



Analytical note

High-precision direct determination of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of bottled Sr-rich natural mineral drinking water using multiple collector inductively coupled plasma mass spectrometry

Yue-Heng Yang^{*}, Fu-Yuan Wu, Lie-Wen Xie, Jin-Hui Yang, Yan-Bin Zhang

State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, China

ARTICLE INFO

Article history:

Received 8 March 2011

Accepted 23 July 2011

Available online 4 August 2011

Keywords:

$^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio

Bottled Sr-rich natural mineral drinking water

Direct determination

Multiple collector ICP-MS

ABSTRACT

We describe a precise and accurate method for the direct determination of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of bottled Sr-rich natural mineral drinking water using multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The method is validated by the comparative analysis of the same water with and without cation-exchange resin purification. The work indicates that isobarically interfering elements can be corrected for when $^{87}\text{Rb}/^{86}\text{Sr} < 0.05$ ($\text{Rb}/\text{Sr} < 0.015$), and that the matrix elements (Ca, Mg, K and Na) have no significant effect on the accuracy of the Sr isotope data. The method is simple, rapid, eliminates sample preparation time, and avoids potential contamination during complicated sample-preparation procedures. Therefore, the high sample throughput inherent to the MC-ICP-MS can be fully exploited.

© 2011 Elsevier B.V. All rights reserved.

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, approximately 7.04, and 82.53 at. %, respectively. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio 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. Thus, the isotopic composition of Sr, expressed as the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio, is dependent on the Rb/Sr ratio and age of the material analyzed. The Rb–Sr system has been extensively used for geochronological studies as well as geochemical tracer [1]. In addition, $^{87}\text{Sr}/^{86}\text{Sr}$ data have been used to track the environmental provenance studies and to trace pathways of animal and human migration [2–8].

Natural mineral water obtained from recycled deep sources of ground water contains many trace elements e.g. Sr, which are necessary for maintaining good health in humans as well as tracking regional water–rock interaction and chemical weathering of ground water flow and water mixing. Analysis for Sr is also required for product quality control. This is important as concerns have been raised about food quality as a consequence of the extent of global environmental pollution [2–8].

Since the 1960s, thermal ionization mass spectrometry (TIMS) has been the common method used for the precise determination of strontium isotopic ratios. This technique requires the efficient chemical separation of Sr from interfering Rb isotopes and other

matrix elements by ion exchange chromatography. Recently, multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has been developed as a routine technique for Sr isotope ratio measurement, with a precision comparable to that of TIMS [3,9–12]. The ICP source eliminates time-dependent fractionation effects, and has the resolution to permit isobaric correction of ^{87}Rb on ^{87}Sr [13–18].

The main objective of the present work is to establish a simple and rapid analytical protocol for direct measurement of Sr isotopic composition in natural mineral drinking water using MC-ICP-MS, thus eliminating the Rb and matrix element (K, Na, Ca, Mg) removal, without comprising the precision and accuracy of the measurements. The method results in significant savings in sample-preparation time and avoids any potential contamination. Therefore, the high sample throughput inherent to the MC-ICP-MS can be fully exploited.

2. Experimental

2.1. Chemical reagents and standards

Milli-Q water (18.2 M Ω .cm) from Millipore (Elix-Millipore, USA) and twice-distilled extra-pure grade reagents were used in this study. Concentrated hydrochloric and nitric acids were purified by the Savillex™ DST-1000 sub-boiling distillation system (Minnetonka, USA).

The isotopic certified reference material SRM 987 strontium carbonate (NIST, Gaithersburg, USA) was used to validate the analytical procedure. This standard was available as a solution of 200 $\mu\text{g L}^{-1}$ for monitoring conditions during actual analytical sessions. The Rb, Mg, Ca, K, and Na standard solutions (1000 $\mu\text{g mL}^{-1}$) were obtained from the National Research Center for Certified

^{*} Corresponding author. Tel.: +86 10 82998599; fax: +86 10 62010846.
E-mail address: yangyueheng@mail.iggcas.ac.cn (Y.-H. Yang).

Table 1

Typical instrumental settings and data acquisition parameters for Sr isotopic measurement using Neptune MC-ICP-MS.

Instrumental settings and data acquisition parameters							
RF power	1300 W			Nebulizer type		Micromist PFA	
Cooling gas flow rate	16.2 L/min			Sample uptake rate		50 $\mu\text{L}/\text{min}$	
Auxiliary gas flow rate	0.6 L/min			Sampling cone		Ni, aperture 1.0 mm	
Nebulizer gas flow rate	1.1 L/min			Skimmer cone		Ni, aperture 0.8 mm	
Extraction voltage	−2000 V			Integration time		4,1494 s	
Focus voltage	−654 V			Number of cycles		5 per block	
Acceleration voltage	10 kV			Number of blocks		9	
Spray chamber	Glass cyclonic			Measurement time		~240 s	
Sr cup configuration							
Cup	L4	L3	L2	L1	C	H1	H2
Mass	82	83	84	85	86	87	88
Sr			^{84}Sr		^{86}Sr	^{87}Sr	^{88}Sr
Kr	^{82}Kr	^{83}Kr	^{84}Kr		^{86}Kr		
Rb				^{85}Rb		^{87}Rb	
Ca	$^{42}\text{Ca}^{40}\text{Ar}$ $^{42}\text{Ca}^{40}\text{Ca}$	$^{43}\text{Ca}^{40}\text{Ar}$ $^{43}\text{Ca}^{40}\text{Ca}$	$^{44}\text{Ca}^{40}\text{Ar}$ $^{44}\text{Ca}^{40}\text{Ca}$ $^{42}\text{Ca}^{42}\text{Ca}$	$^{43}\text{Ca}^{42}\text{Ca}$	$^{46}\text{Ca}^{40}\text{Ar}$ $^{48}\text{Ca}^{38}\text{Ar}$ $^{46}\text{Ca}^{40}\text{Ca}$ $^{44}\text{Ca}^{42}\text{Ca}$ $^{43}\text{Ca}^{43}\text{Ca}$	$^{44}\text{Ca}^{43}\text{Ca}$	$^{48}\text{Ca}^{40}\text{Ar}$ $^{48}\text{Ca}^{40}\text{Ca}$ $^{46}\text{Ca}^{42}\text{Ca}$ $^{44}\text{Ca}^{44}\text{Ca}$

Reference Material, Beijing, and diluted in 2% HNO_3 as necessary. Commercially available cation exchange resin (AG50W-X12, H^+ form, 200–400 mesh size) was obtained from Bio-Rad (Richmond, USA). All bottled Sr-rich natural mineral drinking water used in the study was purchased commercially.

2.2. Sample preparation

All chemical preparations were conducted on special class 100 work benches inside a class 1000 clean laboratory. The seal on the bottled Sr-rich natural mineral drinking water was broken in the clean laboratory and the water acidified with concentrated nitric acid. Considering different Sr concentration (e.g. about 100–5000 $\mu\text{g L}^{-1}$) of bottled Sr-rich natural mineral water, all actual samples were diluted with 2% HNO_3 to ca. 200 $\mu\text{g L}^{-1}$ Sr concentrations for mass spectrometric direct determination. In addition, to validate the MC-ICP-MS direct analysis methods, all water samples were prepared for Sr separation using a standard cation-exchange resin.

10 mL of each sample was put into a pre-cleaned 15 mL round-bottom Savillex™ Teflon-PFA screw-top capsule and gently evaporated to dryness. One milliliter of 2.5 M HCl was added to the residue and dried down again. After cooling, the residue was dissolved in 1.5 mL of 2.5 M HCl. Prior to chemical separation the capsule was resealed and placed on a hotplate at $\sim 100^\circ\text{C}$ overnight.

The method for the separation of Sr using conventional cation exchange resin is briefly summarized here; a detailed description can be found elsewhere [19]. After centrifuging, the solution was loaded into a quartz ion exchange column packed with AG50W-X12 resin, pre-conditioned with 2 mL of 2.5 M HCl. The resin was then washed with a further 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 remove any remaining 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.

2.3. Mass spectrometric procedure

Sr isotope ratio analyses were undertaken using a Neptune MC-ICP-MS [20,21]. A summary of the typical instrumental and data acquisition parameters are presented in Table 1. The Sr isotopic data were acquired in the static, multi-collector mode at low resolution with the Faraday cups configuration array given in Table 1. During the actual Sr isotope analytical session, an aliquot of the international

standard solution of 200 $\mu\text{g L}^{-1}$ NIST SRM 987 was used regularly for optimizing the operation parameters and evaluating the reproducibility and accuracy of the instrument. One international NIST SRM 987 standard was measured proceedingly every five samples analyzed.

The actual water samples for direct determination, and the Sr fractions after chemical purification were taken up with 2% HNO_3 , and aspirated into the ICP source using a Micromist PFA nebulizer in a free aspiration mode after maximizing the signal optimization.

Prior to analysis, the Neptune MC-ICP-MS was allowed to stabilize for at least 1 h under normal operating conditions. Typically, the signal intensities of ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr for the 200 $\mu\text{g L}^{-1}$ standard solution were about 0.05, 0.93, 0.67 and 8.1 V. The actual 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 45 cycles of sample signal collection. The 45 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 between different amplifiers [22]. For Sr measurement, the signal integration time for 1 cycle was 4 s. The total time of one measurement lasted about 5 min and consumed about 50 ng of sample for each measurement. During the period of data acquisition analyses of the NIST SRM 987 standard solution yielded a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710250 ± 20 (2SD, $N = 20$).

2.4. Data reduction protocol

For radiogenic isotope systems, like Rb–Sr, Sm–Nd and Lu–Hf, the use of internal normalization for mass discrimination correction is a commonly-used practice in TIMS and MC-ICP-MS. The exponential law, which initially was developed for TIMS measurement and remains the most widely accepted and utilized with MC-ICP-MS, was also used to assess the instrumental mass discrimination in this study [17].

For Sr standard materials isotope ratios, the remaining $^{87}\text{Rb}^+$ signal was negligible so that further correction for spectral overlap of $^{87}\text{Rb}^+$ on $^{87}\text{Sr}^+$ respectively, was unnecessary. Mass discrimination correction was carried out via internal normalization to a $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194, applying the mass dependent Russell equation [17].

For Sr actual sample isotope analysis, the raw data were also exported and reduced offline in order to correct for instrumental mass bias and isobaric interference correction. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were calculated from the corrected $^{86}\text{Sr}/^{88}\text{Sr}$ ratio using exponential law,

where isobaric interference correction of ^{84}Kr and ^{86}Kr on ^{84}Sr and ^{86}Sr ($^{83}\text{Kr}/^{84}\text{Kr} = 0.20175$, $^{83}\text{Kr}/^{86}\text{Kr} = 0.66474$) and ^{87}Rb on ^{87}Sr was carried out by using $^{85}\text{Rb}/^{87}\text{Rb} = 2.5926$ ratio assuming identical mass bias for Rb and Sr. The data reduction was also performed by a computer using a self-written Excel VBA (Visual Basic for Applications) macro program, within which interference corrections is made, followed by a mass fractionation correction using the exponential law, these calculations are performed cycle by cycle [14,15].

3. Results and discussion

3.1. Isobaric interferences

3.1.1. Monoatomic interferences

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 1). After instrument optimization and prior to the analytical session, determination of potential Kr interferences in the Ar carrier is always monitored. It is particularly important to do this when a new liquid Ar tank is installed. We observed that the signal of ^{84}Kr is typically *ca.* 3–10 mV, corresponding to *ca.* 0.6–2 mV of ^{83}Kr . This decreases significantly to 0.1 mV after the aspiration of 2% HNO_3 into the ICP source. 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 [3,9,10,23,24].

The interference of ^{87}Rb on ^{87}Sr is well-known (Table 1), but is negligible for the NIST SRM 987 standard, and in most fractions of the mineral water after chemical purification. However, Rb has a highly significant effect on the direct determination the Sr isotope ratio of natural mineral drinking water without chemical purification. To assess the extent of potential isobaric interference, a series of NIST SRM 987 solutions spiked with variable amounts of Rb were analyzed. The natural isotopic composition of Rb ($^{85}\text{Rb}/^{87}\text{Rb} = 2.5926$) was used for isobaric correction by the exponential law, assuming that the

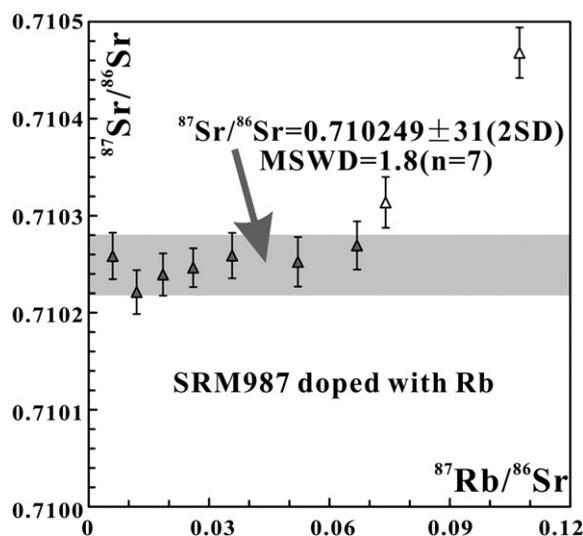


Fig. 1. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of NIST SRM 987 ($200\ \mu\text{g L}^{-1}$) doped with increasing amounts of Rb. Error bars for individual analyses are 2 S.E. (2 standard in-run errors). The isobaric interferences of ^{87}Rb on ^{87}Sr are corrected for mass discrimination by the exponential law assuming the Rb mass discrimination is the same as that of Sr. Gray triangles are used to calculate average values, while white triangles are excluded data points. Gray fields represent the $^{87}\text{Sr}/^{86}\text{Sr}$ mean value of NIST SRM987 doped with Rb and 2SD (standard deviation). The MSWD means the Mean Square of Weighted Deviates. Results indicate that highly accurate and reproducible Sr isotopic ratios can be obtained using the Neptune MC-ICP-MS, even when $^{87}\text{Rb}/^{86}\text{Sr}$ ratios range up to 0.05 (Rb/Sr *ca.* 0.015).

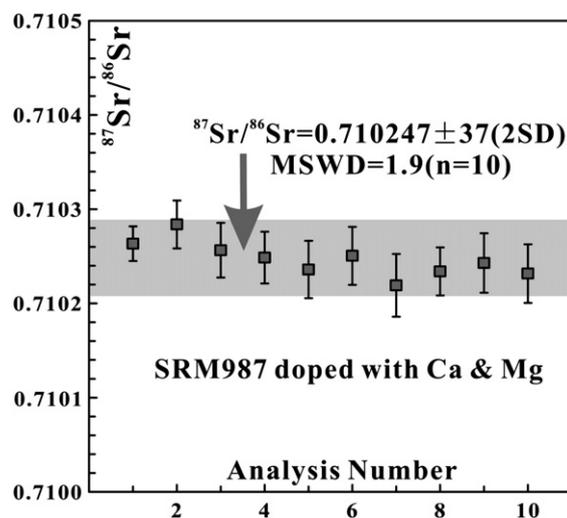


Fig. 2. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of NIST SRM 987 ($200\ \mu\text{g L}^{-1}$) doped with $200\ \mu\text{g mL}^{-1}$ Ca and $100\ \mu\text{g mL}^{-1}$ Mg. Error bars for individual analyses are 2 S.E. (2 standard in-run errors). Gray fields represent the $^{87}\text{Sr}/^{86}\text{Sr}$ mean value of NIST SRM987 doped with Ca and Mg and 2SD (standard deviation). The MSWD means the Mean Square of Weighted Deviates. The horizontal axes represent the sequence of measurements, typically with elapsed times of about 5 min between data points.

rubidium has the same mass discrimination as that of strontium [3,9,10,23,24]. As shown in Fig. 1, our seven analyses of NIST SRM 987 gave a mean value of 0.710249 ± 31 (2SD) for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, which agrees with the recommended value of 0.710248 [10,24]. From these data it was determined that for $^{87}\text{Rb}/^{86}\text{Sr}$ ratios of up to 0.05 (Rb/Sr = 0.015), the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can be effectively corrected for Rb interference by our MC-ICP-MS method, demonstrating that Rb and Sr separation is unnecessary for most Sr-rich natural mineral drinking water.

3.1.2. Polyatomic interferences

Apart from Kr and Rb, the presence of some polyatomic ions such as Ca argides and dimers result in interferences with Sr (Table 1) [23]. In mineral waters Ca is usually a major element with concentrations in the range of 5–200 $\mu\text{g mL}^{-1}$, and Ca/Sr ratio is approximately 100–200. To evaluate instrument performance a series of tests were undertaken to evaluate the Ca-related interference possibilities using $200\ \mu\text{g L}^{-1}$ NIST SRM 987 solutions doped with $200\ \mu\text{g mL}^{-1}$ Ca and $100\ \mu\text{g mL}^{-1}$ Mg standard solutions (Fig. 2). Standard Ca and Mg solutions directly introduced to the plasma were found to have a negligible Sr signal, indicating the high purity of these solutions. Following this analysis, NIST SRM 987 solutions doped with Ca and Mg were measured sequentially. As shown in Fig. 2, the ten analyses yielded a value of 0.710247 ± 37 (2SD) for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, identical to the recommended value of 0.710248 [10,24]. In contrast to Waight et al. [10] and Woodhead et al. [11], the results demonstrate that Ca argides and dimers have an insignificant influence on Sr isotope analysis using our Neptune MC-ICP-MS. The specific reasons for these differences are unknown, but are probably related to the instrumental configurations of the Neptune, relative to those of the Nu ICP-MS used by Waight et al. [10] and Woodhead et al. [11]. On the basis of these data, corrections for Ca and Mg were not applied to our data [18,24].

3.2. Matrix effects

In addition to isobarically interfering elements (Kr, Rb and Ca argides and dimers), other matrix elements, such as Mg, K, and Na, could affect Sr isotope analysis. Fig. 2, shows that Mg and Ca, have negligible effects on Sr isotope analysis. To evaluate the possible interference effects of K and Na, a series of tests were undertaken using $200\ \mu\text{g L}^{-1}$ NIST SRM 987 solutions doped with $100\ \mu\text{g mL}^{-1}$ K

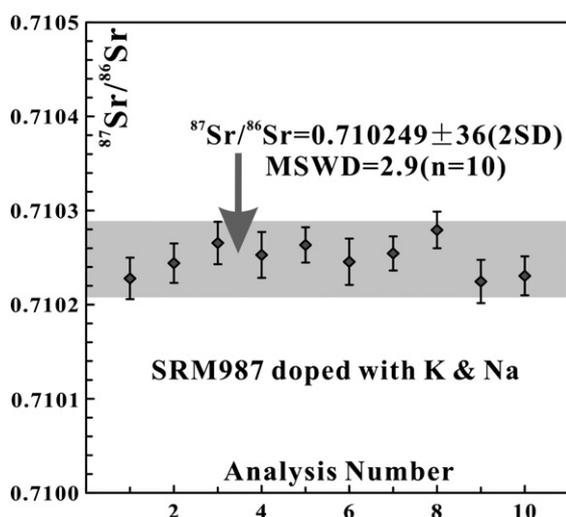


Fig. 3. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of NIST SRM 987 ($200\ \mu\text{g L}^{-1}$) doped with $100\ \mu\text{g mL}^{-1}$ K and Na. Error bars for individual analyses are 2 S.E. (2 standard in-run errors). Gray fields represent the $^{87}\text{Sr}/^{86}\text{Sr}$ mean value of NIST SRM987 doped with K and Na and 2SD (standard deviation). The MSWD means the Mean Square of Weighted Deviates. The horizontal axes represent the sequence of measurements, typically with elapsed times about 5 min between data points.

and Na standard solution. The standard K and Na solution directly introduced to the plasma has a negligible Sr signal, indicating the purity of the standard solution. The NIST SRM 987 solutions doped with K and Na were measured sequentially, as shown in Fig. 3. The ten analyses gave a value of 0.710249 ± 36 (2SD) for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, in good agreement with the recommended value of 0.710248 [10,24]. These data demonstrate that Mg, K and Na, as matrix elements, have an insignificant influence on the determination of Sr isotope ratios analysis using the Neptune MC-ICP-MS. As a result, chemical separation of these matrix elements from Sr is unnecessary, which will greatly avoid complicated and lengthy sample-preparation procedures with low cost [4–8].

Table 2

Comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of bottled Sr-rich natural mineral drinking water using MC-ICP-MS between chemical purification and by direct analysis at different analytical sessions.

Samples	Purification	Direct analysis	
	$^{87}\text{Sr}/^{86}\text{Sr}$ ($\pm 2\sigma$)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ ($\pm 2\sigma$)
N01	0.707 565 (18) ^a	0.0047 ^a 0.0049 ^b	0.707 573 (22) ^a 0.707 569 (20) ^b
N02	0.710 465 (24) ^a	0.0344 ^a 0.0339 ^b	0.710 479 (24) ^a 0.710 452 (28) ^b
N03	0.709 008 (35) ^a	0.0222 ^a	0.709 004 (36) ^a
N04	0.708 202 (31) ^a	0.0061 ^a 0.0061 ^b	0.708 214 (29) ^a 0.708 175 (24) ^b
N05	0.707 458 (26) ^a	0.0018 ^a	0.707 474 (26) ^a
N06	0.714 203 (22) ^a	0.0130 ^a	0.714 186 (22) ^a
N07	0.712 085 (25) ^a	0.0010 ^a 0.0010 ^b	0.712 084 (23) ^a 0.712 054 (20) ^b
N08	0.713 042 (27) ^a	0.0090 ^a	0.713 040 (28) ^a
N09	0.708 859 (34) ^a	0.0010 ^a 0.0010 ^b	0.708 856 (21) ^a 0.708 835 (30) ^b
N10	0.709 240 (23) ^a	0.0143 ^a	0.709 235 (16) ^a
N11	0.708 961 (19) ^a	0.0077 ^a 0.0076 ^b	0.708 956 (17) ^a 0.708 935 (24) ^b
N12	0.708 949 (19) ^a	0.0078 ^a 0.0077 ^b	0.708 962 (22) ^a 0.708 943 (24) ^b
N13	0.707 508 (19) ^a	0.0141 ^a	0.707 540 (24) ^a
N14	0.714 112 (17) ^a	0.0786 ^a	0.714 170 (29) ^a

^a Measurement at June 19, 2010.

^b Measurement at June 24, 2011.

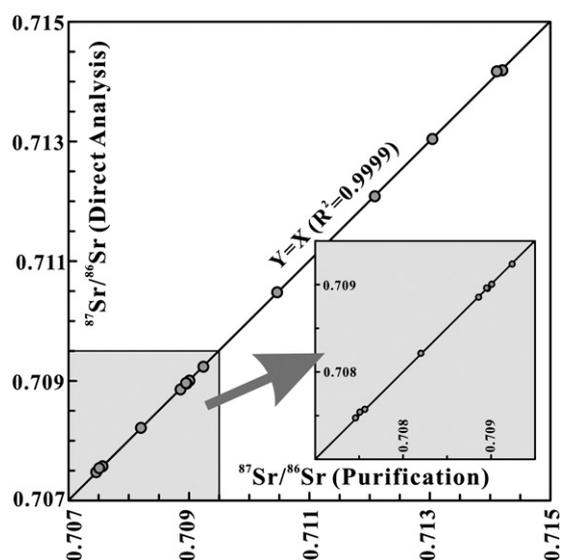


Fig. 4. Comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of bottled Sr-rich natural mineral drinking water between chemical purification and direct analysis using MC-ICP-MS. 2 S.E. error bars are significantly smaller than the symbols and not shown on this scale.

3.3. Direct measurement of bottled Sr-rich natural mineral drinking water

Fourteen bottled Sr-rich natural mineral drinking water were collected and analyzed by direct aspiration into the Neptune MC-ICP-MS (Table 2). In addition, for all samples Sr was also separated from Rb and other matrix elements using standard cation exchange resin methods and analyzed by the same MC-ICP-MS protocol. Table 2 summarizes the results obtained with and without chemical separation and clearly demonstrates agreement between the two analytical methods at different analytical sessions. As shown in Fig. 4, an excellent correlation was found between the results, without any compromise in the precision of the direct determination data. We conclude that separation of Sr from other elements is not always necessary for the analysis of Sr-rich natural-mineral drinking water.

4. Conclusion

A simple and rapid method for the direct determination of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of bottled Sr-rich natural mineral drinking water using MC-ICP-MS has been established. The accuracy of the method was assessed and evaluated by the comparative analysis of identical samples with and without chemical purification. It was demonstrated that without Rb Ca, Mg, K, and Na separation, for most bottled Sr-rich natural mineral drinking waters, direct accurate determination of their Sr isotopic ratio is possible. The method results in significant savings in sample preparation time and avoidance of any potential contamination. Therefore, the high sample throughput inherent to the MC-ICP-MS can be fully exploited.

Acknowledgments

This study was financially supported by the National Natural Science Foundation of China and Institute of Geology and Geophysics, Chinese Academy of Sciences grants 41073009, 40773008 and ZC0903 to Y.H. Yang. We are grateful for critical and constructive comments from two anonymous referees who greatly improved the draft. Valerie Dennison (Almaz Press, Thunder Bay) and Roger Mitchell (Lakehead University) are also greatly thanked for assistance with the preparation of this manuscript.

References

- [1] G. Faure, T.M. Mensing, *Isotopes: principles and applications*, 3rd ed., John Wiley & Sons, New Jersey, 2005, pp. 75–112.
- [2] G. Fortunato, K. Memic, S. Wunderli, L. Pillonel, J.O. Bosset, G. Gremaud, Application of strontium isotope abundance ratios measured by MC-ICP-MS for food authentication, *J. Anal. At. Spectrom.* 19 (2004) 227–234.
- [3] L. Balcaen, I.D. Schrijver, L. Moens, F. Vanhaecke, Determination of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio in USGS silicate reference materials by multi-collector ICP-mass spectrometry, *Int. J. Mass Spectrom.* 242 (2005) 251–255.
- [4] R.C. Capo, B.W. Stewart, O.A. Chadwick, Strontium isotopes as tracers of ecosystem processes: theory and methods, *Geoderma* 82 (1998) 197–225.
- [5] L.N. Christian, J.L. Banner, L.E. Mack, Sr isotopes as tracers of anthropogenic influences on stream water in the Austin, Texas, area, *Chem. Geol.* 282 (2011) 84–97.
- [6] P. Galler, A. Limbeck, S.F. Boulyga, G. Stingeder, T. Hirata, T. Prohaska, Development of an on-line flow injection Sr/matrix separation method for accurate, high-throughput determination of Sr isotope ratios by multiple collector inductively coupled plasma-mass spectrometry, *Anal. Chem.* 79 (2007) 5023–5029.
- [7] P. Galler, A. Limbeck, M. Uveges, T. Prohaska, Automation and miniaturization of an on-line flow injection Sr/matrix separation method for accurate, high throughput determination of Sr isotope ratios by MC-ICP-MS, *J. Anal. At. Spectrom.* 23 (2008) 1388–1391.
- [8] J. Montgomery, J.A. Evans, G. Wildman, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope composition of bottled British mineral waters for environmental and forensic purposes, *Appl. Geochem.* 21 (2006) 1626–1634.
- [9] S. Ehrlich, I. Gavrieli, L.B. Dor, L. Halicz, Direct high-precision measurements of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio in natural water, carbonates and related materials by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), *J. Anal. At. Spectrom.* 16 (2001) 1389–1392.
- [10] T. Waight, J. Baker, D. Peate, Sr isotope ratio measurements by double-focusing MC-ICPMS: techniques, observations and pitfalls, *Int. J. Mass Spectrom.* 221 (2002) 229–244.
- [11] J. Woodhead, S. Swearer, J. Hergt, R. Maas, *In situ* Sr-isotope analysis of carbonates by LA-MC-ICP-MS: interference corrections, high spatial resolution and an example from otolith studies, *J. Anal. At. Spectrom.* 20 (2005) 22–27.
- [12] L. Yang, C. Peter, U. Panne, R.E. Sturgeon, Determination of isotopic composition of Sr in fish liver tissue by MC-ICP-MS, *J. Anal. At. Spectrom.* 23 (2008) 1269–1274.
- [13] A.N. Halliday, D.C. Lee, J.N. Christensen, A.J. Walder, P.A. Freedman, C.E. Jones, C.M. Hall, W. Yi, D. Teagle, Recent developments in inductively coupled plasma magnetic sector multiple collector mass spectrometry, *Int. J. Mass Spectrom. Ion Process* 146/147 (1995) 21–33.
- [14] Y.H. Yang, Z.Y. Chu, F.Y. Wu, L.W. Xie, J.H. Yang, Precise and accurate determination of Sm, Nd concentrations and Nd isotopic compositions in geological samples by MC-ICP-MS, *J. Anal. At. Spectrom.* 26 (2011) 1237–1244.
- [15] Y.H. Yang, F.Y. Wu, L.W. Xie, Y.B. Zhang, High-precision measurements of the $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio in certified reference materials without Nd and Sm separation by multiple collector inductively coupled plasma mass spectrometry, *Anal. Lett.* 43 (2011) 142–150.
- [16] M.F. Thirlwall, R. Anczkiewicz, Multidynamic isotope ratio analysis using MC-ICP-MS and the causes of secular drift in Hf, Nd and Pb isotope ratios, *Int. J. Mass Spectrom.* 235 (2004) 59–81.
- [17] L. Yang, Accurate and precise determination of isotopic ratios by MC-ICP-MS: a review, *Mass Spectrom. Rev.* 28 (2009) 990–1011.
- [18] Y.H. Yang, F.Y. Wu, S.A. Wilde, X.M. Liu, Y.B. Zhang, L.W. Xie, J.H. Yang, *In situ* perovskite Sr–Nd isotopic constraints on petrogenesis of the Mengyin kimberlites in the North China Craton, *Chem. Geol.* 264 (2009) 24–42.
- [19] Y.H. Yang, H.F. Zhang, Z.Y. Chu, L.W. Xie, F.Y. Wu, Combined chemical separation of Lu, Hf, Rb, Sr, Sm and Nd from a single rock digest and precise and accurate isotope determinations of Lu–Hf, Rb–Sr and Sm–Nd isotope systems using Multi-Collector ICP-MS and TIMS, *Int. J. Mass Spectrom.* 290 (2010) 120–126.
- [20] S. Weyer, J.B. Schwieters, High precision Fe isotope measurements with high mass resolution MC-ICPMS, *Int. J. Mass Spectrom.* 226 (2003) 355–368.
- [21] F.Y. Wu, Y.H. Yang, L.W. Xie, J.H. Yang, P. Xu, Hf isotopic compositions of the standard zircons and baddeleyites used in U–Pb geochronology, *Chem. Geol.* 234 (2006) 105–126.
- [22] Z.Y. Chu, Y.H. Yang, G.S. Qiao, A calculation method to eliminate gain effect on isotopic measurement using the virtual amplifier multi-collector mass spectrometer, *Int. J. Mass Spectrom.* 235 (2006) 130–135.
- [23] P.Z. Vroon, B.V.D. Wagt, J.M. Koornneef, G.R. Davies, Problems in obtaining precise and accurate Sr isotope analysis from geological materials using laser ablation MC-ICP-MS, *Anal. Bioanal. Chem.* 390 (2008) 465–476.
- [24] F.C. Ramos, J.A. Wolff, D.L. Tollstrup, Measuring $^{87}\text{Sr}/^{86}\text{Sr}$ variation in minerals and groundmass from basalts using LA-MC-ICP-MS, *Chem. Geol.* 211 (2004) 135–158.