

Precise measurement of stable ($\delta^{88/86}\text{Sr}$) and radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$) strontium isotope ratios in geological standard reference materials using MC-ICP-MS

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Received June 25, 2012; accepted October 8, 2012; published online April 10, 2013

A new method for high-precision measurements of stable ($\delta^{88/86}\text{Sr}$) and radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$) Sr isotope ratios was developed on the MC-ICP-MS using a standard-sample-standard bracketing protocol. By carefully monitoring and controlling the accumulation of the on-peak backgrounds (i.e. the carryover memory) on the instrument, our method can provide an external precision of around $\pm 0.010\text{‰}$ to $\pm 0.014\text{‰}$ for $\delta^{88/86}\text{Sr}$ measurements. Such precision is comparable to that achieved by double-spike TIMS method (DS-TIMS), and 2–3 times better than those of the previously reported results by MC-ICP-MS without spiking. The results of the standard seawater IAPSO are also identical to those by DS-TIMS. However, our method is more advantageous, efficient and convenient to use for routine Sr isotopic analysis than the DS-TIMS method as there is no need to prepare and calibrate the ^{84}Sr - ^{87}Sr double spike. Using this method, we measured the $\delta^{88/86}\text{Sr}$ values in a series of international geological rock standards, which show large variability, with the lowest value (-0.20‰) registered in JG-2, a terrestrial granite, and the highest value (0.539‰) in UB-N, a serpentinite. This may provide an additional means for isotopic characterization of geological processes, adding a new dimension over the traditional use of radiogenic Sr isotopic ratio $^{87}\text{Sr}/^{86}\text{Sr}$.

stable Sr isotopes, $\delta^{88/86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$, IAPSO, geological standards, MC-ICP-MS

Citation: Ma J L, Wei G J, Liu Y, et al. Precise measurement of stable ($\delta^{88/86}\text{Sr}$) and radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$) strontium isotope ratios in geological standard reference materials using MC-ICP-MS. *Chin Sci Bull*, 2013, 58: 3111–3118, doi: 10.1007/s11434-013-5803-5

The Rb-Sr isotopic system is one of the most classical isotopic systematics in isotope geochronology and geochemistry studies [1]. Sr has four naturally occurring isotopes, namely, ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr . ^{84}Sr , ^{86}Sr , and ^{88}Sr are stable, whereas ^{87}Sr is variable, consisting of a radiogenic component derived from the decay of ^{87}Rb through β emission. The ratios among the stable isotopes of ^{84}Sr , ^{86}Sr and ^{88}Sr are generally considered as constants during geological processes, and the value of $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ or $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$ has been widely adopted to correct for mass bias during Sr isotope ratio measurements by mass spectrometry [2]. However, recent studies indicate that the stable $^{88}\text{Sr}/^{86}\text{Sr}$

ratio in many geological bodies may also vary significantly during processes such as chemical weathering and carbonate concretion [3–11].

$\delta^{88/86}\text{Sr}$ has been defined to describe the per-mil deviation of measured $^{88}\text{Sr}/^{86}\text{Sr}$ in a given sample from the Sr metal standard SRM-987, calculated using the following equation [5]:

$$\delta^{88/86}\text{Sr} = \left(\frac{^{88}\text{Sr}/^{86}\text{Sr}_{\text{sample}}}{^{88}\text{Sr}/^{86}\text{Sr}_{\text{standard}}} - 1 \right) \times 1000.$$

The $\delta^{88/86}\text{Sr}$ values in different geological bodies show a large variation. Modern seawater has a value of about 0.38‰ [5,6,12], marine biogenic carbonates generally show

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values of around 0.05‰–0.35‰ [5,6,11], while terrestrial carbonates such as speleothem display quite negative values, –0.1‰ to –0.2‰ [6]. Terrestrial rocks show an average around 0.27‰, while meteorites show a very large range, from –1.73‰ to 0.66‰ [13]. In addition to such large variations, $\delta^{88/86}\text{Sr}$ in marine biogenic carbonates such as corals appears to be temperature dependent, which can potentially be used in paleo-temperature reconstructions [5,11].

Stable Sr isotopes can not only expand our knowledge of Sr isotopic systematics, but also help to better constrain the applications of the radiogenic Sr isotope ratio $^{87}\text{Sr}/^{86}\text{Sr}$ because changes in $^{88}\text{Sr}/^{86}\text{Sr}$ may result in an offset of up to 144×10^{-6} in the measured $^{87}\text{Sr}/^{86}\text{Sr}$ value in IAPSO when a constant $^{88}\text{Sr}/^{86}\text{Sr}$ value was adopted to internally correct for mass bias during mass spectrometric measurement [12]. This would be a serious problem when high-precision $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are needed, such as Sr isotope stratigraphy [14]. It is therefore very important to precisely measure the $\delta^{88/86}\text{Sr}$ and thus the true $^{87}\text{Sr}/^{86}\text{Sr}$ (or $^{87}\text{Sr}/^{86}\text{Sr}^*$), which is free from the influence of $^{88}\text{Sr}/^{86}\text{Sr}$ variation, for a better application of Sr isotopic systematics.

Two methods have been previously used for high-precision $\delta^{88/86}\text{Sr}$ measurement. The first is ^{87}Sr - ^{84}Sr double-spike thermal ionization mass spectrometry method (DS-TIMS) [12]. This method can provide high precision $\delta^{88/86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}^*$ results with external precisions around $\pm 0.01\%$ and 10×10^{-6} , respectively [12]. The double spike TIMS (DS-TIMS) method, however, is very complicated in its essential need for precise calibration of the ^{87}Sr - ^{84}Sr double spike and for precise correction for mass bias during measurement. Moreover, the ^{87}Sr - ^{84}Sr double spike is still not easily available in most laboratories.

The second approach is to measure $\delta^{88/86}\text{Sr}$ using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). This can also be achieved using two different protocols, one adopting a standard bracketing technique in a standard-sample-standard measuring sequence (SSB mode) [5] and the other involving internal correction of mass bias by measuring Zr isotopic ratios, such as $^{91}\text{Zr}/^{90}\text{Zr}$ or $^{92}\text{Zr}/^{90}\text{Zr}$ [10,15,16]. The external precision of the $\delta^{88/86}\text{Sr}$ measurements using the SSB protocol is about $\pm 0.02\%$, which is about 2–3 times poorer than that of the DS-TIMS method [5]. As for the protocol of using measured Zr isotopic ratios for internal mass bias correction, Zr is doped to the sample solution before measurement. The amount of Zr to be added should be carefully controlled to obtain good precisions [15,16]. More importantly, the exact $^{91}\text{Zr}/^{90}\text{Zr}$ or $^{92}\text{Zr}/^{90}\text{Zr}$ values used for mass bias correction are changing in different measurement sessions and in different Zr solutions. Thus they should be calibrated by using $^{88}\text{Sr}/^{86}\text{Sr}$ in the SRM 987 standard along with the measurements of the samples. After carefully calibrating the Zr isotopic ratios, this protocol can achieve an external precision comparable to that by the DS-TIMS method, around

$\pm 0.012\%$ (1SD) for $\delta^{88/86}\text{Sr}$ [15,16]. The only purpose for internal correction using Zr isotopes is to reduce the short-term drift in mass bias of the MC-ICP-MS, but adding Zr to the sample solution may increase the risk of matrix mismatch [15]. Moreover, the ionization efficiencies of Sr and Zr are different, whether this may result in different mass biases between them or not is not known yet. Given that the Zr isotopes need instant calibration using repeated measurements of the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio in SRM987, if the short-term drift in the mass bias of the MC-ICP-MS can be reduced, and the precision of the SSB protocol can be increased to comparable levels, there will be no advantage to employ Zr isotopes for mass bias correction. On the other hand, the SSB protocol has the advantage of simplified chemical procedure, with no extra materials, such as Zr and ^{87}Sr - ^{84}Sr double spike to be added to the sample solutions. In this case, the whole procedure is similar to that for the traditional $^{87}\text{Sr}/^{86}\text{Sr}$ measurement protocol, which is very convenient for applying to related studies.

We herein report our tests over a period of more than 12 months, covering more than 30 measuring sessions. Our results demonstrate that, by carefully controlling the accumulation of the blank or carry-over memory on the MC-ICP-MS using a vigorous in-run washing procedure, the stability of the instrumental mass discrimination can be improved. Using this carefully controlled protocol, we achieve a $\delta^{88/86}\text{Sr}$ external precision better than those previously reported for both MC-ICP-MS and DS-TIMS methods. This new highly efficient protocol will open a new avenue for a wide application of the stable and radiogenic Sr isotopes.

1 Experiments

1.1 Samples and preparation

As seawater $^{88}\text{Sr}/^{86}\text{Sr}$ is significantly different from that of the SRM987 standard, we select two seawater samples to establish the method. One is the IAPSO standard seawater (Batch P153) purchased from the Ocean Scientific International Ltd (OSIL), England. The other seawater sample was collected from Luhuitou Reef in Sanya, southern Hainan Island in the northern South China Sea. The seawater was filtered through 0.4 μm Millipore membrane in the field, and acidified with HNO_3 before sealed in polyethylene bottles.

In addition to the seawater samples, we select a series of international geological standard reference materials with a variety of lithological signatures, including mantle-derived basalts such as BHVO-2, BCR-2 and JB-3; andesite such as JA-2 and AGV-2; diabase such as W-2 and MRG-1; granites such as JG-2 and G-2; serpentinite (UB-N) and polymetallic nodule such as GBW07249, GBW07295 and GBW07296. All the rock standard samples were digested in $\text{HF}+\text{HNO}_3$ acid mixture, and the polymetallic nodule samples were dissolved with aqua regia. The dissolved samples

were dried on a hot-plate and finally re-dissolved in 4 mol/L HNO₃ solution for further Sr purification.

The purification of Sr was carried out by ion chromatography filled with Eichrom-Sr-Resin (50–100 mesh). About 0.3 g Eichrom Sr-Resin was loaded into each Eichrom polypropylene column with an inner diameter of 0.8 cm. The resin was washed with 15 mL 4 mol/L HNO₃, then rinsed with 15 mL milli-Q water, and finally equilibrated with 3 mL 4 mol/L HNO₃. About 1 mL seawater sample (with Sr of about 8 μg) was first mixed with 0.5 mL ultrapure concentrated HNO₃ (~14 mol/L) to make Sr solution in 4 mol/L HNO₃. The acidified seawater, as well as the re-dissolved rock samples was then loaded on the pre-conditioned column. Their matrix was removed by rinsing with 20 mL 4 mol/L HNO₃. The purified Sr was collected using 8 mL milli-Q water, ensuring all the Sr to be eluted. The collected Sr solution was further diluted to achieve a Sr concentration of about 50 ng/mL for MC-ICP-MS measurement.

The milli-Q water was prepared using Millipore[®] system yielding a resistivity of 18.2 MΩ·cm, and all the ultrapure acids were distilled from analytical reagent (AR)-grade acids using DST-1000 sub-boiling acid distillation system purchased from Savillex Company, USA. The Sr procedural blank of the total chemical treatment was at the level of less than 1 ng.

1.2 Instrumentation

The stable Sr isotope analysis in this study was carried out using a Thermo Fisher Scientific Neptune Plus MC-ICP-MS in the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS). This instrument is a double focusing magnetic sector field mass spectrometry equipped with 9 Faraday cups and 4 ion counters. Samples solutions in 2% nitric acid were introduced through a Micromist PFA nebulizer and buffered in a glass cyclonic spray chamber. The spray was inlet to torch directly without any membrane desolvator.

1.3 Measurement procedure

Six Faraday cups were used in our measurement. The axial Faraday cup was assigned to ⁸⁶Sr, and L3, L2, L1, H1 and H2 Faraday cups were assigned to ⁸³Kr, ⁸⁴(Sr+Kr), ⁸⁵Rb, ⁸⁷(Rb+Sr) and ⁸⁸Sr, respectively. ⁸³Kr was measured in order to correct for the isobaric interference of ⁸⁶Kr on ⁸⁶Sr using ⁸⁶Kr = 1.50566×⁸³Kr, and ⁸⁵Rb was measured in order to correct for the isobaric interference of ⁸⁷Rb on ⁸⁷Sr using ⁸⁷Rb = 0.3857×⁸⁵Rb.

The typical instrument parameters during the stable Sr isotope measurement are shown in Table 1. The intensity of ⁸⁸Sr was generally optimized to about 8 V by Sr standard of 50 ng/mL before each measurement session, while the background of 2% HNO₃ on mass 88 was generally lower

Table 1 Typical operating parameters for stable Sr isotope ratio measurement using Neptune MC-ICP-MS

Parameter	Value
RF forward power	1310 W
Cooling gas	15 L/min
Auxiliary gas	0.95 L/min
Sample gas	0.938 L/min
Extraction	−2000 V
Focus	−677 V
Detection system	Nine Faraday collectors
Acceleration voltage	10 kV
Torch setting	
X-pos	−3.310 mm
Y-pos	−3.850 mm
Z-pos	−0.240 mm
Interface cones	Nickel
Spray chamber	Glass cyclonic
Nebulizer type	Micromist PFA nebulizer
Sample uptake rate	100 μL/min
Perri-pump	−12.75 r/min
Instrument resolution	400 (low)
Integration time	4.194 s
Idle time	3 s

than 0.5 mV. Prior to measurement, the measured samples were adjusted to an ⁸⁸Sr intensity of ~8 V, similar to those of the bracketing SRM987 standards. This enables a perfect intensity match between the sample and the bracketing standards, and avoids possible influences from mis-match [15]. Meanwhile, the signal-to-noise ratio for each measurement is >13000. Thus, the influence of the background is negligible and no on-peak-zero correction is needed.

The measurement was carried out in the sequence of SRM987-sample-SRM987. The traditional internal mass bias correction using ⁸⁸Sr/⁸⁶Sr=8.375209 as the normalization value was applied to each of the measurement, including both SRM987 and samples, to obtain ⁸⁷Sr/⁸⁶Sr and marked as ⁸⁷Sr/⁸⁶Sr_{IN}. $\delta^{88/86}\text{Sr}$ and an externally calibrated ⁸⁷Sr/⁸⁶Sr ratio marked as ⁸⁷Sr/⁸⁶Sr* were calculated from the measured ⁸⁸Sr/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr of the sample and the averages of the bracketing SRM987 as

$$\delta^{88/86}\text{Sr} = \left(\frac{2 \times {}^{88}\text{Sr}/{}^{86}\text{Sr}_{\text{sample}}}{{}^{88}\text{Sr}/{}^{86}\text{Sr}_{\text{SRM987B}} + {}^{88}\text{Sr}/{}^{86}\text{Sr}_{\text{SRM987A}}} - 1 \right) \times 1000,$$

$${}^{88}\text{Sr}/{}^{86}\text{Sr}^* = \frac{2 \times 0.710250 \times {}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{sample}}}{{}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{SRM987B}} + {}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{SRM987A}}},$$

where SRM987B and SRM987A refer to the SRM987 standard measured before and after the sample, respectively. The ⁸⁸Sr/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios adopted in these calculations are all the originally measured ratios without any mass bias correction.

Each data acquisition contains 10 blocks with each block containing 10 cycles. The integration time for each cycle is 4.194 s, and the total 100 scans take about 8 min, yielding an internal precision of about $(\pm 5-8) \times 10^{-5}$ for the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio. Such internal precision for $^{88}\text{Sr}/^{86}\text{Sr}$ corresponds to an uncertainty of around $\pm 0.01\%$ for $\delta^{88/86}\text{Sr}$ estimated by Gaussian error propagation equation with the measured errors of both the sample and the bracketing standards being considered.

1.4 Instrumental mass discrimination stability and the influence of background accumulation

Short-term drift in mass bias on MC-ICP-MS between samples and the bracketed standards is believed to influence the precision of the Sr isotopic ratios measured using the direct SSB protocol, which can be overcome by the use of Zr isotopic ratios to instantly correct for the mass bias [15]. The mass discrimination stability of the instruments has been improved in recent years, and the precision of the isotopic ratios without internal correction appears to be not much poorer than that after internal correction. This can be inferred from the internal precision for $^{88}\text{Sr}/^{86}\text{Sr}$ without any mass bias correction and $^{87}\text{Sr}/^{86}\text{Sr}$ after internal correction for mass bias by using $^{88}\text{Sr}/^{86}\text{Sr}=8.375209$ within a single measurement. The relative internal precision for both $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ is generally similar, of about 0.0008% (2σ , RSD).

During the measurement procedure, if the drift paths of the measured $^{88}\text{Sr}/^{86}\text{Sr}$ ratios between the samples and the bracketed SRM987 are in parallel, good external precisions for the Sr isotopic ratios can also be obtained. This can be generally achieved by maintaining constant time intervals between each measurement, such as keeping constant washing time and constant parameters of the instrument after optimization. Figure 1 shows the results of $\delta^{88/86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}^*$ and $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$ of the ~ 10 h continuous measurements of SRM987. The external precision for $\delta^{88/86}\text{Sr}$ is $\pm 0.013\%$, indicating excellent instrumental mass discrimination stability. The external precision for $^{87}\text{Sr}/^{86}\text{Sr}^*$ is $\sim \pm 11 \times 10^{-6}$, while that for $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$ is slightly poorer, of $\pm 15 \times 10^{-6}$. The mean $^{87}\text{Sr}/^{86}\text{Sr}^*$ is identical to the certified value of SRM987, 0.710250, but the mean $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$ is of about 30×10^{-6} deviated from the certified value. This again indicates that the precision for the Sr isotope ratios without internal correction for mass bias is not poorer than that after correction. Measurements using the direct SSB protocol can yield comparable or even better precisions for both stable and radiogenic Sr isotope ratios on our instrument than those after internal correction on mass bias. More importantly, the values of the Sr isotopic ratios after internal correction, not only by $^{88}\text{Sr}/^{86}\text{Sr}$ but also by Zr isotope ratios, are generally $(\sim 20-50) \times 10^{-6}$ deviated from the certified values, and further corrections are needed to compensate for

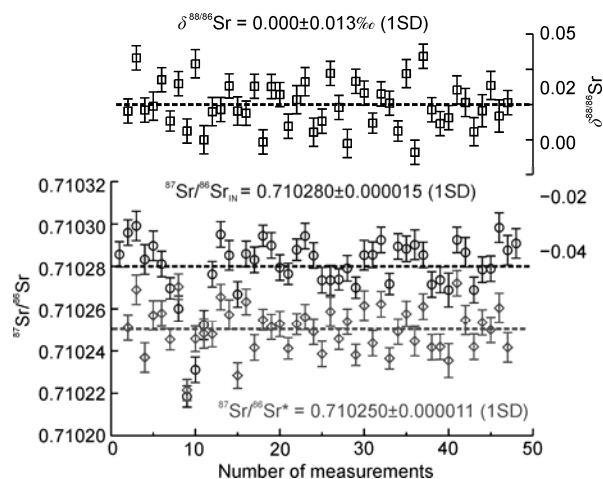


Figure 1 The $\delta^{88/86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$ and $^{87}\text{Sr}/^{86}\text{Sr}^*$ results of 48 continuous measurements of SRM987 during a 10-h period.

such bias [5,16]. The SSB protocol, in which the values of the Sr isotopic ratios are calculated from the measured values of the bracketing SRM987 standards and its certified values, can instantly correct the bias between them, providing accurate results without the need for further compensation correction [15].

As for the measurement of samples with $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ significantly different from SRM987, maintaining parallel drift paths for these ratios may not be as easy as that for the continuous measurement of SRM987 only. The accumulation of Sr memory on the machine (especially from the samples that still contain a trace amount of Ca) is one of the most serious problems. The ^{88}Sr memory can be generally washed to less than 0.5 mV at the beginning of the measurement. The ^{88}Sr intensity can rapidly decrease from 8 V to less than 2 mV in 2 min by flushing with 2% nitric acid after each measurement. Nevertheless, ^{88}Sr can gradually get accumulated during the measurements because of the memory effect of Sr (together with Ca) in the tube, spray cells and cones. As a result, the ^{88}Sr background increases gradually along with repeated sample measurements, which becomes increasingly difficult to be effectively reduced to < 0.5 mV even by flushing with 2% nitric acid for a longer period. In order to obtain a smooth drift in the $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ measurements, the washing time between measurements was set to 5 min. The background can generally become stable after 5 min washing by 2% nitric acid, but gradually increased along with repeated measurements, up to 2 mV in 8–10 h in general. Continuous background accumulation, however, increases the risk of contamination between samples and SRM987. Giving that the measured samples cover a wide range of Sr isotopic compositions, the accumulated Sr background may also show highly variable $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. As a result, such background accumulation or memory build-up may likely ruin the parallel instrumental mass discrimination paths, leading to poor external precisions for $\delta^{88/86}\text{Sr}$.

An easy way to remove the accumulated background is to flush with a 0.2% HF+2% HNO₃ mixture. Probably due to the effect of minor HF, this mixture acid appears to be more aggressive and effective in purging the Sr memory on the sampling tube, nebulizer, chamber or cones. The accumulated ⁸⁸Sr background can be readily reduced from ~5 to <0.5 mV after 2–3 min flushing. The HF flushing, however, can significantly influence the measured ⁸⁸Sr/⁸⁶Sr ratios and interrupt the smooth drift path. Figure 2 shows the typical ⁸⁸Sr/⁸⁶Sr drift path of SRM987 by flushing with 0.2% HF+2% HNO₃ occasionally. The ⁸⁸Sr/⁸⁶Sr increases significantly after flushing, of about 0.002 to 0.004 (Figure 2). This may contribute an uncertainty of ±0.1–0.2‰ to δ^{88/86}Sr and significantly affect the repeatability of the δ^{88/86}Sr results. Fortunately, the parallel drift paths can be re-established in 2–3 measurements after HF flushing.

Therefore a compromise between minimizing sample contamination by background accumulation and maintaining a smooth drift path without HF flushing is needed to obtain good repeatable δ^{88/86}Sr results. The influence of background accumulation could be evaluated by measuring the seawater sample from Sanya, which has much higher ⁸⁸Sr/⁸⁶Sr than that of SRM987. Figure 3 shows the typical drift path of the ⁸⁸Sr/⁸⁶Sr ratios both for SRM987 and Sanya seawater. Measured ⁸⁸Sr/⁸⁶Sr values of SRM987 drift over a fairly large range, from 8.731 to 8.727, during an 8-h measuring period. Meanwhile, measured ⁸⁸Sr/⁸⁶Sr values of the Sanya seawater show a similar drift, from 8.733 to 8.731 (Figure 3). As a result, the drifting paths for SRM987 and Sanya seawater are generally parallel to each other, yielding excellent external precision for the δ^{88/86}Sr of the Sanya seawater, 0.416±0.014‰.

No HF flushing has been carried out during this ~8-h measurement session, and the background on ⁸⁸Sr increased gradually from ~0.3 to ~4 mV (Figure 3). It is worth noting that the Sanya seawater in Figure 3 contains two different Sr concentrations. The blue and green rectangles denote samples with ⁸⁸Sr intensity of ~ 8 and ~4 V, respectively. The two sets of samples with different concentrations show the same drift paths and yield the same δ^{88/86}Sr even though the ⁸⁸Sr background gradually increases to 4 mV. This indicates that the background accumulation by up to 4mV appears to

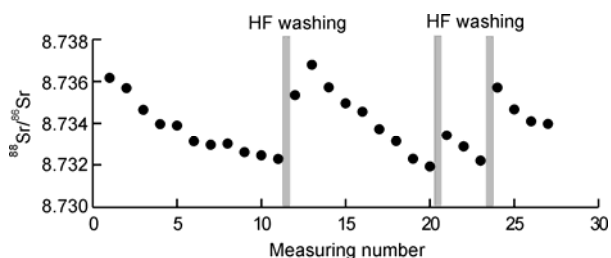


Figure 2 ⁸⁸Sr/⁸⁶Sr drift path for SRM987 by occasionally washing with 0.2% HF+2% HNO₃. Shaded bars marked the HF washing, when ⁸⁸Sr background was readily reduced to less than 0.5 mV, but the ⁸⁸Sr/⁸⁶Sr ratio jumped significantly.

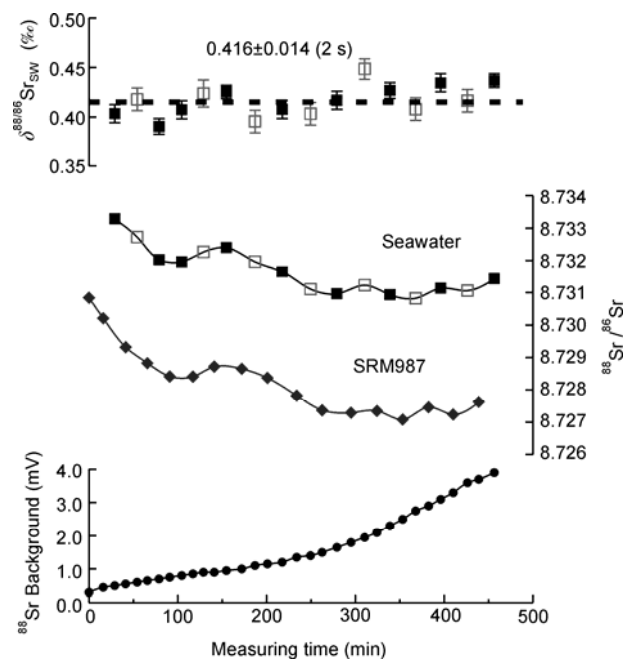


Figure 3 Temporal drifts of ⁸⁸Sr/⁸⁶Sr of SRM987 and Sanya seawater along with the accumulation of ⁸⁸Sr background on MC-ICP-MS. The solid rectangles and the open rectangles indicate the results of the samples with ⁸⁸Sr intensity of 8 and 4 V, respectively.

have not significantly influenced the parallel drift paths of the ⁸⁸Sr/⁸⁶Sr for both SRM987 and seawater samples and the δ^{88/86}Sr results may still be reasonable in a limited background accumulation range. However, there is an apparent increasing trend for the δ^{88/86}Sr of the Sanya seawater along with the background accumulation in Figure 3. The means of the δ^{88/86}Sr before and after 2 mV of the ⁸⁸Sr background are 0.409±0.012‰ (1SD: standard deviation) and 0.431±0.015‰ (1SD), respectively. Such a δ^{88/86}Sr drift is likely contributed from the background accumulation. In order to reduce the potential influence of the background, we herein set a background threshold of about 2.0 mV. Measurement continues if the ⁸⁸Sr background is less than 2 mV. HF flushing is applied to washing the ⁸⁸Sr background to <0.5 mV as soon as this threshold is reached, followed by another continuous measurement session. Such a continuous measurement session generally lasts for 5–6 h, which enables about 20–25 measurements.

2 Results and discussions

2.1 IAPSO and Sanya seawater

Our analytical results, including δ^{88/86}Sr, ⁸⁷Sr/⁸⁶Sr* of the standard seawater IAPSO and the seawater from Sanya coral reef are shown in Figure 4. The results shown in Figure 4 are for both IAPSO and Sanya seawater which were measured on 5 individual sub-samples after different ion chromatographic purification. The δ^{88/86}Sr values of IAPSO and

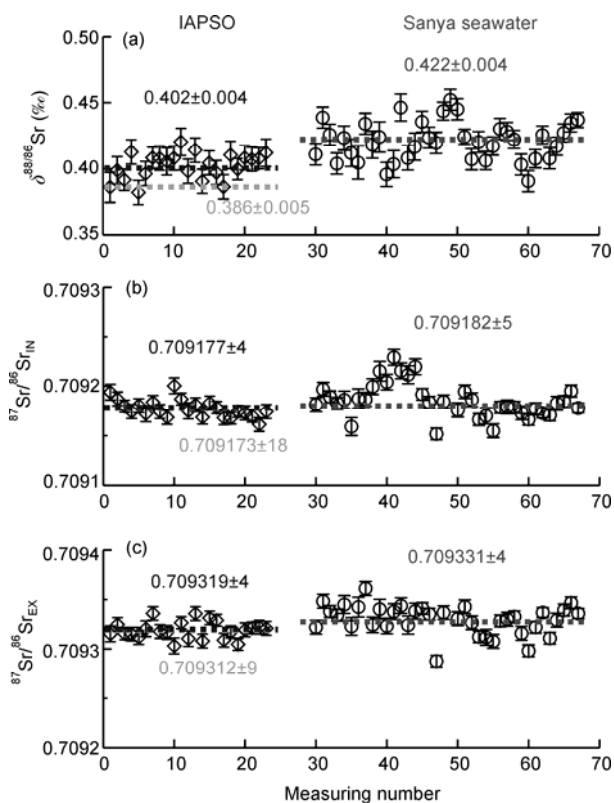


Figure 4 $\delta^{88/86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$ and $^{87}\text{Sr}/^{86}\text{Sr}^*$ results of the standard seawater IAPSO and Sanya seawater. (a) $\delta^{88/86}\text{Sr}$; (b) $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$ after correcting for the systematic offsets between the measured $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$ of SRM987 and its certification value, 0.710250; (c) $^{87}\text{Sr}/^{86}\text{Sr}^*$. The corresponding results of IAPSO by DS-TIMS [12] were also shown for comparison.

Sanya seawater are $0.401\pm 0.010\text{‰}$ (1SD) and $0.422\pm 0.014\text{‰}$ (1SD), respectively. In order to compare the accuracy of our results, the mean $\delta^{88/86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ results for both IAPSO and Sanya seawater, together with the corresponding results for IAPSO by DS-TIMS method are shown in Figure 4 with uncertainties of 2SEM [12]. Our IAPSO $\delta^{88/86}\text{Sr}$ results vary from $0.382\pm 0.009\text{‰}$ to $0.420\pm 0.010\text{‰}$ with an average of $0.402\pm 0.004\text{‰}$. These values are all within the ranges of the previously reported results by both the DS-TIMS [12] and the standard bracketing MC-ICP-MS methods [5]. The mean is slightly higher by 0.016‰ than that by DS-TIMS [12], and higher by 0.021‰ than that of the previously reported mean value obtained by standard bracketing MC-ICP-MS [5]. Such slight difference between our measurements and those by DS-TIMS is very small compared to the large variation range of the current reported $\delta^{88/86}\text{Sr}$ results for IAPSO, with some results being $0.35\pm 0.10\text{‰}$ [6]. The number of the measurements on IAPSO is still not very large currently. Whether such a large deviation is caused by differences in the analytical procedures in different laboratories or is attributed to inhomogeneous $\delta^{88/86}\text{Sr}$ in difference batches of IAPSO is not yet known.

In addition to $\delta^{88/86}\text{Sr}$, our $^{87}\text{Sr}/^{86}\text{Sr}$ results for the IAPSO

after compensating for the offsets between the measured and certified values of SRM987 show an average of 0.709177 ± 4 (Figure 4(b)). This value is the same as that of the $^{87}\text{Sr}/^{86}\text{Sr}_{\text{norm}}$ by DS-TIMS (0.709173 ± 18), after normalization to 0.710250 for SRM987 [12]. The IAPSO $^{87}\text{Sr}/^{86}\text{Sr}^*$ values of our measurements yield an average of 0.709319 ± 4 , which is the same as that by DS-TIMS (0.709312 ± 9) [12]. Therefore, using the standard bracketing method on MC-ICP-MS, it is possible to obtain $\delta^{88/86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}^*$ and traditional $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$ at the same time, which are comparable to those by DS-TIMS in both external precision and accuracy. The standard bracketing MC-ICP-MS method, however, needs no ^{84}Sr - ^{87}Sr double spike, and is very easy for calibration. It may potentially be more broadly used in related studies.

The average $\delta^{88/86}\text{Sr}$ value for Sanya seawater is $0.422\pm 0.004\text{‰}$. It is of 0.02‰ higher than that of the IAPSO, suggesting that there may be spatial variability in seawater $\delta^{88/86}\text{Sr}$. Such slight difference between Sanya seawater and IAPSO is very small in both $^{87}\text{Sr}/^{86}\text{Sr}^*$ and $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$. The average $^{87}\text{Sr}/^{86}\text{Sr}^*$ for Sanya seawater is 0.709331 ± 4 , while that for IAPSO is 0.709319 ± 4 , showing a difference of only about 0.000012 ± 0.000003 . The difference in $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$ between Sanya seawater and IAPSO is negligible, with the averages of 0.709182 ± 4 and 0.709177 ± 4 , respectively. This is in agreement with the generally accepted knowledge that $^{87}\text{Sr}/^{86}\text{Sr}$ is homogeneous in global oceans.

2.2 International rock standards

The $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$, $^{87}\text{Sr}/^{86}\text{Sr}^*$ and $\delta^{88/86}\text{Sr}$ values of the selected international rock standard references were listed in Table 2. There shows a large range for $\delta^{88/86}\text{Sr}$, from -0.20‰ to 0.56‰ (Figure 5). Mantle-derived basalts generally have relative uniform and higher $\delta^{88/86}\text{Sr}$ values, with an average

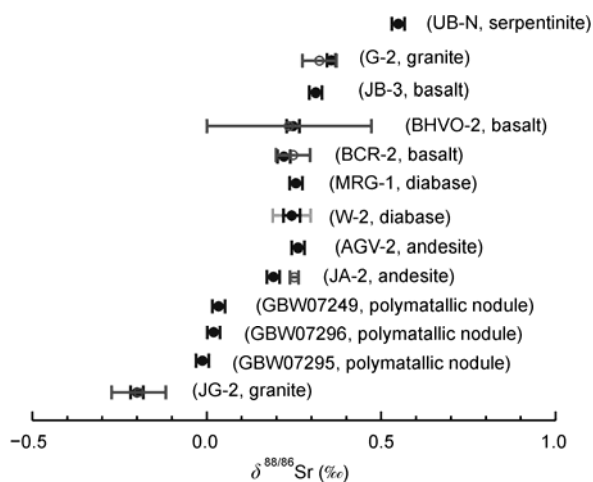


Figure 5 The variations of $\delta^{88/86}\text{Sr}$ for the selected international rock standard references. The solid circles indicate the results of this study, and the open circles indicate the result from [10, 13, 17].

Table 2 $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$, $^{87}\text{Sr}/^{86}\text{Sr}^*$ and $\delta^{88/86}\text{Sr}$ of the selected standard references

Sample ID	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$	$^{87}\text{Sr}/^{86}\text{Sr}^*$	$\delta^{88/86}\text{Sr}$	<i>n</i>	Reference	$^{87}\text{Sr}/^{86}\text{Sr}^{\text{a}}$	Reference
Basalt							
JB-3	0.703429±4	0.703541±5	0.31±0.02	2	This study	0.703417	[18]
BHVO-2	0.703476±5	0.703555±6	0.25±0.02	3	This study	0.703479	[19]
			0.24±0.24	5	[13]		
BCR-2	0.705017±5	0.705102±6	0.22±0.02	2	This study	0.705015	[20]
			0.24±0.09	6	[13]		
Diabase							
W-2	0.706976±4	0.707065±4	0.24±0.03	3	This study	0.706966	[18]
			0.25±0.12	1	[17]		
MRG-1	0.704234±5	0.704321±5	0.25±0.01	1	This study		
Andesite							
JA-2	0.706341±4	0.706405±4	0.19±0.02	2	This study	0.706350	[18]
			0.25±0.01	3	[10]		
AGV-2	0.703986±4	0.704084±4	0.28±0.01	2	This study	0.703981	[19]
Granite							
G-2	0.709753±4	0.709868±5	0.36±0.03	3	This study	0.709770	[19]
			0.31±0.09	3	[13]		
			0.35±0.11	2	[17]		
JG-2	0.758159±4	0.758046±4	-0.20±0.02	2	This study		
			-0.20±0.03		[10]		
Serpentinite							
UB-N	0.709955±4	0.710137±4	0.54±0.03	2	This study		
Polymetallic nodule							
GBW07249	0.709178±4	0.709116±4	0.03±0.02	2	This study		
GBW07295	0.709187±4	0.709124±4	-0.01±0.02	2	This study		
GBW07249	0.709192±4	0.709141±4	0.02±0.02	2	This study		

a) $^{87}\text{Sr}/^{86}\text{Sr}$ denotes recommended reference values.

of $0.254 \pm 0.047\%$. These are consistent with the previously reported results [10,17]. The $\delta^{88/86}\text{Sr}$ of the two andesite rocks, JA-2 and AGV-2, and the two diabase rocks, W-2 and MRG-1, are also similar to those of the basalts, from 0.190% to 0.275% . The $\delta^{88/86}\text{Sr}$ data of the two granite rocks, JG-2 and G-2, differ significantly from each other, with values of -0.204% and 0.321% , respectively. UB-N, a serpentinite rock shows the highest $\delta^{88/86}\text{Sr}$ of 0.539 in all our selected standards.

The $\delta^{88/86}\text{Sr}$ values of three Chinese polymetallic nodule standard references, GBW07249, GBW07295 and GBW-07296 are uniform, from -0.01 to 0.028 . These values are significantly lower than that in seawater, indicating that there is a significant fractionation for $^{88}\text{Sr}/^{86}\text{Sr}$ during the process for Fe-Mn nodule to capture Sr from seawater, with ^{86}Sr being preferentially incorporated.

The measured values of $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$ after normalization to a constant $^{88}\text{Sr}/^{86}\text{Sr}$ value of 8.375209 agree well with their reference values within analytical errors. It is worth noting that there exist obvious differences between the $^{87}\text{Sr}/^{86}\text{Sr}_{\text{IN}}$ and $^{87}\text{Sr}/^{86}\text{Sr}^*$ for these reference materials. These differences are due to the deviation of their respective $^{88}\text{Sr}/^{86}\text{Sr}$

values from the assumed constant value of 8.375209. The variations of $\delta^{88/86}\text{Sr}$ in natural rock samples indicate that the fractionation of $^{88}\text{Sr}/^{86}\text{Sr}$ is significant in geological processes, even though the mechanism for such fractionation is yet unclear. Giving that changes in $^{88}\text{Sr}/^{86}\text{Sr}$ may cause an up to $(100-200) \times 10^{-6}$ bias in the measured $^{87}\text{Sr}/^{86}\text{Sr}$ normalized to an assumed constant $^{88}\text{Sr}/^{86}\text{Sr}$ (8.375209), cautions must be taken in interpreting the $^{87}\text{Sr}/^{86}\text{Sr}$ results obtained by the traditional method.

3 Conclusions

By carefully monitoring and controlling the accumulation of the on-peak backgrounds (carry-over memories) on the instrument, the standard bracketing method on the MC-ICP-MS can achieve a higher analytical precision for the stable Sr isotope ratio measurements ($\delta^{88/86}\text{Sr}$). The results are comparable to those by DS-TIMS in both external precision and accuracy. However, our approach is more advantageous as it avoids the inconvenience of preparing and calibrating ^{84}Sr - ^{87}Sr double spike, providing a more efficient means

that can be easily applied in Sr isotopic studies. The variation of $\delta^{88/86}\text{Sr}$ in natural samples suggests that cautions must be taken to use the traditional method to measure $^{87}\text{Sr}/^{86}\text{Sr}$ whereby the assumed constant value of $^{88}\text{Sr}/^{86}\text{Sr}$ (8.375209) is used to correct for the instrument bias.

The authors thank Wu Lei of the State Key Laboratory of Isotope Geochemistry for her help in MC-ICP-MS measurements. Thanks are also presented to the four anonymous reviewers for their critical and constructive comments, which help to improve this article. The authors are also grateful to Prof. Zhao Jianxin of the University of Queensland, Australia for polishing the English. This work was supported by the Chinese Ministry of Science and Technology Special Scheme (2009CB421206 and 2010CB808900), the Knowledge Innovation Program of the Chinese Academy of Sciences (KZCX2-YW-138), and the National Natural Science Foundation of China (40973008 and 41173006). This is contribution No. IS-1616 from GIGCAS.

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