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Evaluation of Sr chemical purification technique for natural geological samples using common cation-exchange and Sr-specific extraction chromatographic resin prior to MC-ICP-MS or TIMS measurement

Yue-Heng Yang,^{*a} Fu-Yuan Wu,^a Zhi-Chao Liu,^{ab} Zhu-Yin Chu,^a Lie-Wen Xie^a and Jin-Hui Yang^a

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In this paper, sample preparation protocols based on common cation-exchange and Sr-specific extraction chromatographic resin were evaluated and investigated for natural geological samples prior to $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurement using MC-ICP-MS or TIMS. Several CRMs and real geological samples were digested using HF, HNO_3 and HClO_4 in closed vessels prior to sequential chemical purifications and then Sr isotopic ratios were determined by MC-ICP-MS or TIMS. Because HREEs reside in the Sr fraction when common cation-exchange resin is used, this purification technique is unsuitable prior to MC-ICP-MS analysis, as doubly loaded HREE interfere on Sr masses. We observe an obviously positive relationship between the radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and the content of HREEs in the Sr fractions, as well as a negative relationship between un-radiogenic $^{84}\text{Sr}/^{86}\text{Sr}$ or $^{84}\text{Sr}/^{88}\text{Sr}$ ratios and the content of HREEs in the Sr fractions during MC-ICP-MS Sr isotopic measurement. Such effects are insignificant for TIMS measurement, because ionization temperatures are generally lower and can be well controlled during the analyses. In contrast to the traditional Sr purification method (cation exchange resin), Sr-specific extraction chromatographic resin produces high purity Sr fractions, making it feasible for both MC-ICP-MS and TIMS.

1. Introduction

Strontium has four naturally occurring stable isotopes, ^{84}Sr , ^{86}Sr , ^{87}Sr , and ^{88}Sr , with abundances of 0.56, 9.87, 7.04, and 82.53 atomic%, respectively. The abundance of ^{87}Sr is variable due to the addition of radiogenic ^{87}Sr produced by the beta decay of ^{87}Rb with a half-life of 4.88 ± 0.05 Ga.¹ The Sr isotopic ratio, expressed as $^{87}\text{Sr}/^{86}\text{Sr}$, is dependant on the Rb/Sr ratio and age of the material analyzed. Therefore, the Rb-Sr system has been widely applied in the fields of geochronology and geochemistry as well as environmental tracing and archaeological provenance studies.¹

Since the mid 1960s, thermal ionization mass spectrometry (TIMS) is a classic technique for the precise determination of Sr isotopic ratios. Recently, multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has also become a routine technique for Sr isotope analysis with precision comparable to that of TIMS, since its commercial advent in the mid 1990s.²⁻¹⁴ Generally speaking, both methods require the Sr isolation by ion-exchange chromatography techniques to

minimize isobaric interference (*e.g.*, ^{87}Rb on ^{87}Sr) and other matrix elements.^{4,5,13,14}

The approach most commonly used to isolate Sr from Rb and the concomitant matrix elements is cation-exchange chromatography in HCl medium using the AG50W-X8 or 12 ion exchange resin.^{4,13,14} More recently, Sr-specific extraction chromatographic resin is also used for chemical purification of Sr prior to TIMS or MC-ICP-MS measurement.¹⁵⁻¹⁸ Although both techniques have been thoroughly evaluated before,^{17,18} there is no comparison reported in the literature in which the efficiency of Sr purification prior to MC-ICP-MS or TIMS analysis is evaluated.

In the present work we compare common cation-exchange with Sr-specific extraction chromatographic resin using natural geological samples. We apply both MC-ICP-MS and TIMS techniques to evaluate the effect of impurities in the Sr cuts. Our results demonstrate that there are usually residual heavy rare earth elements (HREEs) in the Sr fractions when common cation-exchange resin is used for Sr purification. In contrast, no residual HREEs are observed when Sr-specific extraction chromatographic resin is used.

2. Experimental

2.1. Chemical reagents and standards

Milli-Q H_2O : 18.2 M Ω at 25 °C from Millipore (Elix-Millipore, USA).

^aState Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, P. R. China. E-mail: yangyueheng@mail.iggcas.ac.cn; Fax: +86-010-62010846; Tel: +86-010-82998599

^bSchool of Earth Sciences, Graduate University of Chinese Academy of Sciences, Beijing, 100039, P. R. China

HCl, HF and HNO₃: from Beijing Institute of Chemical Reagent and purified by the Savillex™ DST-1000 sub-boiling distillation system (Minnetonka, USA) and diluted acids were prepared by dilution with Milli-Q water. Double-distilled extra-pure grade reagents were used in this study.

HClO₄: 70% from Acros Organics Belgium.

Strontium isotopic reference material: SRM 987 SrCO₃ (NIST, Gaithersburg, USA) was used to validate the analytical procedure. This standard was available as a solution of 200 µg L⁻¹ for monitoring conditions during real analytical sessions.

Cation-exchange resin column: 10 cm long × 5 mm (internal diameter) with a 25 mL reservoir (quartz construction), filled with ~2.0 mL of Bio-Rad (Richmond, USA) AG50W-X12 resin (200–400 mesh size).

Sr-specific extraction chromatographic resin column: Bio-Rad polypropylene (Richmond, USA) 1 mL columns with an internal diameter of 6 mm were used as the container holding the extraction chromatographic resin, ~0.1 mL of Sr-specific resin (100–150 µm particle size) purchased commercially from Tris-Kem International, France (formerly Eichrom Environment).

Certified Reference Materials (CRMs): BCR-2 (Basalt), BHVO-2 (Basalt), BIR-1 (Basalt), AGV-2 (Andesite), RGM-2 (Rhyolite) and DNC-1 (Dolerite) were obtained commercially from the United States Geological Survey (USGS).

2.2. Sample digestion

All chemical preparations were conducted on class 100 work benches within a class 1000 clean laboratory. About 150 mg of rock powder was weighed into a 15 mL round bottom Savillex™ Teflon/PFA screw-top capsule. Concentrated HF, HNO₃ and HClO₄ acids (2 mL, 1 mL and 0.2 mL) were added to the samples, the capsules capped and then heated on a hotplate at about 120 °C for 1 week. The added amounts of these acids are in excess for the digestion of 200–300 mg of silicate rock samples. After cooling, the capsule was opened and then heated to evaporate HClO₄. One mL of 6 M HCl was added to the residue and subsequently evaporated. This procedure was then repeated. After cooling, the residue was dissolved in 1.5 mL of 2.5 M HCl. The capsule was again sealed and placed on a hot plate at about ~100 °C overnight to re-dissolve the solid residues. Finally, in order to evaluate the performance of the two commonly-used resins for Sr purification, the sample solution was purposely split into two aliquots, ready for cation-exchange and Sr-specific resin isolation, respectively.

2.3. Column chemistry

2.3.1. Cation-exchange resin. After centrifuging, the solution was loaded into a quartz ion exchange column packed with AG50W-X12 resin, pre-conditioned with 25 mL 6 M HCl and 2 mL of 2.5 M HCl, successively. The resin was then washed with 2 mL of 2.5 M HCl, followed by 2.5 mL of 5 M HCl to remove undesirable matrix elements. Rb was then eluted with 1.5 mL of 5 M HCl. To minimize the potential isobaric interference of ⁸⁷Rb on ⁸⁷Sr, the resin was rinsed with 4 mL of 5 M HCl to remove any residual Rb. Finally, the Sr fraction was eluted using 3 mL of 5 M

HCl and gently evaporated to dryness prior to MC-ICP-MS or TIMS measurement.^{19–22}

2.3.2. Sr-specific extraction resin. Considering the strong retention of Sr-specific resin, the sample solution was taken up in 1 mL of 3.0 M HNO₃ medium prior to chemical isolation.^{15–18} The 1 mL of 3 M HNO₃ sample solution was loaded into Bio-Rad polypropylene column newly packed with Sr-specific resin. Subsequently, the resin was rinsed with 20 mL of 3 M HNO₃. Finally, the Sr was stripped from the column with a small volume of 0.05 M HNO₃. The first millilitre was discarded and the next 5 mL was collected for TIMS or MC-ICP-MS analysis.

2.4. Mass spectrometric measurement

2.4.1. MC-ICP-MS. Sr isotope ratio analyses were undertaken using a Thermo Fisher Scientific Neptune MC-ICP-MS.²³ Prior to analyses, the Neptune MC-ICP-MS was allowed to stabilize for at least one hour under normal operating conditions. A summary of the typical instrumental parameters are presented in Table 1. The Sr isotopic data were acquired in the static, multi-collector mode at low resolution of 400 with the Faraday cups configuration array given in Table 2. During the real Sr isotope analytical session, an aliquot of 200 µg L⁻¹ SRM 987 was used regularly for optimizing the operation parameters and evaluating the reproducibility and accuracy of the instrument. The SRM 987 was measured and every ten samples analyzed. The real Sr fractions after either cation-exchange or Sr-specific resin isolation were taken up with 2% HNO₃, and aspirated into the ICP source using a Micromist PFA nebulizer in a free aspiration.

Typically, the signal intensities of ⁸⁴Sr, ⁸⁶Sr, ⁸⁷Sr and ⁸⁸Sr for the 200 µg L⁻¹ standard solutions were about 0.05, 0.93, 0.67 and 8.1 volts. The real sample solution was aspirated for 15 s to obtain a stable signal before starting data acquisition. One run of the Sr isotopic ratio measurement cycle consisted of a baseline measurement at On Peak Zeros (OPZ) and 90 cycles of sample signal collection. The 90 cycles of signals are divided into 9 blocks to complete the 9 rotations of the amplifiers connected to the Faraday cups in order to eliminate amplifier gain errors

Table 1 Typical instrumental parameters for Sr isotopic measurement

Thermo Fisher Scientific Neptune MC-ICP-MS	
RF power	1250 W
Cooling gas flow rate	16.0 L min ⁻¹
Auxiliary gas flow rate	0.6 L min ⁻¹
Sample gas flow rate	~1.1 L min ⁻¹
Extraction voltage	-2000 V
Focus voltage	-630 V
Acceleration voltage	10 kV
Interface cones	Nickel
Spray chamber	Glass cyclonic
Nebulizer type	Micromist PFA nebulizer
Sample uptake rate	50 µl min ⁻¹
Uptake mode	Free aspiration
Instrument Resolution	~400 (Low)
Mass analyzer pressure	4–8 × 10 ⁻⁹ mbar
Typical sensitivity on ⁸⁸ Sr	~40 V/ppm (10 ⁻¹¹ Ω resistors)
Sampling mode	9 × 10 Cycles
Integration time	4.194 Sec
Baseline determination	ca.1 Min on peak in 2% HNO ₃

Table 2 Potential interferences and collector configuration for Sr isotopic measurement^a

Cups	L4	L3	L2	L1	Center	H1	H2	H3
Sr			⁸⁴ Sr ⁺		⁸⁶ Sr ⁺	⁸⁷ Sr ⁺	⁸⁸ Sr ⁺	⁸⁹ Y ⁺
Kr	⁸² Kr ⁺	⁸³ Kr ⁺	⁸⁴ Kr ⁺		⁸⁶ Kr ⁺			
Rb				⁸⁵ Rb ⁺		⁸⁷ Rb ⁺		
Ca Dimers or Ca Ar gides	⁴² Ca ⁴⁰ Ca ⁺ ⁴² Ca ⁴⁰ Ar ⁺	⁴³ Ca ⁴⁰ Ca ⁺ ⁴³ Ca ⁴⁰ Ar ⁺	⁴⁴ Ca ⁴⁰ Ca ⁺ ⁴² Ca ⁴² Ca ⁺ ⁴⁴ Ca ⁴⁰ Ar ⁺	⁴³ Ca ⁴² Ca ⁺	⁴⁶ Ca ⁴⁰ Ca ⁺ ⁴⁴ Ca ⁴² Ca ⁺ ⁴³ Ca ⁴³ Ca ⁺ ⁴⁶ Ca ⁴⁰ Ar ⁺ ⁴⁸ Ca ³⁸ Ar ⁺	⁴⁴ Ca ⁴³ Ca ⁺	⁴⁸ Ca ⁴⁰ Ca ⁺ ⁴⁶ Ca ⁴² Ca ⁺ ⁴⁴ Ca ⁴⁴ Ca ⁺ ⁴⁸ Ca ⁴⁰ Ar ⁺	
Double Charged Ion	¹⁶⁴ Er ²⁺ ¹⁶⁴ Dy ²⁺	¹⁶⁶ Er ²⁺	¹⁶⁸ Er ²⁺ ¹⁶⁸ Yb ²⁺	¹⁷⁰ Er ²⁺ ¹⁷⁰ Yb ²⁺	¹⁷² Yb ²⁺	¹⁷⁴ Hf ²⁺ ¹⁷⁴ Yb ²⁺	¹⁷⁶ Hf ²⁺ ¹⁷⁶ Yb ²⁺ ¹⁷⁶ Lu ²⁺	

^a **Bold** text indicates masses used to determine mass fractionation.

between different amplifiers.²⁴ For Sr measurement, the signal integration time for one cycle was 4 s. The total time of one measurement lasted about 8 min and consumed about 50 ng of sample for each measurement. All Sr isotope ratios were internally corrected for mass fractionation using a constant value of 0.1194 for ⁸⁶Sr/⁸⁸Sr by exponential law. During this analytical session, the SRM 987 standard data yielded an average value of ⁸⁷Sr/⁸⁶Sr ratio of 0.710245 ± 18 (2SD, *n* = 20), consistent within our long-term standard average or other previously reported data.¹⁴

2.4.2. TIMS. Isotopic measurements were performed on an IsoProbe-T TIMS (GV instruments, England). The instrument is equipped with nine Faraday cups, seven Channeltron ion counters, one Daly detector and one ETP multiplier. Single W filament geometry was used to obtain Sr⁺ ion beams.²⁰ All data were acquired by static multi-collection with the collector array of ⁸⁴Sr, ⁸⁵Rb, ⁸⁶Sr, ⁸⁷Sr and ⁸⁸Sr. A solution standard of SRM 987 for Sr was measured during the same TIMS runs as the samples. Prior to sample measurement, the Sr fraction was dissolved using 2 μL 2.5 M HCl and loaded with a 2 μL TaF₅ onto a degassed W filament (0.03 mm thick, 0.72 mm wide) assembly and dried on a clean bench at low temperature and subsequently loaded and dried again. After final drying, the filament was heated up slowly until glowing dull red for about three seconds.

For the mass spectrometric measurement, the W filament was firstly heated at 300 mA min⁻¹ until the signal of ⁸⁸Sr reached 30 mV. The beam was peak centered and roughly focused and the filament was slowly heated to obtain a 4 V for ⁸⁸Sr. When the signal intensity of ⁸⁸Sr reached to 5 V, data acquisition was started. 15 scans with 4 s integration time and 3 s idle time make up one block. For each sample, 12 blocks were run. Prior to mass fractionation correction, the ⁸⁷Sr signal intensity has been corrected for the potential bias caused by remaining isobaric overlap of ⁸⁷Rb on ⁸⁷Sr using an ⁸⁵Rb/⁸⁷Rb value of 2.59265. Then, corrected ⁸⁷Sr/⁸⁶Sr ratios are normalized to ⁸⁶Sr/⁸⁸Sr = 0.1194 using exponential law. The measured ⁸⁷Sr/⁸⁶Sr ratios of SRM 987 reference solution, during all analytical sessions of our data collection, were 0.710249 ± 16 (2SD, *n* = 10), showing good agreement with previously published data.¹⁴

3. Results and discussion

3.1. Results of CRMs and real geological samples

CRMs with well-known isotopic composition are generally used to evaluate and validate analytical protocol.^{19–29} In this work, replicated analyses of six USGS CRMs were conducted after the sample purification described above for Sr isotopic measurement on Neptune or IsoProbe-T. The results for the CRMs together with data cited in the references are summarized in Table 3. As we can see, the ⁸⁷Sr/⁸⁶Sr isotopic ratios of BCR-2, AGV-2, RGM-2, BIR-1 and BHVO-2 are shown to be reproducible within the analytical error of individual analyses after Sr-specific resin purification. Additionally, for Sr-specific resin, our obtained data of Sr isotopic composition using MC-ICP-MS or TIMS are nearly identical to each other within error and in good agreement with other international colleagues' data, indicating good purity of Sr fractions. However, for cation-exchange resin purification,

Table 3 Comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of CRMs using MC-ICP-MS or TIMS between common cation-exchange and Sr-specific extraction chromatographic resin purification

CRMs	Resins	^{82}Kr [mV]	^{83}Kr [mV]	^{85}Rb [mV]	^{88}Sr [V]	^{89}Y [mV]	$^{84}\text{Sr}/^{86}\text{Sr}$	$^{84}\text{Sr}/^{88}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ ($\pm 2\sigma$)	$^{87}\text{Sr}/^{86}\text{Sr}^a$ ($\pm 2\sigma$)	$^{87}\text{Sr}/^{86}\text{Sr}$ Ref. Value
BCR-2	Cation	0.896	0.350	0.47	12.49	650.96	0.0556	0.00664	0.705170(12)	0.704998(12)	0.705015 ¹⁶
	Cation	0.826	0.298	0.10	9.05	489.15	0.0554	0.00662	0.705175(14)		0.705023 ²¹
	Sr-specific	0.061	0.035	0.06	7.76	0.06	0.0565	0.00675	0.705019(17)		
	Sr-specific	0.071	0.052	0.05	7.13	0.05	0.0565	0.00675	0.705010(16)		
AGV-2	Sr-specific	0.076	0.043	0.05	5.20	0.03	0.0564	0.00675	0.703994(15)	0.703985(15)	0.703978 ²¹
	Sr-specific	0.060	0.030	0.02	5.32	0.01	0.0565	0.00674	0.704001(17)		0.703981 ²⁷
RGM-2	Sr-specific	0.066	0.037	0.04	3.98	0.07	0.0565	0.00674	0.704234(23)	0.704230(16)	0.704219 ²⁷
	Sr-specific	0.058	0.030	0.05	4.36	0.02	0.0565	0.00675	0.704241(20)		
BHVO-2	Sr-specific	0.071	0.039	0.03	4.92	0.03	0.0565	0.00675	0.703479(20)	0.703468(14)	0.703487 ²⁸
BIR-1	Sr-specific	0.073	0.041	0.03	2.20	0.03	0.0565	0.00675	0.703130(28)	0.703108(15)	0.703130 ²⁹
DNC-1	Sr-specific	0.067	0.039	0.02	5.29	0.02	0.0565	0.00674	0.705834(23)		

^a Measurement by IsoProbe-T TIMS.

our obtained Sr isotopic data of BCR-2 using MC-ICP-MS is obviously less radiogenic than TIMS and literature data.^{4-9,16-18} Similar systematics is observed for twelve granite samples (Table 4 and Fig. 1). Analyses after cation-exchange resin isolation shows significant deviations from those obtained after Sr-specific extraction resin purification. Not only the radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio but also the naturally constant $^{84}\text{Sr}/^{86}\text{Sr}$ (0.0565) and $^{84}\text{Sr}/^{88}\text{Sr}$ (0.00675) are affected. The reason for these discrepancies is discussed and evaluated in the following.

3.2. Chemical purity comparison of Sr fractions between cation-exchange and Sr-specific extraction resin

It is well recognized that high-precision isotope ratio determination by either TIMS or MC-ICP-MS requires quantitative purification of the analyte from its matrix as complete as possible. Ion-exchange chromatography method is widely used to isolate the element of interest from the matrix in the field of geochemistry and geochronology. As previously stated, common Sr isolation techniques include the common cation-exchange

Table 4 Comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios in real granite geological samples using MC-ICP-MS between common cation-exchange and Sr-specific extraction chromatographic resin purification^a

No.	Resins	^{82}Kr [mV]	^{83}Kr [mV]	^{85}Rb [mV]	^{88}Sr [V]	^{89}Y [mV]	$^{84}\text{Sr}/^{86}\text{Sr}$	$^{84}\text{Sr}/^{88}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ ($\pm 2\sigma$)	Δ [ppm]
1	Sr-specific	0.053	0.027	0.03	8.43	0.05	0.0565	0.00675	0.707824 (14)	26
	Cation	0.088	0.050	0.10	7.62	7.14	0.0564	0.00673	0.707850 (13)	
2	Sr-specific	0.054	0.030	0.07	4.51	0.07	0.0565	0.00675	0.707866 (21)	44
	Cation	0.157	0.056	0.29	3.74	19.01	0.0563	0.00672	0.707910 (20)	
3	Sr-specific	0.050	0.031	0.07	5.14	0.05	0.0565	0.00675	0.709264 (17)	45
	Cation	0.109	0.050	0.20	5.69	20.54	0.0564	0.00673	0.709309 (15)	
4	Sr-specific	0.064	0.042	0.06	5.45	0.07	0.0564	0.00674	0.707353 (16)	56
	Cation	0.157	0.054	0.12	5.45	22.83	0.0564	0.00673	0.707409 (14)	
5	Sr-specific	0.058	0.036	0.05	4.44	0.06	0.0565	0.00674	0.710796 (23)	51
	Cation	0.346	0.058	0.37	5.48	40.81	0.0564	0.00673	0.710846 (16)	
6	Sr-specific	0.061	0.034	0.03	6.56	0.07	0.0565	0.00674	0.707872 (16)	29
	Cation	0.167	0.059	0.25	4.80	48.31	0.0563	0.00673	0.707901 (17)	
7	Sr-specific	0.057	0.030	0.04	5.28	0.06	0.0565	0.00675	0.708952 (16)	31
	Cation	0.295	0.052	0.29	4.30	56.16	0.0564	0.00673	0.708983 (18)	
8	Sr-specific	0.056	0.035	0.20	4.25	0.05	0.0564	0.00674	0.708048 (17)	38
	Cation	0.340	0.058	0.14	5.19	61.61	0.0563	0.00673	0.708086 (15)	
9	Sr-specific	0.065	0.037	0.09	4.23	0.06	0.0564	0.00674	0.705023 (19)	48
	Cation	0.268	0.075	0.20	4.88	136.10	0.0562	0.00671	0.705071 (17)	
10	Sr-specific	0.076	0.041	0.08	5.16	0.08	0.0564	0.00674	0.707747 (13)	75
	Cation	0.882	0.114	0.15	4.00	269.30	0.0558	0.00667	0.707822 (18)	
11	Sr-specific	0.074	0.040	0.14	5.55	0.09	0.0564	0.00674	0.712981 (14)	101
	Cation	1.147	0.236	0.67	7.39	564.38	0.0555	0.00663	0.713082 (12)	
12	Sr-specific	0.076	0.039	0.06	2.23	0.10	0.0564	0.00674	0.769647 (28)	232
	Cation	0.848	0.314	0.96	3.98	651.23	0.0540	0.00645	0.769880 (19)	

^a $\Delta = (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Cation}} - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Sr-specific}}$.

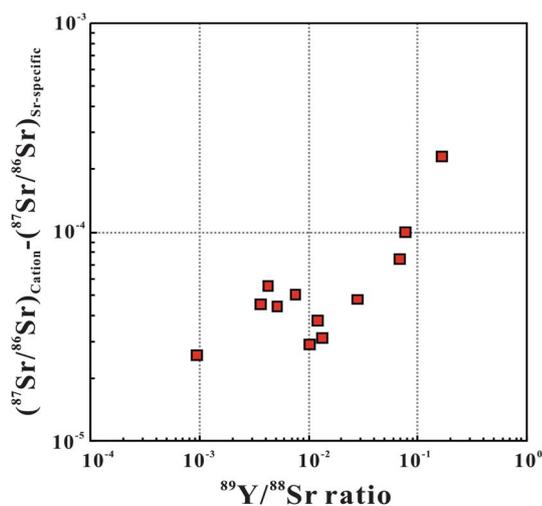


Fig. 1 Relationship between the $^{89}\text{Y}/^{88}\text{Sr}$ ratios (cation resin) and $\Delta = [(^{87}\text{Sr}/^{86}\text{Sr})_{\text{Cation}} - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Sr-specific}}]$ for twelve real geological samples analyzed by MC-ICP-MS in this study (Table 4). Residual HREEs in the Sr fraction after common cation-exchange resin purification have significant effect on Sr isotopic composition when measured by Neptune MC-ICP-MS. There is obviously a positive relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio and content of HREEs in Sr fractions. Error bars (internal precisions) are smaller than symbols in all cases and not shown on this scale.

resin (*e.g.*, AG50W-X12)^{4,14,21,22} or extraction chromatographic Sr-specific resin.^{15–18}

Since the 1960s, cation-exchange resin using HCl as an eluting acid has served as a reliable method to purify Sr for TIMS measurements. In this study, we use the resin AG50W-X12 for purification and our obtained $^{87}\text{Sr}/^{86}\text{Sr}$ ratios using TIMS agree well with those using either cation resin or Sr-specific resin by other workers.^{15–18} We therefore concluded that most major elements (K, Ca, Mg, Na, Al) and isobaric elements (^{87}Rb on ^{87}Sr) are usually isolated from the Sr fraction using the common cation-exchange resin AG50W-X8 or 12. Naturally, it is difficult to completely separate Sr from Rb for those special minerals with high Rb/Sr ratios (*e.g.*, mica) but repeating the purification procedure significantly improves the purity of Sr cuts.^{4,15–18}

However, the REEs are eluted in the reverse order of mass on the cation resin (AG50W-X8 or 12) using HCl medium. Therefore, Lu, Yb and Er (HREEs) are eluted as a group and usually overlap with the Sr cut which is eluted prior to collecting the LREEs for further purification of Sm and Nd.^{19–22} Waight *et al.*⁴ first observed that the presence of HREEs in the Sr fraction can produce significant isobaric interferences on Sr masses, due to doubly charged HREE ions. Such effects are usually insignificant using classic TIMS, because of the substantial differences between ionization temperatures between Sr (*ca.* 1300 °C) and HREEs (*ca.* 1750 °C). However, they are significant after using MC-ICP-MS, because the hot plasma (*ca.* 8000 °C) efficiently ionizes both Sr and the HREEs.^{19–29}

In order to eliminate residual HREEs in the Sr fraction after AG50W-X12 resin, these fractions were usually further purified using Sr-specific resin.⁴ Additionally, ^{89}Y was used to monitor any residual HREE in the final Sr fractions in this work (Table 2, 3 and 4), because Y (Y^{3+}) chemically behaves like a REEs during

ion-exchange chromatography. As shown in Table 3 and Fig. 2, the signal intensity of ^{82}M (M means atomic mass unit) and ^{83}M of the Sr fraction after cation resin isolation differs significantly from those of Sr specific resin or high purity SRM 987, indicating that doubly charged ions (*i.e.*, $^{164}\text{Dy}^{2+}$, $^{164}\text{Er}^{2+}$, $^{166}\text{Er}^{2+}$) interfere on the masses 82 and 83, respectively. Clearly, Sr-specific resin isolation efficiently removed any HREEs from the Sr cut. The difference of ^{82}M , ^{83}M and $^{89}\text{Y}/^{88}\text{Sr}$ ratios between the Sr fraction after Sr-specific isolations and SRM 987 are insignificant. This demonstrates high purity of the Sr cuts after special extraction chromatographic resin.^{15–18}

3.3. Analyte recovery, procedural blanks and memory effects

Besides the high degree of purity required for the analyte, chemical yields of the element of interest must be as high as possible to enable analyses of small sample quantities (*e.g.*, for limited sample size). The recoveries of Sr using both resins are usually higher than 90%, which is sufficient for most natural geological samples. In addition, the procedural blanks must be negligible compared to the amount of analyzed element. In this study, a Teflon Savillex™ DST-1000 sub-boiling distillation system was used to doubly purify HCl, HF and HNO_3 reagents, and the sample preparation was conducted within a class 100 environment. The typical procedural blank values using common cation and Sr-specific resins, including sample digestion, column chemistry and mass spectrometric measurement were less than 80 pg and 50 pg, respectively, which are at the lower end of recently-published results. Therefore, the total procedure blank contribution in this work is negligible and requires no correction of the measured isotopic ratios.

In this work, common cation-exchange resin was reused repeatedly and preconditioned using 30 mL of 6 M HCl prior to loading another new sample solution. In order to evaluate the Sr contamination extent and column memory effect during the whole sample preparation procedure, SRM 987 with 500 ng was processed identically to the samples, including digestion procedure. The chemical separation of these SRM 987 samples was conducted on columns, which had been used for samples before. Repeated analysis of $^{87}\text{Sr}/^{86}\text{Sr}$ of SRM 987 yielded a mean value of 0.710245 ± 15 (2SD, $n = 5$), indicating negligible contamination due to memory effects during these steps. However, considering strong memory character of Sr-specific resin, new 0.1 mL Sr-specific resin was used for each new real sample solution.^{4,15–18}

3.4. Difference between TIMS and MC-ICP-MS for Sr isotopic mass spectrometric measurements

Usually, isobaric interference correction is the key issue for accurate Sr isotopic ratios determination. The main isobaric interference regarding $^{87}\text{Sr}/^{86}\text{Sr}$ comes from ^{87}Rb . Depending on the Rb/Sr ratio in the samples and the efficiency of the separation on the columns, the $^{85}\text{Rb}/^{88}\text{Sr}$ ratios in the final samples varied between 10^{-4} and 10^{-5} , which can be accepted. For classic TIMS, residual Rb in the Sr fraction can be easily be burned off before Sr data acquisition because of its lower ionization temperature (*ca.* 700 °C) from that of Sr (*ca.* 1300 °C). In contrast to TIMS, all elements are ionized simultaneously in ICP source. Therefore,

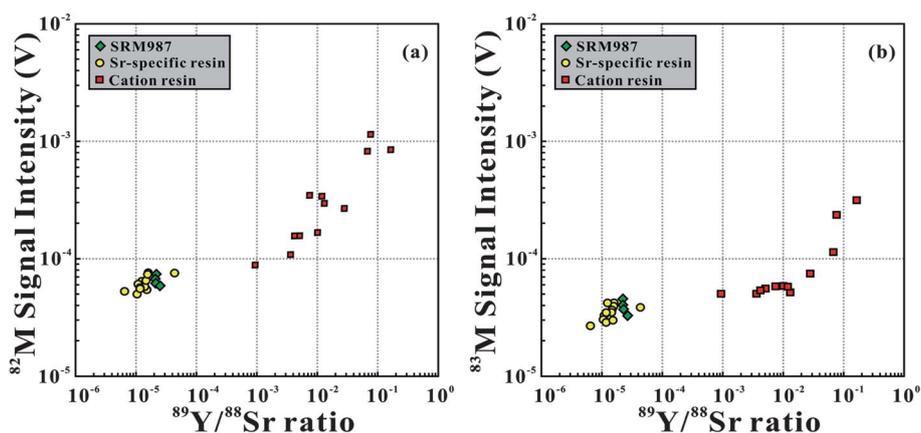


Fig. 2 Relationship between the $^{89}\text{Y}/^{88}\text{Sr}$ ratios and ^{82}M ($^{82}\text{Kr}^+ + ^{164}\text{Dy}^{2+} + ^{164}\text{Er}^{2+}$) (a) and ^{83}M ($^{83}\text{Kr}^+ + ^{166}\text{Er}^{2+}$) (b) signal intensity for twelve real geological samples of different Sr fractions analyzed by MC-ICP-MS in this study (Table 4). Doubly charged HREE ions have significant effects on Sr isotopic composition measurement using Neptune MC-ICP-MS. HREE clearly remain in the Sr cuts after common cation-exchange resin purification. Error bars (internal precisions) are smaller than symbols in all cases and not shown on this scale.

the natural isotopic composition of Rb ($^{85}\text{Rb}/^{87}\text{Rb} = 2.59265$) was usually used for isobaric correction by the exponential law, assuming that Rb has the same mass discrimination as that of Sr in this study.^{3,6,13,14} Actually, $^{85}\text{Rb}/^{88}\text{Sr}$ ratios for all real samples in this work were lower than 1×10^{-4} demonstrating negligible isobaric interference from ^{87}Rb and showing our robust separation based on common cation exchanger resin or Sr-specific resin (Tables 3 and 4).

Besides Rb, there are other interferences for MC-ICP-MS Sr isotopic analysis. Krypton (Kr), is a common contaminant in ICP Ar carrier gas. The interference of ^{84}Kr and ^{86}Kr on ^{84}Sr and ^{86}Sr , respectively, cannot be eliminated but can be monitored by simultaneously collecting ^{82}Kr and ^{83}Kr during the Sr isotopic measurement (Table 2). Hence the natural Kr isotopic ratios: ($^{83}\text{Kr}/^{84}\text{Kr} = 0.20175$, $^{83}\text{Kr}/^{86}\text{Kr} = 0.66474$) were directly used for overlap correction and no mass discrimination corrections were needed because of the low intensity of the Kr beam.^{3,14} Apart from Kr and Rb, the presence of some polyatomic ions such as

Ca argides and dimers also potentially result in interferences with Sr isotopic analysis (Table 2). In contrast to Waight *et al.*⁴ and Woodhead *et al.*,⁹ our previous work demonstrated that Ca argides and dimers had an insignificant influence on Sr isotope analysis using our Neptune. This observation is also strongly supported by Ramos *et al.*⁶ The real reason for these differences is still unknown, but is probably related to the instrumental configurations. Therefore, we did not conduct any correction for Ca argides and dimers applied to our data.¹⁴

As mentioned above, there are inevitably residual HREEs in the Sr fraction during common cation-exchange resin isolation. Because of TIMS' selective and unique ionization of a specific element species in different temperature conditions, Sr isotopic ratio can be easily measured with ideal ionization temperature of about 1300 °C. Therefore, the residual HREEs in the Sr fractions are not ionized and thus doubly charged HREE ions are not produced at this relatively lower temperature. In contrast to TIMS, the main characteristic of MC-ICP-MS is its combination

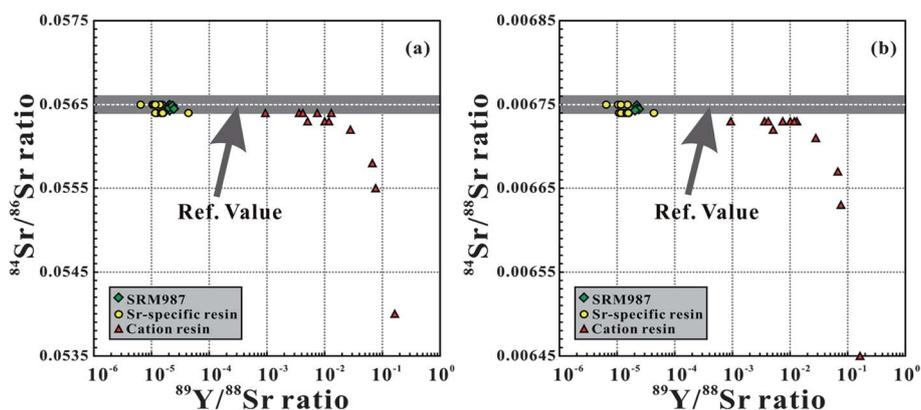


Fig. 3 Relationship between the $^{89}\text{Y}/^{88}\text{Sr}$ ratios and invariant $^{84}\text{Sr}/^{86}\text{Sr}$ (a) (Ref. Value 0.0565 (white dashed line)) and $^{84}\text{Sr}/^{88}\text{Sr}$ (b) (Ref. Value 0.00675 (white dashed line)) isotopic ratios for twelve real granite geological samples of different Sr fractions analyzed by MC-ICP-MS in this study (Table 4), indicating existence of doubly charged ion after common cation-exchange resin purification has a significant effect on Sr isotopic composition measurements using Neptune MC-ICP-MS. There is a negative relationship between $^{84}\text{Sr}/^{86}\text{Sr}$ or $^{84}\text{Sr}/^{88}\text{Sr}$ isotopic ratio and content of HREEs in Sr fractions during MC-ICP-MS Sr isotopic measurement. Error bars (internal precisions) are smaller than symbols in all cases and are not shown on this scale.

of magnetic sector multi-collector Faraday cup array and highly efficient ICP ion source, which can ionize almost any element in the periodic table even those with high first ionization potential elements (e.g., Hf, W). Therefore, the residual HREEs in the Sr fraction will usually produce doubly charged ion ($^{166}\text{Er}^{2+}$ ($m/z = ^{83}\text{M}^+$), $^{168}\text{Er}^{2+}$ ($m/z = ^{84}\text{M}^+$), $^{170}\text{Er}^{2+}$ ($m/z = ^{85}\text{M}^+$), $^{168}\text{Yb}^{2+}$ ($m/z = ^{84}\text{M}^+$), $^{170}\text{Yb}^{2+}$ ($m/z = ^{85}\text{M}^+$), $^{172}\text{Yb}^{2+}$ ($m/z = ^{86}\text{M}^+$), $^{174}\text{Yb}^{2+}$ ($m/z = ^{87}\text{M}^+$), $^{176}\text{Yb}^{2+}$ ($m/z = ^{86}\text{M}^+$)), which significantly interferes Sr isotopic measurement (Table 2).^{4,6}

As shown in Fig. 2, there is insignificant difference of ^{82}M , ^{83}M and $^{89}\text{Y}/^{88}\text{Sr}$ ratios of real granite samples between Sr fraction and SRM 987, indicating the high purity of Sr cuts after Sr-specific resin. Similarly, our obtained $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of CRMs either by TIMS or MC-ICP-MS are in excellent agreement with each other and the literature preferred isotopic data (Table 3). As shown in Fig. 3, the obtained $^{84}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{88}\text{Sr}$ ratios are also in good agreement with those recommended values, respectively (Table 3 and 4).

4. Conclusion

We have evaluated and investigated sample chemical purification techniques based on common cation-exchange and Sr-specific extraction chromatographic resins prior to MC-ICP-MS or TIMS measurements. Our evaluation and investigation can draw the following conclusions. (1) Common cation-exchange resin is not suitable for Sr chemical purification prior to MC-ICP-MS because of residual HREEs in the Sr fraction and simultaneous ionization, which interferes with Sr masses. Residual HREEs do not significantly bias TIMS measurements, due to the lower ionization temperatures of Sr compared to HREEs. (2) Sr-specific extraction chromatographic resin is not only suitable for MC-ICP-MS but also for TIMS because high purity Sr fractions can be obtained. (3) There is a positive relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio and content of HREEs in Sr fractions and a negative relationship between $^{84}\text{Sr}/^{86}\text{Sr}$ or $^{84}\text{Sr}/^{88}\text{Sr}$ isotopic ratio and content of HREEs in Sr fractions during MC-ICP-MS Sr isotopic measurement, while there are insignificant effects on Sr isotopic ratio analysis with the residual HREEs in the Sr fractions for TIMS mass spectrometric measurement.

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References

- 1 G. Faure and T. M. Mensing, *Principles of Isotope Geology (3rd edition)*, New Jersey, John Wiley & Sons, 2005, pp. 75–112.
- 2 A. N. Halliday, D. C. Lee, J. N. Christensen, A. J. Walder, P. A. Freedman, C. E. Jone, C. M. Hall, W. Yi and D. Teagle, *Int. J. Mass Spectrom. Ion Processes*, 1995, **146/147**, 21–33.
- 3 S. Ehrlich, I. Gavrieli, L. B. Dor and L. Halicz, *J. Anal. At. Spectrom.*, 2001, **16**, 1389–1392.
- 4 T. Waight, J. Baker and D. Peate, *Int. J. Mass Spectrom.*, 2002, **221**, 229–244.
- 5 G. Fortunato, K. Mucic, S. Wunderli, L. Pillonel, J. O. Bosset and G. Gremaud, *J. Anal. At. Spectrom.*, 2004, **19**, 227–234.
- 6 F. C. Ramos, J. A. Wolff and D. L. Tollstrup, *Chem. Geol.*, 2004, **211**, 135–158.
- 7 M. F. Thirlwall and R. Anczkiewicz, *Int. J. Mass Spectrom.*, 2004, **235**, 59–81.
- 8 O. Nebel, K. Mezger, E. E. Scherer and C. Munker, *Int. J. Mass Spectrom.*, 2005, **246**, 10–18.
- 9 J. Woodhead, S. Swearer, J. Hergt and R. Maas, *J. Anal. At. Spectrom.*, 2005, **20**, 22–27.
- 10 P. Z. Vroon, B. van der Wagt and J. M. Koornneef, *Anal. Bioanal. Chem.*, 2008, **390**, 465–476.
- 11 L. Yang, C. Peter, U. Panne and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 2008, **23**, 1269–1274.
- 12 L. Yang, *Mass Spectrom. Rev.*, 2009, **28**, 990–1011.
- 13 Y.-H. Yang, F.-Y. Wu, S. A. Wilde, X.-M. Liu, Y.-B. Zhang, L.-W. Xie and J.-H. Yang, *Chem. Geol.*, 2009, **264**, 24–42.
- 14 Y.-H. Yang, F.-Y. Wu, L.-W. Xie, J.-H. Yang and Y.-B. Zhang, *Spectrochim. Acta, Part B*, 2011, **66**, 656–660.
- 15 E. P. Horwitz, M. L. Dietz and D. E. Fisher, *Anal. Chem.*, 1991, **63**, 522–525.
- 16 L. Balcaen, I. D. Schrijver, L. Moens and F. Vanhaecke, *Int. J. Mass Spectrom.*, 2005, **242**, 251–255.
- 17 D. Muynck, G. De Huelga-Suarez, L. Van Heghe, P. Degryse and F. Vanhaecke, *J. Anal. At. Spectrom.*, 2009, **24**, 1498–1510.
- 18 I. Smet, D. D. Muynck, F. Vanhaecke and M. Elburg, *J. Anal. At. Spectrom.*, 2010, **25**, 1025–1032.
- 19 C.-F. Li, F.-K. Chen and X.-H. Li, *Int. J. Mass Spectrom.*, 2007, **226**, 34–41.
- 20 Z.-Y. Chu, F.-K. Chen, Y.-H. Yang and J.-H. Guo, *J. Anal. At. Spectrom.*, 2009, **24**, 1534–1544.
- 21 Y.-H. Yang, H.-F. Zhang, Z.-Y. Chu, L.-W. Xie and F.-Y. Wu, *Int. J. Mass Spectrom.*, 2010, **290**, 120–126.
- 22 Y.-H. Yang, Z.-Y. Chu, F.-Y. Wu, L.-W. Xie and J.-H. Yang, *J. Anal. At. Spectrom.*, 2011, **26**, 1237–1244.
- 23 S. Weyer and J. B. Schwieters, *Int. J. Mass Spectrom.*, 2003, **226**, 355–368.
- 24 Z.-Y. Chu, Y.-H. Yang and G.-S. Qiao, *Int. J. Mass Spectrom.*, 2006, **23**, 130–135.
- 25 Y.-H. Yang, F.-Y. Wu, S. A. Wilde and L.-W. Xie, *Int. J. Mass Spectrom.*, 2011, **299**, 47–52.
- 26 Y.-H. Yang, F.-Y. Wu, L.-W. Xie and Y.-B. Zhang, *Anal. Lett.*, 2010, **43**, 142–150.
- 27 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.
- 28 I. Raczek, K. P. Jochum and A. W. Hofmann, *Geostand. Geoanal. Res.*, 2003, **27**, 173–179.
- 29 C. Pin, D. Briot, C. Bassin and F. Poitrasson, *Anal. Chim. Acta*, 1994, **298**, 209–217.