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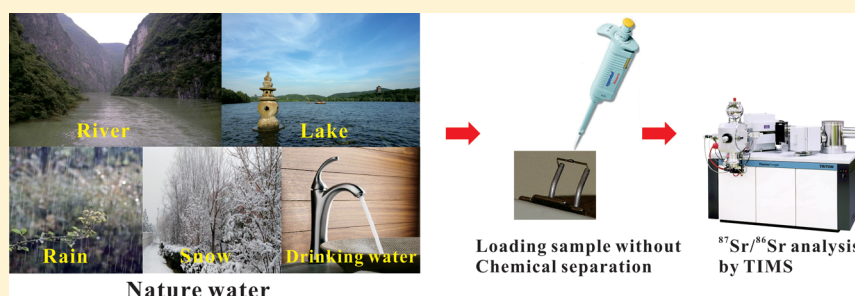
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# Direct High-Precision Measurements of the $^{87}\text{Sr}/^{86}\text{Sr}$ Isotope Ratio in Natural Water without Chemical Separation Using Thermal Ionization Mass Spectrometry Equipped with $10^{12} \Omega$ Resistors

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**ABSTRACT:** Thermal ionization mass spectrometry (TIMS) allows excellent precision for determining Sr isotope ratios in natural water samples. Traditionally, a chemical separation procedure using cation exchange resin has been employed to obtain a high purity Sr fraction from natural water, which makes sample preparation time-consuming. In this study, we present a rapid and precise method for the direct determination of the Sr isotope ratio of natural water using TIMS equipped with amplifiers with two  $10^{12} \Omega$  resistors. To eliminate the  $^{87}\text{Rb}$  isobaric interference, Re ribbons are used as filaments, providing a significant advantage over W ribbons in the inhibition of  $\text{Rb}^+$  emission, based on systematically examining a series of NIST SRM987 standard doping with various amounts of Rb using Re and W ribbons. To validate the applicability of our method, twenty-two natural water samples, including different water types (rain, snow, river, lake and drinking water), that show a large range in Sr content variations (2.54–922.8 ppb), were collected and analyzed from North and South China. Analytical results show good precision (0.003–0.005%, 2 RSE) and the method was further validated by comparative analysis of the same water with and without chemical separation. The method is simple and rapid, eliminates sample preparation time, and prevents potential contamination during complicated sample-preparation procedures. Therefore, a high sample throughput inherent to the TIMS can be fully utilized.

Sr isotopic ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) compositions are routinely measured and extensively applied in hydrochemical studies to determine sources and mixing relationships in river water, lake water, snow water, rainwater, groundwater, and drinking water.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios have proved particularly useful in determining weathering processes and quantifying end-member mixing processes.<sup>1–4</sup> However, high precision isotopic measurements better than 0.005% (2 RSE) are required when using a Sr isotopic tracer.<sup>5–7</sup> At present, thermal ionization mass spectrometry (TIMS) and (MC-ICP-MS) exhibit high accuracy, excellent sensitivity, and low memory effect, and they are regarded as benchmark techniques for Sr isotope ratio analysis. The TIMS and MC-ICP-MS techniques therefore are extensively used for tracing water chemistry.<sup>1–7</sup> Unfortunately, these aforementioned techniques generally require efficient chemical separation of Sr from the interfering rubidium ( $^{87}\text{Rb}$ ) isotope and other matrix elements in the water samples by ion exchange chromatography, such as AG50W<sup>8,9</sup> or Sr Spec resin.<sup>10,11</sup> Separation procedures using traditional methods are tedious, and sample throughput is slow. In addition, traditional

methods increase the chance of contamination from the experimental environments and cross-operation in the column chemistry because of complex operation steps. In order to obtain higher analysis efficiency for natural water samples, Ehrlich et al.<sup>5</sup> and Yang et al.<sup>6</sup> reported the direct determination of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios using MC-ICP-MS after monatomic ( $^{86}\text{Kr}^+$ ), polyatomic ( $^{48}\text{Ca}^{40}\text{Ar}^+$ ), and  $^{87}\text{Rb}$  isobaric interference corrections. Therefore, the high sample throughput inherent to MC-ICP-MS has been fully utilized to relatively high Sr concentrations (>50 ppb). However, to the best of our knowledge, no direct Sr isotope analytical protocol for natural water samples using TIMS has yet been reported in the literature. This is because the intensity and stability of the Sr signal is strongly inhibited by matrix elements (such as K, Na, Ca, and Mg), and the accuracy of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is

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Figure 1. Geographical sketch and location of the sampling stations in this study.

Table 1. Na, K, Mg, Ca, Rb, and Sr Contents in Natural Water Samples

Sample No. <sup>a</sup>	Sample location	Water type	Na (ppm)	K (ppm)	Mg (ppm)	Ca (ppm)	Rb (ppb)	Sr (ppb)
L1	Shanghai	Drinking water	50.4	2.70	10.9	46.0	2.70	267.1
L2	Hongkong	Drinking water	7.12	3.24	1.66	16.7	10.1	43.4
L3	Tianjin	Drinking water	37.9	4.72	21.2	41.7	2.27	334.5
L4	Xiameng	Drinking water	9.86	5.12	2.40	16.0	13.5	82.9
L5	Beijing	Drinking water	13.2	1.97	18.9	47.3	0.47	277.8
L6	Nanjing	Drinking water	17.3	2.42	9.23	44.0	3.28	253.2
L7	Beijing	Rain water	2.02	2.08	1.28	18.2	3.60	43.8
L8	Qinhuangdao	Rain water	1.06	0.19	0.13	1.31	0.37	7.11
L9	Datong	Rain water	0.52	0.23	0.30	2.18	0.54	12.9
L10	Xiameng	Rain water	0.22	0.22	0.08	0.71	0.46	2.54
L11	Hangzhou	Rain water	16.3	9.05	2.60	41.1	12.9	141.1
L12	Hangzhou	Lake water	9.33	2.09	2.51	29.7	3.24	94.3
L13	Yangzhou	Lake water	42.8	4.84	13.1	39.7	1.69	294.2
L14	Datong	Snow water	1.19	0.58	0.66	2.68	1.92	25.2
L15	Beijing	Snow water	1.43	2.99	0.68	3.91	2.29	41.5
L16	Yichang	River water	11.3	1.54	7.66	42.1	0.99	245.6
L17	Nanjing	River water	19.0	2.86	9.38	46.8	3.41	244.7
L18	Shishou	River water	14.6	1.73	9.12	43.4	1.62	266.5
L19	Zhengzhou	River water	90.6	4.12	26.6	45.3	0.81	896.7
L20	Kaifeng	River water	93.1	4.17	26.7	42.0	0.64	922.8
L21	Jinan	River water	93.2	4.25	26.4	60.2	0.56	881.7
L22	Guilin	River water	6.89	2.33	2.40	39.4	3.85	52.4

<sup>a</sup>Note: L16, L17, and L18 were collected from the Changjiang River. L19, L20, and L21 were collected from the Yellow River. L22 was collected from the Lijiang River. L12 and L13 were collected from West Lake in Hangzhou city and from Slender west Lake in Yangzhou, respectively.

significantly affected by  $^{87}\text{Rb}$  isobaric interference. The key for direct measurements of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in natural water is to improve instrumental sensitivity and reduce the  $^{87}\text{Rb}$  isobaric interference. Recently, the use of a new design of current amplifiers equipped with  $10^{12} \Omega$  feedback resistors in TIMS has provided good applications in high-precision isotopic analysis

using small beam sizes, such as  $\text{S}$ ,  $^{12}\text{Hf}$ ,  $^{13}\text{Sr}$ ,  $^{14,15}\text{Nd}$ ,  $^{14-16}\text{Pb}$ .<sup>13,17</sup> Compared with the default  $10^{11} \Omega$  resistors,  $10^{12} \Omega$  amplifiers theoretically result in a three times higher signal-to-noise ratio.<sup>14,16,18</sup> For signal intensities lower than 100 mV, analysis using  $10^{12} \Omega$  resistors is more precise.<sup>14</sup> These improvements provided the impetus to test the feasibility of

directly determining the Sr isotope ratio of natural water samples using TIMS.

In this study, the analytical performances of TIMS employing the new amplifiers with two  $10^{12} \Omega$  resistors and three  $10^{11} \Omega$  resistors are systematically examined to directly determine the Sr isotope ratios of natural water samples.  $^{87}\text{Rb}$  isobaric interference is eliminated using Re ribbon as the filament material rather than W ribbon. The  $^{85}\text{Rb}/^{86}\text{Sr}$  ratios of all natural water samples are lower than 0.00008 when Re filaments are used, indicating negligible  $^{87}\text{Rb}$  isobaric interference. The application of new amplifiers ensures high precision and accuracy for Sr isotope determination. To demonstrate the applicability of this method, twenty-two natural water samples (rain, snow, river, lake, and drinking water), collected from North and South China (see Figure 1 for sample locations) and encompassing an extensive range of natural water chemical compositions and Sr analyte concentrations (2.54–922.8 ppb), were analyzed.

## EXPERIMENTAL SECTION

**Reagents, Chemicals Materials and Standards.** Re and W ribbons: 0.035 mm thick, 0.77 mm wide and 99.98% pure, H.Cross Company.

**Table 2. Cup Setting of the Static Multicollector Mode in Triton Plus TIMS**

Element	L2	L1	CC	H1	H2
Sr	$^{84}\text{Sr}$	$^{85}\text{Rb}$	$^{86}\text{Sr}$	$^{87}\text{Sr}$	$^{88}\text{Sr}$
Amp1 ( $\Omega$ )	$10^{11}$	$10^{11}$	$10^{11}$	$10^{11}$	$10^{11}$
Amp2 ( $\Omega$ )	$10^{11}$	$10^{11}$	$10^{12}$	$10^{12}$	$10^{11}$

**Resin.** Commercially available Sr Spec resin (100–150  $\mu\text{m}$ ) was obtained from Eichrom company.

**Column.** The cation-exchange polypropylene column was 5 cm long and had a 2 mm internal diameter and 1 mL reservoir. The column was packed with 0.25 mL of Sr Spec resin.

**Natural water samples.** Rain water, snow, drinking water, lake water and river water samples were filtered through 0.45  $\mu\text{m}$  Millipore membrane filters using precleaned Nalgene filter apparatus and stored in precleaned polyethylene bottles for Sr isotope analysis.

**Labware.** The labware used included 3.0 and 7.0 mL PFA Teflon vials with screw top lids (Savillex Corporation, USA). These vials were used for solution collection, and evaporation and cleaned prior to use with a degreasing agent followed by sequential washing in AR grade  $\text{HNO}_3$ ,  $\text{HCl}$ , and ultrapure  $\text{H}_2\text{O}$ .

**Standard solutions.** A stock solution of 2 ppm of Sr was gravimetrically prepared to monitor the Triton Plus TIMS using NIST SRM-987 reference materials. The Rb, Mg, Ca, K, and Na standard solutions (1000 ppm) were obtained from the National Research Center for Certified Reference Material, Beijing, China, and diluted in 2%  $\text{HNO}_3$  as necessary.

**Water Chemistry Composition Measurements.** To obtain the optimal sample loading conditions, the contents of K, Na, Ca, Mg, Rb, and Sr were predetermined before loading sample. Major cation (K, Na, Ca and Mg) contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES Thermo IRIS Intrepid II). The contents of Sr and Rb were measured by the isotope dilution method using a Triton Plus TIMS following the method as reported by Yang et al.<sup>8</sup> As shown in Table 1, the water

chemical compositions and Rb and Sr contents of the natural water samples exhibited large variations.

**Sample Loading.** The single Re filament geometries were used to obtain  $\text{Sr}^+$  ion beams. As shown in Table 1, the Sr content in natural water samples exhibited large variations. Approximately 2.2–1575  $\mu\text{L}$  of natural water, depending on the Sr concentration, was evaporated in precleaned PFA vials. Approximately 2–4 ng of Sr from each water sample was loaded onto the Re filament. First, 1  $\mu\text{L}$  of 0.2 M phosphoric acid and  $\text{TaF}_5$  solution was loaded onto a degassed Re filament and dried at 0.8 A. Sr samples then were dissolved and loaded in 1  $\mu\text{L}$  of 2 M  $\text{HCl}$  and dried at 0.8 A. Finally, after loading and drying 1  $\mu\text{L}$  of  $\text{TaF}_5$  solution, the filaments were heated to a dull red glow at 2.2 A for 4 s. Loading blank was 0.6–1.1 pg for Sr, determined by isotope dilution by loading 5  $\mu\text{L}$  of pure  $^{84}\text{Sr}$  spike.

**Thermal Ionization Mass Spectrometry Analysis.** Sr isotope compositions were measured using a Triton Plus TIMS (Thermo Fisher Scientific) at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS) in Beijing, China. All Sr data were acquired in static multicollection mode. The collector array is shown in Table 2.

The optimized ionization temperature is 500–600  $^\circ\text{C}$  for Rb and 1250–1450  $^\circ\text{C}$  for Sr in TIMS measurements. Hence, as to minor Rb that coexisted in the Sr fraction is easily burned off using a warm up procedure (90–120 s at 1100–1150  $^\circ\text{C}$ ) prior to starting Sr measurements, due to the huge temperature gap between evaporation at Sr and Rb.

For Sr isotope ratio measurements, the filament was heated at 500 mA/min until the  $^{86}\text{Sr}$  signal reached approximately 5 mV. The beam was centered and roughly focused, and the filament was slowly heated to obtain a signal of approximately 50 mV for  $^{86}\text{Sr}$ . During direct measurement of the Sr isotope in natural water, the actual signal intensity can be kept stable at a relatively low level (60–90 mV) as a result of the matrix effect on Sr signal sensitivity. Thus, all measurements are conducted using Amp2 cup configuration containing two  $10^{12} \Omega$  resistors, as shown in Table 2. The connection scheme between the amplifiers and Faraday cups is software controlled and the gain calibration of the  $10^{12} \Omega$  and  $10^{11} \Omega$  current amplifiers is performed by software configuration at the start of each day. Before data acquisition, a peak-center routine was run. The baseline was then measured by deflecting the beams using the x-symmetry lens. Afterward, the baselines were measured every three blocks. Data acquisition began when the signal intensity of  $^{86}\text{Sr}$  reached approximately 65 mV. The typical intensity of  $^{86}\text{Sr}$  was approximately 70 mV during data acquisition. The measurement run consisted of 20 blocks of data with 20 cycles per block. The integration time per cycle was 4 s. Before mass fractionation correction, the  $^{87}\text{Sr}$  signal intensity was corrected for the potential interference caused by the remaining isobaric overlap of  $^{87}\text{Rb}$  on  $^{87}\text{Sr}$  using a  $^{87}\text{Rb}/^{85}\text{Rb}$  value of 0.385041.<sup>11</sup> After implementing the rapid sample warming program (90–120 s) at 1100–1150  $^\circ\text{C}$ , the  $^{85}\text{Rb}/^{86}\text{Sr}$  ratios obtained during natural water sample analysis were  $\leq 8 \times 10^{-5}$ , indicating negligible isobaric interferences. Finally, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio data were normalized to  $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$  for mass fractionation correction using the exponential law. Most data were obtained at an internal precision of  $\leq 0.000030$  (2 SE). The total time of one measurement lasted approximately 45 min and consumed 2–4 ng of Sr for each measurement. NIST SRM-987 standard was analyzed during the sample measurement period to monitor instrument status. The NIST SRM-987 standard

gave a mean  $^{87}\text{Sr}/^{86}\text{Sr}$  of  $0.710245 \pm 18$  (2 SD,  $n = 8$ ), showing good agreement with previously reported values.<sup>5–13,16,17</sup>

## RESULTS AND DISCUSSION

**Rb Isobaric Interference Evaluation and the Choice of Filament Materials.** It is well-known that the interference of

**Table 3.** Measured  $^{87}\text{Sr}/^{86}\text{Sr}$  Ratios of NIST SRM987 (2 ng) Doped with Various Sample Sizes of Rb

Sample No.	$^{87}\text{Sr}/^{86}\text{Sr}$	2 SE	Doped Rb (ng)
RS-1	0.710263	0.000011	0.2
RS-2	0.710271	0.000012	0.4
RS-3	0.710249	0.000015	0.8
RS-4	0.710260	0.000012	1
RS-5	0.710244	0.000013	2
RS-6	0.710254	0.000014	4
RS-7	0.710269	0.000011	8
RS-8	0.710235	0.000013	10
RS-9	0.710244	0.000013	16
Mean $\pm$ 2 SD	0.710254	0.000024	

**Table 4.** Measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of NIST SRM987 (2 ng) doped with various sample sizes (800, 1200, and 1600 ng) of Ca, Mg, K, Na, respectively

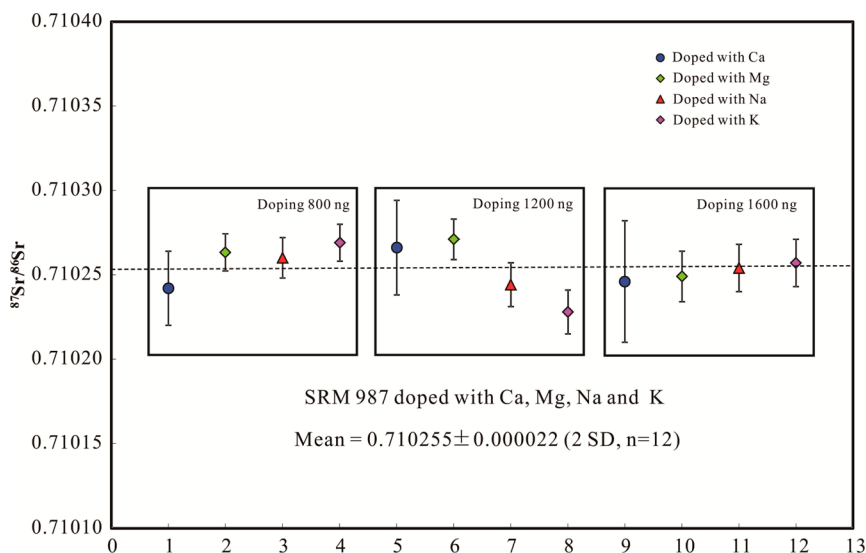
Sample No.	$^{87}\text{Sr}/^{86}\text{Sr}$	2 SE	Doped elements
Ca-1	0.710242	0.000022	Ca 800 ng
Ca-2	0.710266	0.000028	Ca 1200 ng
Ca-3	0.710246	0.000036	Ca 1600 ng
Mg-1	0.710263	0.000011	Mg 800 ng
Mg-2	0.710271	0.000012	Mg 1200 ng
Mg-3	0.710249	0.000015	Mg 1600 ng
Na-1	0.710260	0.000012	Na 800 ng
Na-2	0.710244	0.000013	Na 1200 ng
Na-3	0.710254	0.000014	Na 1600 ng
K-1	0.710269	0.000011	K 800 ng
K-2	0.710235	0.000013	K 1200 ng
K-3	0.710257	0.000014	K 1600 ng

$^{87}\text{Rb}$  on  $^{87}\text{Sr}$  directly affects  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio measurements. If the sample is purified by column chemistry,<sup>8–11</sup> the effect of  $^{87}\text{Rb}$  is negligible for purified samples because the  $^{85}\text{Rb}/^{86}\text{Sr}$  value is always lower than 0.00006. However, using our direct determination method without any chemical purification, Rb has a potentially significant effect on the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio measurements in natural water. In previous investigations, analysts obtained the optimal ionization efficiency of Sr using Re or W ribbon materials which showed excellent performance to enhance Sr ionization, especially for small sample sizes ( $\leq 10$  ng).<sup>11,14,15,19–21</sup> Considering that the analytes show high purity after chemical purification, few analysts have investigated what material showed the stronger inhibitory emission of  $\text{Rb}^+$  during Sr isotope measurement.

A series of NIST SRM 987 solutions (2 ppm) doped with various amounts of Rb were loaded onto the single Re and W filaments and analyzed to check which exerts the better inhibitory effect on  $\text{Rb}^+$  emission. We conducted all Rb interference evaluation experiments using  $10^{11} \Omega$  resistors (Amp1 cup setting) rather than  $10^{12} \Omega$  resistors (Amp2 cup setting) because no matrix elements inhibit the Sr signal and the intensity of  $^{86}\text{Sr}$  is high ( $\geq 500$  mV) and stable.

We observed the signal intensity of  $^{85}\text{Rb}$  was strong ( $\geq 2$  mV) and lasted for a long time with stable emission after filament warming even when a small sample size of Rb (1 ng) was loaded onto a single W filament. By contrast, no Rb signal after filament warming was detected even when a large sample size of Rb (16 ng) was loaded on the single Re filament. As shown in Table 3, nine measurements of  $^{87}\text{Sr}/^{86}\text{Sr}$  from the mixed NIST SRM 987 solutions, doped with various amounts of Rb using a Re filament, yielded a value of  $0.710254 \pm 0.000024$  (2 SD), which agreed with the recommended values of 0.710235–0.710260.<sup>6–12,15,16</sup> Thus, the measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for these mixed NIST SRM987 solutions can be effectively corrected for Rb interference by TIMS. These experiments indicate that a Re filament is the best material for direct Sr isotope measurement of nature water. The Re ribbon results in excellent sensitivity for  $\text{Sr}^+$  and strong inhibition for  $\text{Rb}^+$ .

The Rb/Sr ratios of most natural water samples are never higher than 1.0. Thus, the Rb loading size should not exceed 4



**Figure 2.** Measured Sr isotope ratios of NIST SRM 987 (2 ng) doped with different K, Na, Ca, and Mg loading sizes.



Table 5. Comparison of Sr Ratios of Natural Water between Chemical Purification and Direct Analysis

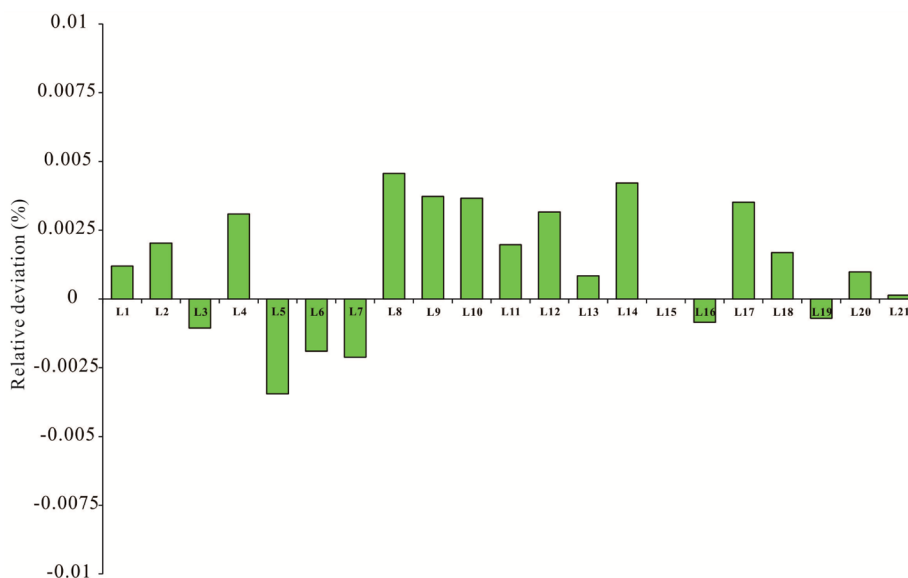
Sample No. <sup>a</sup>	Direct analysis		Analysis after purification		Sample No. <sup>a</sup>	Direct analysis		Analysis after purification	
	<sup>87</sup> Sr/ <sup>86</sup> Sr	2 SE	<sup>87</sup> Sr/ <sup>86</sup> Sr	2 SE		<sup>87</sup> Sr/ <sup>86</sup> Sr	2 SE	<sup>87</sup> Sr/ <sup>86</sup> Sr	2 SE
L1a	0.710458	0.000026	0.710461	0.000011	L14a	0.711176	0.000022	0.711143	0.000012
L1b	0.710481	0.000031			L14b	0.711170	0.000022		
Mean	0.710470				Mean	0.711173			
L2a	0.713853	0.000026	0.713861	0.000011	L15a	0.709026	0.000022	0.709037	0.000012
L2b	0.713898	0.000034			L15b	0.709047	0.000022		
Mean	0.713876				Mean	0.709037			
L3a	0.710442	0.000022	0.710445	0.000011	L16a	0.710377	0.000033	0.710393	0.000011
L3b	0.710433	0.000026			L16b	0.710396	0.000031		
Mean	0.710438				Mean	0.710387			
L4a	0.711672	0.000024	0.711653	0.000011	L17a	0.710469	0.000023	0.710470	0.000010
L4b	0.711678	0.000027			L17b	0.710505	0.000024		
Mean	0.711675				L17-6 ng	0.710510	0.000026		
L5a	0.710543	0.000022	0.710547	0.000011	L17-8 ng	0.710501	0.000030		
L5b	0.710502	0.000024			L17-10 ng	0.710492	0.000036		
Mean	0.710523				Mean	0.710495			
L6a	0.710449	0.000025	0.710480	0.000010	L18a	0.710347	0.000033	0.710357	0.000009
L6b	0.710484	0.000028			L18b	0.710390	0.000022		
Mean	0.710467				Mean	0.710369			
L7a	0.709370	0.000025	0.709395	0.000009	L19a	0.711266	0.000025	0.711267	0.000012
L7b	0.709390	0.000033			L19b	0.711258	0.000020		
Mean	0.709380				Mean	0.711262			
L8a	0.711769	0.000030	0.711758	0.000010	L20a	0.711242	0.000024	0.711256	0.000013
L8b	0.711772	0.000026			L20b	0.711255	0.000021		
Mean	0.711771				L20-3	0.711262	0.000022		
L9a	0.710877	0.000026	0.710831	0.000011	L20-4	0.711287	0.000022		
L9b	0.710838	0.000026			L20-5	0.711273	0.000022		
Mean	0.710858				L20-6	0.711249	0.000022		
L10a	0.710648	0.000024	0.710626	0.000011	L20-7	0.711255	0.000026		
L10b	0.710656	0.000032			L20-8	0.711260	0.000022		
Mean	0.710652				L20-9	0.711275	0.000022		
L11a	0.710131	0.000034	0.710122	0.000011	L20-10	0.711269	0.000022		
L11b	0.710121	0.000032			Mean ±2 SD	0.711263	0.000027		
Mean	0.710126								
L12a	0.711202	0.000030	0.711192	0.000011	L21a	0.711290	0.000026	0.711254	0.000010
L12b	0.711227	0.000025			L21b	0.711220	0.000020		
Mean	0.711215				Mean	0.711255			
L13a	0.711552	0.000024	0.711526	0.000012	L22a	0.711921	0.000049	0.711869	0.000011
L13b	0.711512	0.000024			L22b	0.711913	0.000086		
Mean	0.711532				Mean	0.711917			

<sup>a</sup>Note: a and b marked in each water sample represent loading amounts of 2 ng and 4 ng, respectively. The sample size in L20-3 to L20-10 is 2 ng.

ng because the maximum Sr loading size is 4 ng in this study. As shown in Table 1, all Rb/Sr ratios are lower than 0.23 and the actual Rb loading size is never higher than 1 ng. During direct measurement of Sr isotope of natural water, all <sup>85</sup>Rb/<sup>86</sup>Sr ratios are lower than 0.00008, which indicates that Rb and Sr separation by cation resin exchange column is unnecessary for natural water.

**Evaluation of Matrix Elements Interference.** Ca, Mg, Na, and K are the major matrix elements in natural water and cause severe suppression of the signal intensity of Sr and unstable ion beam emission. Thus, the interference from matrix elements must be carefully examined to obtain the optimal measurement conditions. To evaluate which element exerts the most severe signal suppression for Sr, as shown in Table 4, we prepared a series of 2 ppm of NIST SRM 987 solutions doped with various amounts of Ca, Mg, Na, and K. These mixed solution samples, containing 2 ng NIST SRM987 doped with various sample sizes (800, 1200, and 1600 ng) of Ca, Mg, Na,

and K, were evaporated to dryness and loaded onto the single Re filaments. We found the matrix effects from Mg, K, and Na are obviously less than that from Ca at the same sample loading size. In mixtures doped with K, Mg, and Na, the signal intensity of <sup>88</sup>Sr is stable and high ( $\geq 2.8$  V). Thus, we measured these samples employing the  $10^{11}$   $\Omega$  resistor (Amp1 cup setting) rather than the  $10^{12}$   $\Omega$  resistor (Amp2 cup setting). However, in mixtures doped with Ca, the signal intensity of Sr is obviously suppressed with increasing the amount of Ca from 800 ng to 1600 ng. In particular, the signal intensity of <sup>88</sup>Sr in the sample doped with 1600 ng of Ca is maintained between 370 and 480 mV, and only 320 cycles could be collected. Thus, the internal precision of <sup>87</sup>Sr/<sup>86</sup>Sr is worse than 35 ppm. This phenomenon indicates that the method is unsuitable for water samples with high Ca/Sr ratios. As shown in Table 4 and Figure 2, most of the mixed solution samples give good precision ( $\leq 0.004\%$ , 2 RSE) and accuracy, except for the sample doped with 1600 ng of Ca.



**Figure 3.** Comparison of  $^{87}\text{Sr}/^{86}\text{Sr}$  values of natural water samples between chemical purification and direct analysis, except for L22, because of bad internal precision for the unpurified sample. Relative Deviation (%) =  $(\text{The mean value of } ^{87}\text{Sr}/^{86}\text{Sr}_{\text{unpurified}} - ^{87}\text{Sr}/^{86}\text{Sr}_{\text{purified}}) / ^{87}\text{Sr}/^{86}\text{Sr}_{\text{purified}} \times 100\%$ .

In spite of performing sufficient preanalysis evaluation of the artificial samples, simulating the matrix compositions of all natural water samples is difficult because different water types exhibit significant differences in water chemistry. In the following section, we employ natural water samples to further check the actual matrix effects during Sr isotope measurements.

**Ideal Sample Loading Size for Sr Direct Measurements.** Compared with the  $10^{11} \Omega$  resistor system, the  $10^{12} \Omega$  resistor can provide more precise data, especially for small signal measurements, because the  $10^{12} \Omega$  resistor has a better signal-to-noise ratio.<sup>14–18</sup> However, because matrix elements can strongly inhibit the Sr signal, increasing the amount of sample that is loaded will result in stronger inhibition of the Sr signal. Thus, investigating the optimized sample loading size for Sr analysis is important. In the present study, half of the samples of natural water come from river samples. A Changjiang River sample (L17) from Nanjing, with a relatively high Ca content, was employed to verify Sr isotope ratio precision under different sample loading sizes (2–10 ng). As shown in Table 5, the internal precision of the Sr isotope ratio for L17 fluctuates from 22 to 30 ppm when the Sr loading size is smaller than 8 ng. Data precision shows obvious deterioration from 30 to 36 ppm when the Sr sample size exceeds 8 ng. These findings indicate that the Sr sample loading size must be smaller than 8 ng. During measurements, a more stable signal of  $^{86}\text{Sr}$  (60–75 mV) can be achieved when the sample size is 2–4 ng. For a complex natural water system, it is therefore unwise to load too much sample because of the strong matrix inhibition effects. For samples with high Ca/Sr ratio, the  $^{87}\text{Sr}/^{86}\text{Sr}$  precision exhibits significant deterioration with the increase in sample size, such as L22 in Table 5. Based on Table 5, we recommended the maximum loading amount of Ca in the filaments should be less than 1500 ng. Thus, in this study, we conducted all measurements with Sr sample size of 2 ng and 4 ng for each natural water sample to reduce the matrix effect. Most samples show good data precision ( $\leq 30$  ppm, 2 SE), indicating the 2–4 ng sample size may be suitable for most water samples. For most Sr isotope applications in hydrochemical studies, the basic water chemical compositional data and Sr element contents are usually indispensable and

measured preferentially by ICP-MS or ICP-OES. Thus, calculating the amount of water needed to conduct direct Sr isotope measurements using TIMS is easy.

**Sr Isotopic Data for Natural Water Samples.** To assess the analytical reproducibility and feasibility of direct analysis, twenty-two natural water samples were determined using Triton Plus by Amp2 cup configurations containing two  $10^{12} \Omega$  resistors. The typical intensity of  $^{86}\text{Sr}$  is approximately 65–80 mV. As shown in Table 1 and Figure 1, these samples covered different water types (river, lake, rain, snow, and drinking water) and were obtained widely across China. As shown in Table 5, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of all analyzed natural water samples were obtained with an internal precision better than 0.000033 (2 SE); except for L22, with a high Ca/Sr ratio ( $\sim 752$ ), most internal precision was better than 0.000028 (2 SE). Based on L22 data and the matrix interference evaluation discussed above, the proposed method is unsuitable for those samples with high Ca/Sr ratios ( $\geq 700$ ). To further verify the reliability of our method, all water samples were also purified using the Sr Spec resin method.<sup>19</sup> All samples with high purity Sr were measured using the same Triton Plus TIMS with the Amp1 cup setting. The typical intensity of  $^{86}\text{Sr}$  is approximately 500–600 mV for these purified samples. As indicated in Table 5 and Figure 3, the results obtained with and without chemical separation clearly demonstrate good agreement within analytical error.

The reproducibility of our procedure was validated by ten different runs of a Yellow River sample (L20) from Kaifeng city without chemical separation. As shown in Table 5, ten replicate measurements of L20 yielded a  $^{87}\text{Sr}/^{86}\text{Sr}$  value of  $0.701263 \pm 0.000027$  (2 SD) which is consistent with the purified data  $0.701256 \pm 0.000013$ . The external reproducibility of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of L20 was better than  $\pm 0.000027$  (2 SD). In general, the data reproducibility and precision of the proposed method are satisfactory and completely fit the demands of geochemical tracing in natural water.

**Merits and Limitations.** This method shows significant improvements in analytical efficiency compared with previous protocols.<sup>1–4,9</sup> This improvement is time saving and results in low experimental costs. First, it is not necessary to conduct

complex chemical separation procedures. Thus, it is time-saving. In addition, potential cross-contamination risks are eliminated during chemical separation. Second, the analytical cost is significantly reduced. Considering that no chemical separation is performed, relevant experimental resources are saved such as the purchase of expensive resin materials and reagents.

Despite its suitability for application to most natural water samples, the proposed method suffers two limitations. First, applying the method to all natural water samples is impossible because water chemical compositions are complex in nature. The method is unsuitable for samples with Ca/Sr values higher than 700 because strong matrix effects lead to low Sr signal intensity and poor precision. Second, the precision (0.003%~0.005%, 2 RSE) of  $^{87}\text{Sr}/^{86}\text{Sr}$  is less than that of the traditional method (0.001%~0.003%, 2 RSE) after Sr chemical separation.

## CONCLUSIONS

A direct determination method using TIMS has been developed for measuring  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios in natural water samples. The proposed method achieves high precision Sr isotope data (0.003%~0.005%, 2 RSE). The feasibility of the method was validated using a series of natural water samples collected across China, thus covering a wide distribution and different types of water. With the new protocol, the bottleneck and cost associated with sample preparation prior to TIMS measurements can be significantly reduced.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Shand, P.; Darbyshire, D. P. F.; Love, A. J.; Edmunds, W. M. *Appl. Geochem.* **2009**, *24*, 574–586.
- (2) Frost, C. D.; Toner, R. N. *Ground Water*. **2004**, *42*, 418–432.
- (3) Semhi, K.; Clauer, N.; Probst, J. L. *Chem. Geol.* **2000**, *168*, 173–193.
- (4) Palmer, M. R.; Edmond, J. M. *Geochim. Cosmochim. Acta* **1992**, *56*, 2099–2111.
- (5) Ehrlich, S.; Gavrieli, I.; Dor, L. B.; Halicz, L. J. *Anal. At. Spectrom.* **2001**, *16*, 1389–1392.
- (6) Yang, Y. H.; Wu, F. Y.; Xie, L. W.; Yang, J. H.; Zhang, Y. B. *Spectrochim. Acta Part B* **2011**, *66*, 656–660.
- (7) Brach-Papa, C.; Bockstaele, M.; Van Ponzevera, E.; Quételet, C. R. *Spectrochim. Acta Part B* **2009**, *64*, 229–234.
- (8) Yang, Y. H.; Zhang, H. F.; Chu, Z. Y.; Xie, L. W.; Wu, F. Y. *Int. J. Mass Spectrom.* **2010**, *290*, 120–126.
- (9) Li, C. F.; Li, X. H.; Li, Q. L.; Guo, J. H.; Li, X. H.; Yang, Y. H. *Anal. Chim. Acta* **2012**, *727*, 54–60.
- (10) Deniel, C.; Pin, C. *Anal. Chim. Acta* **2001**, *426*, 95–103.
- (11) Charlie, B. L. A.; Ginibre, C.; Morgan, D.; Nowell, G. M.; Pearson, D. G.; Davidson, J. P.; Ottley, C. J. *Chem. Geol.* **2006**, *32*, 114–133.
- (12) Makishima, A.; Nakamura, E. J. *Anal. At. Spectrom.* **2012**, *27*, 891–895.
- (13) Makishima, A.; Nakamura, E. J. *Anal. At. Spectrom.* **2010**, *25*, 1712–1716.
- (14) Koornneef, J. M.; Boumanb, C.; Schwietersb, J. B.; Davies, G. R. *Anal. Chim. Acta* **2014**, *819*, 49–55.
- (15) Koornneef, J. M.; Boumanb, C.; Schwietersb, J. B.; Davies, G. R. *J. Anal. At. Spectrom.* **2013**, *28*, 749–754.
- (16) Chu, Z. Y.; Li, C. F.; Hegner, E.; Chen, Z.; Yan, Y.; Guo, J. H. *Anal. Chem.* **2014**, *86*, 11141–11150.
- (17) Sarkar, C.; Pearson, D. G.; Heaman, L. M.; Woodland, S. J. *Chem. Geol.* **2015**, *395*, 27–40.
- (18) Wieser, M. E.; Schwieters, J. B. *Int. J. Mass Spectrom.* **2005**, *242*, 97–115.
- (19) Li, Q. L.; Chen, F. K.; Wang, X. L.; Li, X. H.; Li, C. F. *Chin. Sci. Bull.* **2005**, *50*, 2861–2865.
- (20) Liu, T.; Li, C. F.; Lin, Y. T. *Meteoritics & Planetary Sci.* **2011**, *46*, 681–689.
- (21) Misawa, K.; Yamazaki, Y.; Ihira, N.; Nakamura, N. *Geochem. J.* **2000**, *34*, 11–21.