Analytical Note

Re-evaluation of interferences of doubly charged ions of heavy rare earth elements on Sr isotopic analysis using multi-collector inductively coupled plasma mass spectrometry

Yue-Heng Yang *, Fu-Yuan Wu, Lie-Wen Xie, Zhu-Yin Chu, Jin-Hui Yang

State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, P. O. Box 9825, Beijing 100029, PR China

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ABSTRACT

We re-evaluate the interference of doubly charged heavy rare earth elements during Sr isotopic analysis using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). A series of mixed solutions of standard reference material SRM 987, rare earth elements, and Sr separated from rock reference materials are measured to assess the influence of isobaric interferences on the MC-ICP-MS analysis of Sr isotopes. After sample dissolution, conventional cation-exchange chromatography is employed for Sr purification of rock reference materials prior to MC-ICP-MS measurement. It has been demonstrated that if the natural abundances of Er and Yb are used to correct for doubly charged ion interferences on Sr, an overcorrection results. In contrast, the use of measured doubly charged ion ratios results in an accurate and precise correction of isobaric interference. This finding is confirmed by analytical results for several certified reference materials from mafic (basaltic) to felsic (granitic) silicate rocks. It is noteworthy that, because Er is more prone to doubly charged ion formation, it dominates over Yb doubly charged ions as an interference source.

1. Introduction

Radiogenic $^{87}Sr/^{86}Sr$ ratio is an important geochemical tracer in solid earth sciences [1]. Because of its high precision, thermal ionization mass spectrometry (TIMS), which has been used for Sr isotopic analysis since the mid-1960s, is still regarded as a benchmark technique. Nevertheless, this technique requires a time-consuming analytical procedure, including extensive source filament preparation, including degassing and chemical purification of Sr [2]. More recently, multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has become a routine technique for $^{87}Sr/^{86}Sr$ measurement because of a faster and simpler sample throughput [3–8]. The isotopic fractionation within the ICP source is time-independent and stable, allowing precise and accurate correction of isobaric interferences. As the ICP ion source is under atmospheric pressure, liquid samples can be easily and sequentially introduced. Moreover, Sr-enriched accessory minerals (*e.g.*, apatite, plagioclase, calcite, and perovskite) can be directly analyzed using MC-ICP-MS coupled with a laser-ablation system [9–15].

However, the presence of isobaric interferences on masses of interest is a challenge to accurate and precise isotopic ratio measurements by MC-ICP-MS. To minimize isobaric interferences and matrix effects, Sr should be separated from the sample matrix as completely as possible using ion-exchange chromatography. Commonly, Sr purification is achieved by two-step chemical isolation [2–6,14,15]. In the first step, Sr and the rare earth elements (REE) are separated from the matrix elements using a common cation resin (*i.e.*, AG50W-X8 or AG50W-X12). Second, the Sr fraction is then further purified by a Sr-specific resin to remove residual heavy REE (HREE) [13,15,16,18,19].

In this study, after the reinvestigation of the interferences of doubly charged HREE ions on Sr isotopic analysis using MC-ICP-MS, two primary contributions of these interferences are identified. The first is that the use of the natural abundance of Er and Yb to correct the interference leads to an overcorrection, whereas using the measured doubly charged ion ratios allows a more accurate correction. The second finding is that Er is more prone to doubly charged ion formation than Yb.

2. Experimental

2.1. Chemical reagents and materials

HCl, HF, and HNO_3 from Beijing Institute of Chemical Reagents were purified in a Savillex™ DST-1000 sub-boiling distillation system. Only double-distilled extra-pure grade reagents were used in this study, except for $HClO_4$ (70%), which was obtained from Acros Organics, Belgium.

Aliquots of standard reference material SRM 987 solution (200 μg/L) were used during each analytical session. Multi-element solution 1 from SPEX Certi Prep (Lot # 34-139AS, Cat # CLMS-1) included 10 mg/L of 17

* Corresponding author.
E-mail address: yangyueheng@mail.iggcas.ac.cn (Y.-H. Yang).

Table 1
Typical instrumental parameter for Sr isotopic measurement using MC-ICP-MS.

Thermo Fisher Scientific Neptune MC-ICP-MS	
RF power	1300 W
Cooling gas flow rate	16.0 L/min
Auxiliary gas flow rate	0.8 L/min
Sample gas flow rate	~1.1 L/min (optimized daily)
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
Uptake mode	Free aspiration
Instrument resolution	~400 (low)
Mass analyzer pressure	4–8×10^{-9} mbar
Typical sensitivity	~ 40 V/ppm for ^{88}Sr
Sampling mode	9×10 cycles
Integration time	4.194 s
Baseline determination	*ca.* 1 min on peak in 2% HNO_3

elements (*i.e.*, Y, Sc, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th).

AG50W-X12 (200–400 mesh) from Bio-Rad and Sr-specific extraction chromatographic resin (100–150 μm) from Eichrom Technologies were employed for Sr chemical purification.

Eight certified reference materials (CRMs) of natural silicate rocks, commercially available from United States Geological Survey (USGS) and Geological Survey of Japan (GSJ), were used.

2.2. Sample digestion

All chemical preparations were performed on class 100 work benches within a class 1000 over-pressured clean laboratory. Approximately 150 mg of rock powder was weighed into a 15 mL round-bottom Savillex^{TM} Teflon/PFA screw-top capsule. Concentrated HF, HNO_3, and $HClO_4$ (2 mL, 1 mL, and 0.2 mL, respectively) were added to the samples. The capsules were capped and then heated on a hot plate at approximately 120 °C for five days. The amounts of acids added were in excess of that required for the digestion of 200–300 mg of silicate rock samples. After cooling, the capsule was opened and then heated to 180 °C to completely evaporate $HClO_4$. One milliliter of 6 M HCl was added to the residue and then evaporated. This procedure was performed twice, and after cooling, the sample was dissolved in

1.5 mL of 2.5 M HCl. The capsule was sealed again and placed on a hot plate at approximately 100 °C overnight.

2.3. Column chemistry

2.3.1. Cation-exchange resin

After centrifugation, the supernatant solution was loaded into a quartz ion-exchange column (*ca.* 100 mm × 5 mm) packed with 2 mL AG50W-X12 resin and pre-conditioned with 25 mL of 6 M HCl and then 2 mL of 2.5 M HCl [2]. The resin was washed with an additional 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 ^{87}Rb on ^{87}Sr, the resin was rinsed with 4 mL of 5 M HCl to eliminate residual Rb. Finally, the Sr fraction was eluted using 3 mL of 5 M HCl and gently evaporated to dryness prior to mass-spectrometric measurement.

For the evaluation and validation of the proposed protocol, some samples were split into two aliquots, one for the direct mass-spectrometric analysis and other for further purification using the Sr-specific extraction resin.

2.3.2. Sr-specific resin extraction

Considering the strong retention of Sr on the Sr-specific resin, Sr fraction was converted to 1 mL of 3 M HNO_3 solution [7,16–19]. This solution was loaded into a Bio-Rad polypropylene column that was newly packed with 0.1 mL Sr-specific resin. The resin was then rinsed with 20 mL of 3 M HNO_3, and Sr was stripped from the column with 6 mL of 0.05 M HNO_3. The first milliliter was discarded and the next 5 mL was collected, dried, and then re-dissolved with 2–5 mL of 2% HNO_3 for Sr analysis [18,19].

2.4. Mass-spectrometric measurement

A Thermo Fisher Scientific (Bremen, Germany) Neptune MC-ICP-MS was used for all measurements [20]. Instrument signal intensity was peak-centered and aligned by setting the L1 Faraday cup at mass ^{86}Sr using SRM 987 doped with some Rb standard solution, whereas the 83.5, 85.5, and 86.5 mass units of the doubly charged ions were aligned using a single 10 mg/L Alfa Er or Yb standard solution. The typical instrumental operating conditions, data acquisition parameters, and cup configuration for Sr measurements are summarized in Tables 1 and 2. The Sr fraction was gently evaporated and taken up with 2% HNO_3 for MC-ICP-MS analysis. Further dilution just prior to the analysis was adjusted to obtain appropriate ion-beam intensity during mass-spectrometric measurement. After each measurement, the sample

Table 2
Potential interferences and collector configuration for Sr isotopic measurement using MC-ICP-MS.

Faraday cups	L4	L3	L2	L1	Center	H1	H2	H3	H4
Interest element					*Sr*				
Mass	83	83.5	84	85	85.5	86	86.5	87	88
Sr			^{84}Sr$^+$			^{86}**Sr**$^+$		^{87}Sr$^+$	^{88}**Sr**$^+$
Kr	^{83}Kr$^+$		^{84}Kr$^+$			^{86}Kr$^+$			
Rb				^{85}Rb$^+$				^{87}Rb$^+$	
Ca dimers or Ca argides	^{43}Ca^{40}Ca$^+$		^{44}Ca^{40}Ca$^+$	^{43}Ca^{42}Ca$^+$		^{46}Ca^{40}Ca$^+$		^{44}Ca^{43}Ca$^+$	^{48}Ca^{40}Ca$^+$
	^{43}Ca^{40}Ar$^+$		^{42}Ca^{42}Ca$^+$			^{44}Ca^{42}Ca$^+$			^{46}Ca^{42}Ca$^+$
			^{44}Ca^{40}Ar$^+$			^{43}Ca^{43}Ca$^+$			^{44}Ca^{44}Ca$^+$
						^{46}Ca^{40}Ar$^+$			^{48}Ca^{40}Ar$^+$
						^{48}Ca^{38}Ar$^+$			
Doubly charged ion	^{166}Er^{2+}	^{167}Er^{2+}	^{168}Er^{2+}	^{170}Er^{2+}				^{174}Hf^{2+}	^{176}Hf^{2+}
	(33.6%)	(22.95%)	(26.8%)	(14.9%)				(0.162%)	(5.206%)
			^{168}Yb^{2+}	^{170}Yb^{2+}	^{171}Yb^{2+}	^{172}Yb^{2+}	^{173}Yb^{2+}	^{174}Yb^{2+}	^{176}Yb^{2+}
			(0.13%)	(3.05%)	(14.3%)	(21.9%)	(16.12%)	(31.8%)	(12.7%)
									^{176}Lu^{2+}
									(2.59%)

Bold text indicates masses used to determine mass fractionation. The elemental natural abundance of doubly charged ion is shown in the parentheses and under the chemical symbol.

Table 3
Comparison of $^{87}Sr/^{86}Sr$ of CRMs between analysis of Sr and HREE cut after cation resin and corresponding purified Sr cut after further Sr-Spec resin.

CRMs	No.	$^{167}Er^{2+}$ (83.5) [mV]	$^{173}Yb^{2+}$ (86.5) [mV]	$^{88}Sr^+$ (88) [V]	$^{87}Sr/^{86}Sr$ ($\pm 2\sigma_m$) Un-HREE corr.	Natural ratio HREE corr.	Measured ratio HREE corr.	$^{87}Sr/^{86}Sr$ Refer. value
BCR-2	1[a]	0.251	0.148	9.2	0.705179 (12)	0.704855 (13)	0.704997 (12)	0.705023[02]; 0.705015[07];
	2[a]	0.291	0.192	12.6	0.705159 (13)	0.704865 (13)	0.705002 (12)	0.704998[18]; 0.705019[22];
	3[a]	0.278	0.134	8.8	0.705206 (18)	0.704871 (18)	0.705005 (16)	0.705003[23];
	3[b]	0.004	0.004	8.6	0.705022 (17)	0.705005 (17)	0.705016 (18)	
	4[a]	0.271	0.094	6.8	0.705257 (23)	0.704904 (23)	0.705013 (22)	
	4[b]	0.003	0.004	8.2	0.705006 (16)	0.704996 (16)	0.705007 (16)	
BHVO-2	1[a]	0.104	0.161	9.4	0.703521 (14)	0.703434 (14)	0.703489 (13)	0.703468[18]; 0.703487[23];
	2[a]	0.111	0.168	9.3	0.703526 (15)	0.703433 (14)	0.703491 (14)	0.703479[24];
	2[b]	0.005	0.006	9.5	0.703503 (14)	0.703496 (14)	0.703498 (13)	
BIR-1	1[a]	0.280	0.079	12.2	0.703229 (12)	0.703045 (12)	0.703095 (12)	0.703130[19]; 0.703104[24];
W-2	1[a]	0.025	0.033	5.8	0.707031 (23)	0.706942 (22)	0.706996 (22)	0.706966[02]; 0.706973[24];
	1[b]	0.005	0.006	8.0	0.707002 (15)	0.706986 (15)	0.706989 (14)	
JB-3	1[a]	0.016	0.042	7.7	0.703485 (18)	0.703268 (18)	0.703421 (17)	0.703396[02];
AGV-2	1[a]	0.055	0.025	9.9	0.704046 (12)	0.703952 (12)	0.703988 (12)	0.703978[02]; 0.703976[23];
	1[b]	0.006	0.002	11.0	0.703979 (11)	0.703987 (11)	0.703989 (11)	0.703985[18]; 0.703981[22];
GSP-2	1[b]	0.003	0.002	9.0	0.765170 (13)	0.765165 (13)	0.765175 (13)	0.765151[22]; 0.765177[24];
RGM-2	1[b]	0.004	0.003	7.9	0.704225 (18)	0.704215 (18)	0.704227 (18)	0.704230[18]; 0.704219[22];

[a] Means purification only by cation resin.
[b] Means purification by further Sr-Spec resin after cation resin isolation.

introduction system was washed with 2% HNO_3 for 5 min to minimize memory effects. The Sr cup configuration in this study is identical to that of Ramos et al. (Table 2) [10]. The Sr data consist of 9 blocks of 10 cycles per block with an integration time of 4 s per cycle. The SRM 987 standard was remeasured after every five samples [8,18]. During the data acquisition period, replicate analyses of approximately 200 µg/L SRM 987 isotopic standard solution gave an average value of $^{87}Sr/^{86}Sr =$ 0.710250 ± 11 (2SD, $n = 12$) and $^{84}Sr/^{86}Sr = 0.05648 \pm 3$ (2SD, $n = 12$). These values and their reproducibilities are comparable with those obtained by high-precision TIMS techniques [22–25] and are consistent with other Sr isotope data analyzed by MC-ICP-MS [7–11,16,17–19].

2.5. Data-reduction protocol

After Sr isotopic analysis, the raw data was exported and reduced offline to correct for instrumental mass bias and isobaric interference. First, the doubly charged ion isobaric interferences of $^{166}Er^{2+}$ (at m/z 83), $^{168}Er^{2+}$ (at m/z 84), and $^{170}Er^{2+}$ (at m/z 85) on $^{83}Kr^+$, $^{84}Sr^+$, and $^{85}Rb^+$, respectively, were evaluated and corrected by monitoring interference-free $^{167}Er^{2+}$ (at m/z 83.5) signal intensity. Similarly, the doubly charged ion isobaric interferences of $^{170}Yb^{2+}$ (at m/z 85), $^{172}Yb^{2+}$ (at m/z 86), $^{174}Yb^{2+}$ (at m/z 87), and $^{176}Yb^{2+}$ (at m/z 88) on $^{85}Rb^+$, $^{86}Sr^+$, $^{87}Sr^+$, and $^{88}Sr^+$, were assessed and corrected by monitoring interference-free $^{173}Yb^{2+}$ (at m/z 86.5) signal intensity. Second, isobaric interference correction of ^{84}Kr on ^{84}Sr and ^{86}Kr on ^{86}Sr was conducted using natural Kr isotopic ratios ($^{83}Kr/^{84}Kr =$ 0.20175, $^{83}Kr/^{86}Kr = 0.66474$) where no mass discrimination corrections were required because of the low intensity of the Kr beam [8,10,18]. Generally, the signal intensity of ^{84}Kr is *ca.* 3–10 mV, corresponding to *ca.* 0.6–2 mV of ^{83}Kr. It then decreases significantly to 0.1 mV after the 2% HNO_3 solution is aspirated into the ICP. The isobaric interference of ^{87}Rb on ^{87}Sr was corrected using $^{85}Rb/^{87}Rb = 2.59262$, assuming an identical mass bias for Rb and Sr [8,10,18]. Finally, the $^{87}Sr/^{86}Sr$ ratios were calculated and normalized to the interference-corrected $^{86}Sr/^{88}Sr$ ratio using the exponential law [21]. The data-reduction procedure was performed using a self-written Excel Visual Basic for Applications macro program.

3. Results and discussion

3.1. Results

The well-known isotopic compositions of CRMs are commonly employed for validating and investigating analytical protocols.

However, as deviations of single analyses are probably biased because of heterogeneity of these geological materials, we analyzed one to four aliquots per silicate rock CRMs powder. The respective $^{87}Sr/^{86}Sr$ results, together with literature data, are summarized in Table 3.

As shown in Table 3, the $^{87}Sr/^{86}Sr$ data for the CRMs are in good agreement with published values using TIMS or MC-ICP-MS [7,17,22]. Our new $^{87}Sr/^{86}Sr$ data for BCR-2, BHVO-2, W-2, and AGV-2 is also in good agreement with our previous data obtained using a Sr-specific resin-purification protocol [18]. Furthermore, the $^{87}Sr/^{86}Sr$ data determined for replicate analyses of the basalt, andesite, and diabase all show high precision. The $^{87}Sr/^{86}Sr$ reproducibility of CRMs is approximately 0.003% (2 RSD). Generally, the reproducibility and precision are satisfactory and completely fit the demands of geosciences [22].
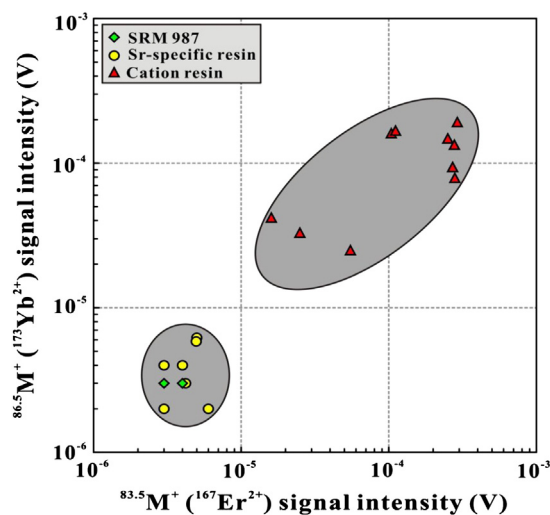
Fig. 1. Relationship between the $^{83.5}M$ ($^{167}Er^{2+}$) and $^{86.5}M$ ($^{173}Yb^{2+}$) signal intensity for SRM 987 or CRMs of different Sr fractions (Sr-specific extraction chromatographic or common cation-exchange resin) analyzed by MC-ICP-MS in this study (Table 3). These demonstrate the existence of doubly charged HREE ions after common cation-exchange resin purification that have significant effects on the Sr isotopic composition measurement using MC-ICP-MS, while the purity of Sr cut after Sr-specific resin is almost identical to that of standard reference solution (*e.g.*, SRM 987). Error bars (internal precisions) are smaller than symbols in all cases and not shown on this scale.

Fig. 2. Mass scan illustration of SRM 987 (200 ppb) and REE mixture standard solutions (10 ppm) using the present cup configuration (Table 2). Our result demonstrated that there are some obvious mass differences between Sr and doubly charged ions (*ca.* 0.05–0.07 AMU), indicating that natural abundance of Er and Yb is unfeasible for isobaric correction and generally results in overcorrection (Table 4). Additionally, Er doubly charged ion dominates over Yb doubly charged ion as source of doubly charged ion interferences on Sr isotopic data (*e.g.*, L4(^{166}Er^{2+}), L3(^{167}Er^{2+})), indicating that Er is more prone to doubly charged ion formation than Yb during the Sr isotopic composition measurement using MC-ICP-MS.

3.2. Isobaric interference corrections for Sr isotope analysis

3.2.1. Singly charged monoatomic and polyatomic ions

The protocol for the correction of Kr and Rb on Sr has been previously described in detail [5–10,18]; hence, only a brief overview is provided here. 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 ^{83}Kr during the Sr isotopic measurement (Table 2). Because of ^{87}Rb interference on ^{87}Sr, the natural isotopic composition of Rb is generally used for isobaric interference by the exponential law. It is usually observed that the ^{85}Rb signal intensity is less than 5×10^{-5} V for most geological samples after common cation resin isolation [5,8,10,11,18]. Our previous observation demonstrated that the measured ^{87}Sr/^{86}Sr ratios can be effectively corrected for Rb interference by the Neptune MC-ICP-MS when the Rb/Sr ratio is less than 0.015 [8,25].

Apart from Kr and Rb, the presence of polyatomic ions, such as Ca argides and dimers, also interferes with Sr masses (Table 2). However, in contrast to the results of Waight et al. [9] and Woodhead et al. [11], our previous study demonstrated that the influence of Ca argides and dimers on Sr isotope analysis using our Neptune MC-ICP-MS was insignificant [8,25]. Furthermore, this observation is supported by other findings [10,13,25]. The reason for these differences is still unknown; however, it could be related to different instrument design concepts (*e.g.*, movable or fixed Faraday cups) or different operating parameters. No corrections for Ca argides and dimers were performed for our dataset [8,25].

3.2.2. Doubly charged monoatomic ions

As previously reported [9,10,18], HREE-produced doubly charged ions can interfere with Sr masses and thus significantly alter Sr data during MC-ICP-MS measurement. Our previous study demonstrated that there are inevitably residual HREE in Sr fractions when using a common cation resin (AG50W-X12) because of their overlapping elution curves, which lead to positive deviations in measured ^{87}Sr/^{86}Sr data [18]. This observation is also reported by Waight et al. [9, Fig. 4A], and usually indicates poor calibration of common cation column chemistry. Further evidence is observed from our present data as shown in Fig. 1, in which differences in signal intensities at 83.5 and 86.5 AMU between the cation and Sr-specific resin fractions demonstrate the presence of residual HREE in the Sr fraction of samples separated by the common cation resin. To eliminate residual HREE in the Sr fraction, this fraction is usually further purified by a Sr-specific extraction chromatographic resin [7,9,17]. Because such a purification step is not conducted in our proposed one-step cation purification procedure, accurate correction for doubly charged Er and Yb ions is crucial for determining accurate and precise ^{87}Sr/^{86}Sr ratios.

Table 4
The potential and obvious mass dispersion of isobaric interference correction during Sr isotope measurement.

Real AMU	L4	L3	L2	L1	Center	H1	H2	H3	H4
Nominal mass	83	83.5	84	85	85.5	86	86.5	87	88
Sr$^+$			83.913			85.909		86.909	87.906
Kr$^+$	82.914		83.912			85.911			
Rb$^+$				84.912				86.909	
Er^{2+}	82.965	83.466	83.966	84.968					
Yb^{2+}			83.967	84.967	85.468	85.968	86.469	86.969	87.971
Lu^{2+}								86.970	87.971
Hf^{2+}									87.971
Mass difference = M$^+$(Kr or Rb) − Sr$^+$ or M^{2+}(Er, Yb, Lu and Hf) − Sr$^+$									
Kr$^+$			−0.001			0.002			
Rb$^+$								0.000	
Er^{2+}	0.051		0.053	0.056					
Yb^{2+}			0.054	0.056		0.059		0.060	0.065
Lu^{2+}								0.061	0.065
Hf^{2+}									0.065

After the pioneering work by Ramos et al. [10], several colleagues have adopted the same or similar cup array, in which half masses, such as 83.5, 85.8, and 86.5 atomic mass unit (AMU) cups are used to monitor doubly charged ions like $^{167}Er^{2+}$, $^{170}Er^{2+}$, and $^{173}Yb^{2+}$ [12, 13]. We also adopted this Faraday cup configuration, which is ideal for interference monitoring while measuring all Sr and Rb isotope masses with some assumption of the same atomic masses for Er^{2+}, Yb^{2+}, and Sr^+ [e.g., $^{84}Sr^+(^{168}Er^{2+})$, $^{86}Sr^+(^{172}Yb^{2+})$, $^{87}Sr^+(^{174}Yb^{2+})$, and $^{88}Sr^+(^{176}Yb^{2+})$]. However, the doubly charged Er and Yb peaks are not aligned in the Sr cup and the full peak height is not measured simultaneously considering the preferred dominant Sr mass of interest. As shown in Fig. 2, and as reported earlier, the Rb and Sr Faraday cup signal intensities were peak-centered and aligned by setting the L1 Faraday cup at mass $^{86}Sr^+$. Nevertheless, there are some obvious differences between singly charged Kr, Rb, and Sr ions and doubly charged Er and Yb ions (ca. 0.05–0.07 AMU), which is further strongly supported and demonstrated in Table 4. Furthermore, in the range from lower mass (83 AMU) to higher mass (88 AMU), the mass difference between the Sr ion and the doubly charged Er and Yb ions changes evidently from 0.051 AMU to 0.065 AMU in Table 4 (Fig. 2), suggesting that the higher the mass, the greater the dispersion (i.e., 0.053 AMU difference between $^{168}Er^{2+}$ and $^{84}Sr^+$, whereas there is a 0.065 AMU difference between $^{176}Er^{2+}$ and $^{88}Sr^+$). More importantly, as also shown in Fig. 2, using the same concentrations of Er and Yb (10 mg/L) in a mixed REE standard solution at the same operating parameters, the signal intensity of Er^{2+} is considerably higher than that of Yb^{2+} (e.g., 0.08 V on L3 cup ($^{83.5}M^+$, [$^{167}Er^{2+}$, 22.95%]) > 0.05 V on the H3 cup ($^{87}M^+$, [$^{174}Yb^{2+}$, 31.8%]), 0.06 V on the L1 cup ($^{85}M^+$, [$^{170}Er^{2+}$, 14.9%]) > 0.02 V on the center cup ($^{85.5}M^+$, [$^{171}Yb^{2+}$, 14.3%])), although they have the same natural abundance (abundance of Yb may even be a slightly higher than that of Er) (Table 2 and Fig. 2). This implies that Er doubly charged ions dominate over Yb doubly charged ions as a source of interference because Er is more prone to doubly charged ion formation. Yb has a slightly smaller ionic radius than Er and the ionization efficiency or elemental signal intensity tends to increase with increasing mass [14,15]; thus, our observation seems contradictory with this, and the real reason is still unknown.

As presented in an earlier study, $^{87}Sr/^{86}Sr$ will be higher than the recommended values (Table 3 and Fig. 3), if no doubly charged ion isobaric interference correction is applied [18]. In contrast, as shown in Figs. 2 and 3, isobaric interferences are overcorrected if natural Er and Yb ratios are used for interference corrections. Only the use of the actual measured Er and Yb ratios, as shown in this study, results in accurate Sr isotopic compositions (Fig. 3). The Er and Yb ratios were usually measured regularly every ten real samples using a multi-element mixed REE standard solution at the same operating parameter settings. Hence residual HREE in Sr cuts can be accurately corrected for when using the Er and Yb ratios measured in-run, rather than literature values. This method allows "impure" Sr cuts to be measured at good precision and accuracy; thus, costly and time-consuming purification steps in the lab can be avoided [10,13,25].

4. Conclusion

Interference by doubly charged HREE ions on MC-ICP-MS Sr isotopic composition measurement is re-investigated in this study. Two primary contributions to doubly charged HREE ion interferences are observed. The first is that the use of the natural abundance of Er and Yb for doubly charged ion interference correction leads to an overcorrection, whereas measured doubly charged ion ratios are reasonable and provide accurate isobaric interference corrections. The analytical feasibility and reproducibility of the analytical protocol are evaluated and validated for several CRMs. More importantly, Er dominates over Yb as a source of doubly charged ions, indicating that Er is more prone to doubly charged ion formation than Yb during Sr isotopic composition measurements using MC-ICP-MS.
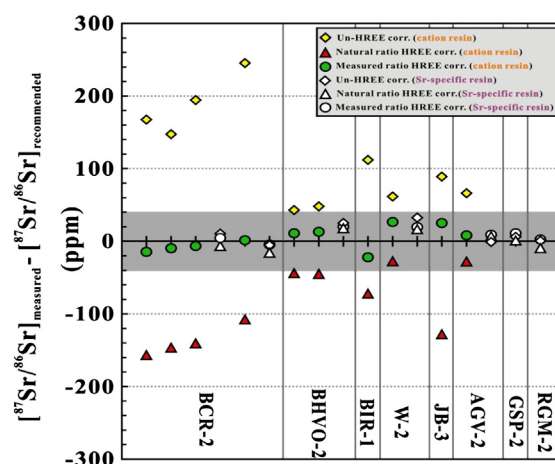

Fig. 3. Comparison of the $^{87}Sr/^{86}Sr$ data for CRMs from this study using different correction protocols with the recommended mean values from published data compilations (Table 3). Specifically, solid diamonds are un-HREE corrected data; solid triangles are data corrected using the natural HREE ratio; and solid circles are corrected using the measured HREE ratio. Empty diamonds, triangles and circles represent samples that had been purified by Sr-Spec resin prior to MC-ICP-MS analyses. Gray field represents the preferred value ± 40 ppm (2SD). These demonstrate that the natural abundance of Er and Yb used to doubly charged ion interference correction leads to an overcorrection, while measured doubly charged ion ratios provide more accurate correction. Error bar (2SE) (internal precision are approximately the symbols size in all case and not shown on this scale).

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