 5	Collecting K 3 M HNO ₃ 3 mL \times 5
Step 6	Washing 8 M HNO ₃ 5.5 mL
Step 7	Collecting Ba 8 M HNO ₃ 3 mL \times 6
Step 8	Collecting Sr Milli-Q water 5 mL
Step 9	Collecting Sr and reducing the memory effect on the resin 3 M HNO ₃ 4 mL Milli-Q water 3 mL \times 2

9.80 μ g g⁻¹ to 170 μ g g⁻¹, including BHVO-2 (basalt), AGV-2 (andesite), W-2a (diabase) and G-2 (granite), were obtained are shown together in Fig. 1. Meanwhile we set the same column and followed all the steps without loading any rock sample to test the procedural blanks, and the results indicated that the total procedural blanks for Rb, K, Ba and Sr were generally lower than 1 ng.

Instrumentation

The measurement of Rb isotopes was carried out on a Thermo Fisher Scientific Neptune Plus MC-ICP-MS at the GIG-CAS. This instrument is a double focusing magnetic sector field mass spectrometer equipped with 9 Faraday cups and 8 ion counters. All Faraday cups were connected to amplifiers with 10¹¹ Ω resistance. Sample solutions in 2% nitric acid were introduced through a PFA nebulizer (\sim 50 μ L min⁻¹, ESI) and a quartz dual cyclonic-Scott spray chamber from Thermo Fisher Scientific. An X skimmer cone instead of an H skimmer cone was used at the interface to improve the sensitivity of the instrument. The total Rb isotope intensity for 100 ng mL⁻¹ solution is about 5 V on mass 85. Details of the typical operating parameters are reported in Table 2.

Measurement strategies

The L2, the axial and the H1 Faraday cups were assigned to collect the signals of ⁸⁵Rb, ⁸⁷Rb and ⁸⁸Sr, respectively. The intensity of ⁸⁸Sr was used to monitor the interference of ⁸⁷Sr on ⁸⁷Rb. The isobaric interference of ⁸⁷Sr on ⁸⁷Rb was corrected by monitoring ⁸⁸Sr as $^{87}\text{Sr} = 0.085 \times ^{88}\text{Sr}$.¹⁶ Although the ⁸⁸Sr/⁸⁷Sr ratio of geological samples should not be constant, the signal of

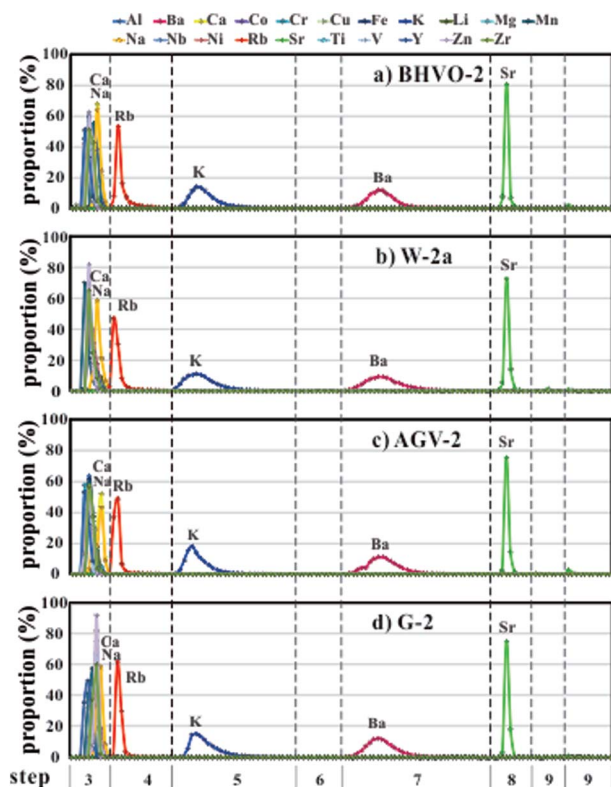


Fig. 1 The elution curves of four international reference materials: (a) BHVO-2, (b) W-2a, (c) AGV-2, and (d) G-2 on Sr-spec resin. The proportions for all elements represented the percentage content in each elution fraction relative to the total Rb content loaded onto the column.

Table 2 Typical operating parameters for Rb isotope measurement on a Neptune

Parameter	Value
RF forward power	1145 W (optimized daily)
Ar cooling gas flow	16.00 L min ⁻¹
Ar auxiliary gas flow	1.00 L min ⁻¹ (optimized daily)
Ar sample gas flow	0.99 L min ⁻¹ (optimized daily)
Measurement mode	Static
Extraction voltage	-2000 V
Acceleration voltage	10 kV
Detection system	Faraday cups
Nebulizer	ESI PFA-50 (~50 μL min ⁻¹)
Spray chamber	Quartz dual cyclonic-Scott spray chamber
Sample cone	H sample cone (Ni)
Skimmer cone	X skimmer cone (Ni)
Instrument resolution	400
Integration time	4.194 s
Idle time	3 s

⁸⁸Sr was generally less than 1 mV during our experiment; so it is feasible to choose a ⁸⁷Sr/⁸⁸Sr ratio of 0.085 (ratio of most geological samples) for reduction of interference of ⁸⁷Sr on ⁸⁷Rb.

Given that Rb has only two isotopes, the technique of double spike can not work. So, two methods were employed in previous studies: (1) adding Zr to calibrate the mass bias during Rb

isotope measurement,^{11,12} and (2) using sample-standard bracketing (SSB) mode for mass bias corrections.¹³ Here, we preferentially use method 2 to measure Rb isotopes because adding Zr can increase the memory effects of both Zr and Rb on our MC-ICP-MS. NIST SRM 984 was selected as the calibrator. The $\delta^{87}\text{Rb}$ of the sample was calculated from the measured $\text{Rb}_{\text{sample}}$ isotope ratio and the average results of the bracketed NIST SRM 984 from the equation below:

$$\delta^{87}\text{Rb}_{\text{‰}} = \left(\frac{2 \times {}^{87}\text{Rb}/{}^{85}\text{Rb}_{\text{sample}}}{{}^{87}\text{Rb}/{}^{85}\text{Rb}_{\text{SRM984A}} + {}^{87}\text{Rb}/{}^{85}\text{Rb}_{\text{SRM984B}}} - 1 \right) \times 1000$$

where SRM 984A and SRM 984B indicate the standard measured after and before the sample, respectively. All ⁸⁷Rb/⁸⁵Rb ratios in this equation are originally measured ratios without any mass bias correction.

In order to decrease the difference of mass bias between the sample and the standard solution during Rb isotope measurement, prior to measuring Rb isotopes, the concentrations of Rb of both the NIST SRM 984 standard solution and sample were adjusted to 100 ng mL⁻¹, which yielded a ⁸⁵Rb intensity of ~5 V, and a ⁸⁷Rb intensity of ~2 V. The signal of ⁸⁵Rb rapidly decreased to 0.4 mV after 5 min of washing with 2% HNO₃ at the end of each Rb isotope measurement. The minor Rb memory will be gradually increased up to 1 mV on mass 85 after a whole day of operation. However, as a consequence of the signal-to-background ratio for each measurement reaching values greater than 5000, the influence of the background on Rb isotope measurement can be assumed to be negligible, and no on-peak-zero correction is needed in our experiment.

The data acquisition contained a block with 60 cycles. The integration time for each cycle was 4.194 s. All 60 scans took about 5 minutes, yielding an internal precision of about (2–5) × 10⁻⁶ for ⁸⁷Rb/⁸⁵Rb. From the measured errors of both the sample and the bracketing standards, calculated using the Gaussian-error-propagation equation, the internal precision for $\delta^{87}\text{Rb}$ was estimated to be better than 0.03‰.

Results and discussion

Recovery of Rb, Ba, K and Sr

In order to test whether the recoveries of the four elements were close to 100% in our procedure, we mixed 400 ng of Rb into an Alfa-42885 elemental standard solution which contains 100 μg of Al, Ba, Ca, K, Li, Mg, Na, Sr and some other elements. The mixture was dried first, and then re-dissolved in 200 μL of 3 M HNO₃. 100 μL of the solution was loaded onto the resin and Rb, Ba, K and Sr were subsequently collected following our procedures described above. Another 100 μL was diluted into different concentrations as external standards to calculate the Rb, Ba, K and Sr concentrations and recovery of the purified aliquot. All four elements were measured 3 times using ICP-MS and the mean concentrations in the purified solution were 201 ± 9 ng for Rb and 50.1 ± 0.4 μg, 50.0 ± 0.1 μg, and 50.0 ± 0.3 μg for Ba, K and Sr, respectively, while their contents in the synthetic solution were 198 ± 8 ng, 49.8 ± 0.1 μg, 49.5 ± 0.3 μg, and 49.4 ± 0.5 μg, respectively. The concentrations in the synthetic solution

were slightly lower than those in the purified solution, which was perhaps the result of different matrix effects or minor differences in the diluted volumes. Calculated from these results, the recovery of the four elements purified by our procedure is close to 100% (100.8–101.8%).

Memory effect on Sr-spec resin

As mentioned in a previous study, the strong memory effect for Sr observed on Eichrom Sr-spec resin,¹⁷ like that for Sr and Rb memory on Sr-spec resin, can also be a problem. In order to evaluate the influence of the memory effect, we here chose a Chinese national reference material, GSR-1 (granite with a high Rb content of $466 \mu\text{g g}^{-1}$ and a negative $\delta^{87}\text{Rb}$ of -0.2‰). Firstly, we loaded GSR-1 solution onto a new Sr-spec resin column and separated the Rb using the above procedure. Then the same resin column was washed according to step 1 (Table 1). After that, 0.1 mL of $2 \mu\text{g mL}^{-1}$ NIST SRM 984 was loaded onto the same column, all the steps of the Rb separation procedures were carried out and the Rb for MC-ICP-MS measurements was collected. The $\delta^{87}\text{Rb}$ result of this column chemistry treated NIST SRM 984 is $0.00 \pm 0.04\text{‰}$, indicating that the Rb memory effect was negligible and the Sr-spec resin could be re-used at least two times after being carefully cleaned following our procedures. Also all the geological samples were repeatedly separated with the re-used Sr resin, and the data are consistent with the results obtained for samples treated with new resin within analytical error. This suggested that Sr-spec resin can be re-used at least twice after being carefully cleaned. However, when the leaching curves of Rb, Ba, K and Sr on Sr-spec resin were continuously monitored, we observed that the tails of these elements on Sr-spec resin became stronger and stronger with the increasing number of times the resin was re-used. As we have to collect these elements with close to full recovery, larger eluting volumes for Rb, K, Ba and Sr were needed after the resin was used twice. For example, 0.5 mL , 1.5 mL , 5 mL and 3 mL more of the eluents are needed for these elements, respectively, when the resin was re-used 3 times. We therefore suggest that Sr-spec resin can not be re-used more than three times in this work.

However, Sr-spec resin is very expensive, and it is quite wasteful to discard it after being used only very few times. In our lab, after tests with more than three rounds of rinsing by alternating $3\text{--}8 \text{ M HNO}_3$ and warm Milli-Q water, Rb, K, Ba and Sr residues on Sr-spec resin can be effectively removed. Conventional Sr separation (aiming to measure $^{87}\text{Sr}/^{86}\text{Sr}$, not the stable Sr isotope) can be performed in these reused Sr-spec resins, considering that it is not necessary to achieve full Sr recovery because a constant value of $^{88}\text{Sr}/^{86}\text{Sr}$ was used to calibrate the mass bias during $^{87}\text{Sr}/^{86}\text{Sr}$ measurements. A lot of Sr isotope data on rock standards have been tested in our lab, and all the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are consistent with the reference values within analytical error.

Rb isotope fractionation during column chemistry

Significant isotope fractionation has been observed during column purification for many isotopes such as Sr, Mg and Nd.^{19,21–23} Thus, it is of critical importance to ensure that no

artificial mass fractionation occurred during Rb purification using column chemistry. To investigate this, we loaded $100 \mu\text{L}$ of $15 \mu\text{g mL}^{-1}$ NIST SRM 984 Rb standard solution onto the Sr-spec resin, and the Rb was collected in 6 fractions by eluting with 0.5 mL of 3 M HNO_3 in each of the former 5 fractions and 5 mL of 3 M HNO_3 in the sixth fraction. The Rb isotope composition of each fraction was measured against the NIST SRM 984 Rb solution, and the results are shown in Fig. 2. A significant Rb isotope fractionation can be observed during column chemistry except for the first fraction, which contains an amount of Rb too small to be measured by MC-ICP-MS. It is interesting that, unlike Sr, Mg and Nd isotope fractionation during chromatography,^{18–20} the lighter Rb isotope was preferentially leached from the Sr-spec resin and the heavier Rb isotope left on the resin.²¹ We calculated the mean $\delta^{87}\text{Rb}$ with a weight average from all the collected fractions, yielding a value of $0.00 \pm 0.03\text{‰}$. This further indicates that the recovery of Rb was close to 100% and no artificial Rb isotope fractionation occurred during the column chemistry of our study.

Na, Ca and K matrix effects on Rb isotope measurement

During the Rb separation from the major matrix, there was still a small amount of Na ($<0.20\%$) and Ca ($<0.40\%$) remaining in the Rb fraction, whereas other major elements, such as Fe, Al, Mg, Ti, Mn, *etc.* had been entirely rinsed in advance and were not found in the Rb cutting solution. In order to evaluate the matrix effect of Na and Ca on Rb isotope measurement, Na and Ca standard solutions were added into NIST SRM 984 standard solution respectively. Besides, considering that K could not be removed effectively in previous procedures^{11,12} and trace amounts of K were likely collected together with Rb solution when the Sr spec resin was reused, K was evaluated together. As shown in Fig. 3, when the Na/Rb ratio was less than 2, the Ca/Rb ratio less than 4 and K/Rb less than 25, all the measured $\delta^{87}\text{Rb}$ values of NIST SRM 984 were close to 0.00 within analytical error, whereas negative drifts of $\delta^{87}\text{Rb}$ were induced when the Na/Rb ratio was >2 , the Ca/Rb ratio was >4 and K/Rb was >25 . Thus, the Na/Rb ratio should be controlled to <2 , the Ca/Rb ratio to <4 and K/Rb to <25 for a high-precision measurement of Rb isotopes. Na, Ca and K are major elements in most silicate

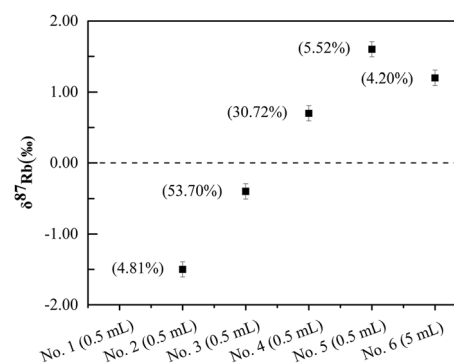


Fig. 2 Rb isotope fractionation in each fraction during the column chemistry. The percentage of Rb content in each fraction was relative to the total content loaded onto the Sr-spec resin.

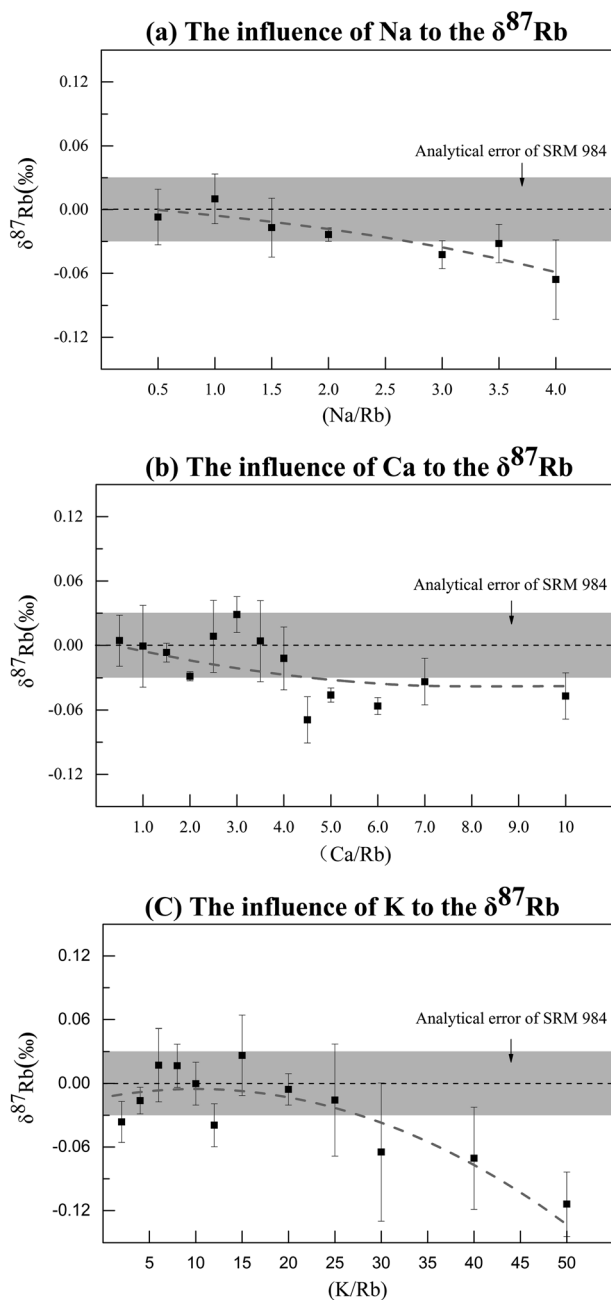


Fig. 3 The influence of (a) Na, (b) Ca and (c) K on $\delta^{87}\text{Rb}$.

rocks and their contents are generally higher than 1%. Rb content is more than $100 \mu\text{g g}^{-1}$ for most granites, but quite low for basalts; for example the USGS basalt reference BHVO-2 contains only $9.80 \mu\text{g g}^{-1}$ Rb. As a result, the Na/Rb, Ca/Rb and K/Rb ratios are generally lower than 200 in granites (such as G-2) but significantly high in basalts (such as BHVO-2), with Na/Rb, Ca/Rb and K/Rb ratios being larger than 1500, 8000, and 400, respectively. As mentioned above, <0.20% of Na and <0.40% of Ca were collected into the Rb fraction in our procedure. Therefore, the Na/Rb ratio in the collected Rb fraction decreases to about 0.30 for granite and to about 3.40 for basalts, and the Ca/Rb ratio decreases to about 0.32 for granite and to about 4.71

for basalts. In this respect, for most granite rocks or samples with low Na/Rb and low Ca/Rb ratios, the collected Rb could be directly measured for Rb isotopes by MC-ICP-MS after a single column chemical separation. As for most basaltic samples and those samples with high Na/Rb and Ca/Rb ratios (Na/Rb > 1000 and Ca/Rb > 1000), a repeated column chemistry step on the same column was needed to further decrease the Na and Ca contents remaining in the Rb solution. The K/Rb ratio is generally <25 in the Rb fraction for all the rocks after separation by our method. Thus its effect on Rb isotope measurement can be neglected in our work.

Instrument stability

The performance of the instrument for the determination of Rb isotope composition has been assessed by repeated measurement of NIST SRM 984 Rb standard solution. In order to decrease the short-term drift in mass bias during instrument measurement, we kept the washing time constant and maintained the same Rb concentration between the sample and the standard solution. The average results of $\delta^{87}\text{Rb}$ were $0.00 \pm 0.03\text{‰}$ (2SD, $n = 20$) for ~15 h measurements of NIST SRM 984 (Fig. 4(a)) and $0.00 \pm 0.06\text{‰}$ (2SD, $n = 120$) during the past 12 months (Fig. 4(b)), which suggests that our method is robust enough to measure high-precision Rb isotopic composition. The $\delta^{87}\text{Rb}$ values of some geological references were measured at different times during the past year and their standard deviation was found to be generally better than 0.06‰ (2SD), indicating an ideal external reproducibility.

Rb and Sr isotope compositions of geological reference materials

Rb isotope compositions of a series of geological reference materials have been measured using the above method. All the samples were repeated both for the column chemistry and instrument measurement at least twice. The results are listed in Table 3 and Fig. 5. According to our data, we can observe that two basalts (BHVO-2 and GSR-3) have relatively high $\delta^{87}\text{Rb}$ values, with an average of -0.06‰ , one andesite (AGV-2) and a diabase (W-2a) have relative $\delta^{87}\text{Rb}$ values, with averages of $-0.10 \pm 0.06\text{‰}$ and $-0.11 \pm 0.02\text{‰}$, respectively, whereas three granite samples (G-2, JG-2 and GSR-1) show much lower $\delta^{87}\text{Rb}$ values, with an average of -0.22‰ . These results again suggest that the SSB method is robust enough to measure high-precision Rb isotopes by MC-ICP-MS and Rb isotopes can serve as a promising new tracer to probe different geological processes.

The collected Sr solution in this study was also used to measure Sr isotopes by MC-ICP-MS following the method proposed by Ma *et al.*⁵ The results were consistent with the references published previously,^{4,22,23} within analytical error, which indicated that our method can also be suitable for Sr isotope measurement. The determination of Ba and K isotopes was not fully developed in our lab. Theoretically, Rb and Sr, as well as K and Ba purified using this method, can be satisfactorily used to measure the corresponding isotope compositions, and this needs to be confirmed in our future work.

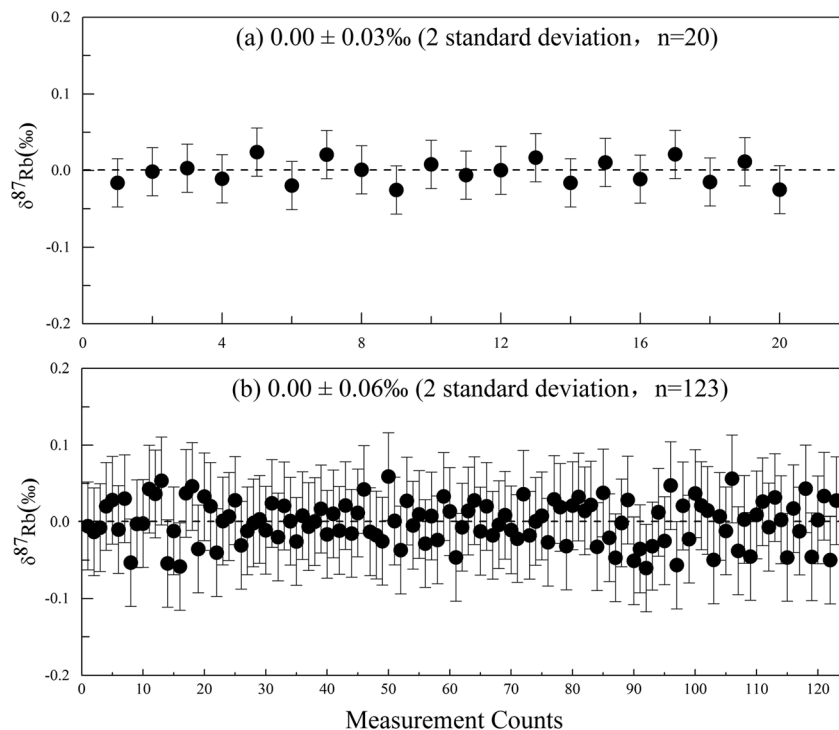


Fig. 4 The instrument stability during Rb isotope measurement for NIST SRM 984: (a) representing ~ 15 h of continuous measurement and (b) representing measurements for more than one year.

Table 3 Summary of measured $\delta^{87}\text{Rb}$ and Sr isotopes in the geological materials

Sample name	Sample type	Source	Rb ($\mu\text{g g}^{-1}$)	$\delta^{87}\text{Rb}$ (‰, 2SD)	Number ^d	Sr ($\mu\text{g g}^{-1}$)	$^{87}\text{Sr}/^{86}\text{Sr}$ (2SD)	$\delta^{88/86}\text{Sr}$ (‰, 2SD)	Number
G-2	Granite	USGS ^a	170	-0.27 ± 0.06	5	478	0.709794	0.33	1
JG-2	Granite	GSJ ^b	301	-0.18 ± 0.03	5	17.9	0.759189 ± 10	-0.19 ± 0.09	2
GSR-1	Granite	NRCCRM ^c	466	-0.20 ± 0.03	6	106	0.741954	0.27	1
BHVO-2	Basalt	USGS	9.80	-0.07 ± 0.04	4	389	0.703522 ± 32	0.24 ± 0.02	3
GSR-3	Basalt	NRCCRM	37.0	-0.05 ± 0.03	5	1100	0.703868	0.20	1
AGV-2	Andesite	USGS	67.3	-0.10 ± 0.06	7	662	0.703996 ± 23	0.34 ± 0.03	2
W-2a	Diabase	USGS	20.0	-0.11 ± 0.02	5	194	0.706997 ± 10	0.25 ± 0.02	2

^a USGS: United States Geological Survey. ^b GSJ: Geological Survey of Japan. ^c NRCCRM: National Research Center for Certified Reference Materials (China). ^d Number denotes the number of repetitions including chemical separation and measurement on the MC-ICP-MS.

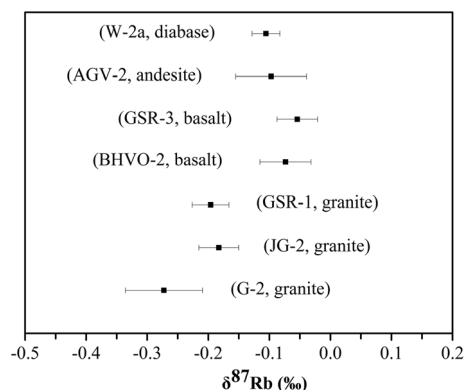


Fig. 5 The $\delta^{87}\text{Rb}$ values of geological reference materials. The analytical error was 2 standard deviations, and all samples for Rb isotope compositions were repeated at least twice including column and measurement.

Conclusions

An efficient method of Rb, K, Ba and Sr purification using larger volumes of Sr-spec resin *via* a single chemical column has been developed in this study and high-precision Rb isotope measurements were carried out using MC-ICP-MS by a SSB method. Controlling Na/Rb to <2 , Ca/Rb to <4 and K/Rb to <25 is necessary to ensure the reliability of Rb isotopes. The precision of Rb isotope measurements is better than $\pm 0.03\text{‰}$ (2SD) in the short term (15 hours) and better than $\pm 0.06\text{‰}$ (2SD) in the long term (12 months) in this study. Rb isotope compositions of a series of geological reference materials were reported here and the data showed that distinguishable Rb isotope composition differences were observed in different geological samples which would make Rb isotopes a promising proxy to probe different geological processes.

Author contributions

All authors participated in the discussion and gave approval to the final version of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

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