# Precise and accurate analysis of deep and surface seawater Sr stable isotopic composition by double-spike thermal ionization mass spectrometry

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This paper describes an analytical technique for highly precise and accurate determination of radiogenic and stable Sr isotopic composition using double-spike thermal ionization mass spectrometry. Repeated analyses of the in-house isotopic reference Wako-9999 against NIST SRM-987 gave an average $\delta^{88}$Sr of +0.32‰, with a long-term 2 SD external reproducibility of ±0.02‰ ($n = 15$). Detailed evaluation of the Sr isotope fractionation behavior during a column chromatographic Sr separation process using Sr spec resin showed systematic variation of $\delta^{88}$Sr in the eluate, from +1.05‰ to –0.64‰, as the Sr elution progressed. The Sr isotope fractionation factor between the Sr spec resin and 0.05M $HNO_3$ was estimated as 0.999947 ± 0.000001. During the chemical separation procedure, a very small amount of Sr with a highly fractionated isotopic composition was found to be lost in the sample loading and purification stage prior to Sr collection. This may cause a small but significant systematic mass bias in high-precision non-double-spike analyses. The analysis of 11 seawater samples from the Pacific and Atlantic oceans, including four deep seawater samples taken below the carbonate compensation depth (CCD) in the North Pacific Ocean, gave consistent results, with an average $\delta^{88}$Sr of 0.407 ± 0.012‰ (2 SD). All analyzed data agreed with literature values, demonstrating the accuracy of the stable Sr analysis in this study. The $\delta^{88}$Sr values of deep seawater, which were consistent with those of surface water, showed that seawater stable Sr isotopic composition is homogeneous to depths below the CCD.

Keywords: double-spike TIMS, Sr isotope fractionation, seawater Sr isotopes, column chromatography, non-traditional isotope geochemistry

## INTRODUCTION

The Rb-Sr isotope system is a major long-lived radioactive decay system applied in earth and planetary sciences. The $^{87}$Sr/$^{86}$Sr ratio is widely used as a dating tool and an isotopic tracer to investigate petrogenesis of rocks across various geological settings and timescales. In the analysis of the $^{87}$Sr/$^{86}$Sr ratio, it has long been assumed that isotope fractionation in terms of stable $^{88}$Sr/$^{86}$Sr ratio in terrestrial environments is negligible and that the $^{88}$Sr/$^{86}$Sr ratio is as a constant (Steiger and Jäger, 1977). The discussion on natural Sr isotope fractionation ($^{88}$Sr/$^{86}$Sr) has been limited to CAIs and chondrules from primitive meteorites, which show large stable Sr isotope variation up to 3 permil (Patchett, 1980a, b; Moynier et al., 2010). However, recent advances in mass spectrometric techniques have revealed the existence of sub-permil-order heterogeneity in $\delta^{88}$Sr (the relative $^{88}$Sr/$^{86}$Sr ratio against standard material in parts per thousand) across various terrestrial samples (Fietzke and Eisenhauer, 2006; Ohno and Hirata, 2007; Ohno et al., 2008; Halicz et al., 2008; Charlier et al., 2012). Temperature-dependent stable Sr isotope fractionation has been documented for both inorganic and biogenic carbonate formation processes (Fietzke and Eisenhauer, 2006; Rüggeberg et al., 2008; Böhm et al., 2012). Strontium isotope fractionation behavior has also been studied for chemical weathering processes (de Souza et al., 2010; Wei et al., 2013). These studies demonstrate that $\delta^{88}$Sr can be used as a tracer to investigate various geochemical processes. Combined use of the $^{87}$Sr/$^{86}$Sr ratio and stable $\delta^{88}$Sr allows the evaluation of both the source and the process; thus, it may be a powerful geochemical tool for investigating global-scale Sr cycling such as marine Sr cycling (Krabbenhöft et al., 2010).

Two mass spectrometric techniques, multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) and double-spike thermal ionization mass

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spectrometry (DS-TIMS), has been applied to simultaneously analyze the radiogenic and stable Sr isotope ratios (Fietzke and Eisenhauer, 2006; Ohno and Hirata, 2007; Krabbenhöft *et al.*, 2009; Liu *et al.*, 2012; Neymark *et al.*, 2014). The advantage of MC-ICPMS is high sample throughput, while those of DS-TIMS are high accuracy (resulting from rigorous correction of the instrumental isotope fractionation) and relatively higher analytical precision. Both high precision and high accuracy are required to determine small isotopic differences in natural samples on the order of 0.01‰. An apparent analytical error in Sr isotope measurement can be reduced by analyzing the sample multiple times and estimating the analytical error by standard errors of the mean (SE). Some of the high-precision stable Sr isotopic data has been reported in this manner (e.g., Fietzke and Eisenhauer, 2006). However, note that such apparent error reduction is effective only for random errors and does not apply to systematic errors. A possible source of systematic error in Sr stable isotope analysis is the Sr chemical separation process by column chromatography. Because of the isotope fractionation during column chromatography (Russell and Papanastassiou, 1978; Ohno and Hirata, 2007; Charlier *et al.*, 2012), incomplete recovery of Sr in the chemical separation process induces systematic bias in the Sr stable isotope ratios for non-DS analysis. Although some recent MC-ICPMS studies claim to have obtained high precision with reported errors down to *ca.* 0.02‰ (e.g., Fietzke and Eisenhauer, 2006; de Souza *et al.*, 2010), the column chromatography-induced Sr isotope fractionation seems to be insufficiently assessed in their analytical routines for eliminating such possible systematic biases.

This paper presents a methodology for the high-precision and high-accuracy analysis of radiogenic ($^{87}Sr/^{86}Sr$) and stable ($\delta^{88}Sr$) Sr isotope ratios using the DS-TIMS technique. The technique is distinct from the previous DS-TIMS analyses (Krabbenhöft *et al.*, 2009; Neymark *et al.*, 2014; Stevenson *et al.*, 2014) by using an $^{84}Sr$-$^{86}Sr$ double spike as well as the data reduction scheme that consists of the matrix approach and iterative calculations. Using this technique, we evaluate the Sr isotope fractionation during column chromatography, and its related systematic bias, in detail. We also report $\delta^{88}Sr$ values for seven surface seawater samples from the Pacific and Atlantic oceans. The radiogenic Sr isotope ratio is homogenous in the modern ocean (Veizer, 1989). Although the investigated samples are mostly limited to surface waters, literature data for modern ocean $\delta^{88}Sr$ values also show homogeneous stable Sr isotopic distribution of the ocean (e.g., Scher *et al.*, 2013). Therefore, seawater seems to be an adequate reference sample to assess the precision and accuracy of $\delta^{88}Sr$ analyses, including both chemical separation and mass spectrometry. We report $\delta^{88}Sr$ results not only for surface seawater but

*Table 1. Locations of seawater samples*

| Sample | Sampling location | | Depth |
|---|---|---|---|
| | Latitude | Longitude | |
| Pacific (nearshore) | | | |
| 1310316-2 | 32°47.194′ N | 132°52.126′ E | surface |
| 1310316-3 | 32°46.623′ N | 132°52.267′ E | surface |
| 1310316-4 | 32°45.548′ N | 132°50.832′ E | surface |
| | | | |
| Pacific (deep sea) | | | |
| BD-7 4000 m | 47°00′ N | 160°05′ E | 4000 m |
| BD-7 5000 m | 47°00′ N | 160°05′ E | 5000 m |
| BD-14 4000 m | 47°00′ N | 170°00′ W | 4000 m |
| BD-14 5000 m | 47°00′ N | 170°00′ W | 5000 m |

also, for the first time, for deep seawater taken below the carbonate compensation depth (CCD). The homogeneity of the seawater $\delta^{88}Sr$ is discussed.

## MATERIALS AND METHODS

### Samples and reference materials

Eleven modern seawater samples from the Atlantic and Pacific oceans, including four seawater reference materials, were analyzed in this study. All four seawater reference materials—IAEA BCR-403, NASS-6 (issued by the National Research Council Canada), CASS-5 (near-shore seawater issued by the National Research Council Canada), and IAPSO standard seawater—were taken from the Atlantic Ocean. Three batches of IAPSO standard seawater (P147, P152, and P153) were analyzed separately to check Sr isotopic homogeneity among them.

Near-shore water of the Pacific Ocean was collected along the coast of Tatsukushi (Kochi Prefecture), southwest Japan. Details of the sampling points are summarized in Table 1. Sample 130316-2 was collected from the mouth of Misaki River. Sampling points 130316-3 and 130316-4 were, respectively, 1.2 km and 3.9 km away from sampling point 130316-2. Seawater was directly sampled from the surface without filtering. Ultrapure $HNO_3$ was added to the sample just after the sampling, to obtain a $HNO_3$ concentration of *ca.* 0.15M.

Four deep seawater samples from the North Pacific Ocean taken during the Hakuho Maru Cruise KH-12-4 were used in this study. These samples were taken from 4000 m and 5000 m depths at stations BD-7 and BD-14 (Table 1) by the CTD-Carousel Multi sampling system. The sampling is detailed in Gamo *et al.* (2012) and Kim *et al.* (2015).

The Sr isotopic reference material NIST SRM-987 was used as a reference standard for Sr stable isotope analysis. In addition to SRM-987, a commercially supplied high-purity (99.99%) $SrCO_3$ reagent (Lot # DPM5413,

*Table 2. Isotope ratios of NIST SRM-987 and the Sr double spike*

|  | $^{84}Sr/^{86}Sr$ | $^{87}Sr/^{86}Sr$ | $^{88}Sr/^{86}Sr$ | $^{86}Sr/^{88}Sr$ | n |
|---|---|---|---|---|---|
| SRM-987 | 0.0564914 (4) | 0.7102595 (16) |  | $\equiv 0.1194$ | 6 |
| $^{84}Sr$-$^{86}Sr$ double spike | 3.09260 (3) | 0.01486056 (17) | 0.0295206 (11) |  | 6 |

*Errors in parentheses represent 2 SE of multiple analyses.*

Wako Pure Chemical Industries, Ltd.) was dissolved with high-purity $HNO_3$ to obtain a stock standard solution. This solution, Wako-9999, was used as an in-house Sr stable isotopic reference and analyzed throughout this study.

*Strontium double spike*

An $^{84}Sr$-$^{86}Sr$ double spike was used in this study. The error propagation simulation by Wakaki (2012) showed that the $^{84}Sr/^{86}Sr$ ratio of *ca.* 3 gives the smallest error propagation in the double spike data correction algorithm. Thus, the double-spike solution was prepared by mixing $^{84}Sr$ and $^{86}Sr$ spikes at a proportion of *ca.* 3:1. Precise isotopic composition and Sr concentration of the double spike were determined and calibrated against SRM-987 by inverse double-spike analysis, similar to that described in Wakaki and Tanaka (2012). First, the Sr isotopic composition of SRM-987 was measured using internal normalization with an assumption of $^{86}Sr/^{88}Sr_{SRM-987} = 0.1194$ (Table 2), which was treated as the isotopic composition of the spike ($R_S$). Then, the double spike was treated as an unknown sample and the isotope ratios were determined by the double-spike analysis procedure (see Mass spectrometry and double-spike analysis section), as shown in Table 2.

*Strontium separation chemistry*

Strontium was separated from major cations (e.g., Na, Mg, and Ca) by extraction chromatography using Sr spec resin (Eichrom). A teflon column with a diameter of 3.66 mm was filled with 0.2 mL of Sr spec resin (particle size of 50–100 $\mu m$). The column height under this condition was *ca.* 19 mm. Approximately 50 $\mu L$ of each seawater sample solution, containing *ca.* 400 ng Sr, was dried, dissolved in 1.0 mL of 3M $HNO_3$, and then loaded onto the column. Major cations and Ba were washed out from the column with 2 mL of 6M $HNO_3$, and subsequently, 0.5 mL of 3M $HNO_3$. Strontium fractions were collected with 2 mL of 0.05M $HNO_3$. The resin was used only once. Under this separation chemistry the total procedural blank was <10 pg. The total recovery yield is estimated from elution curves obtained experimentally using GSJ reference rock JB-2 as a test sample. The amount of Sr released form the column during sample loading and washing phases (using 3M and 6M $HNO_3$) was smaller than 1% of the total Sr. However, we observed that 3–5% of

*Table 3. Faraday-cup configuration for the Sr isotope ratio measurements*

| Collector | L1 | C | H1 | H2 | H3 |
|---|---|---|---|---|---|
| Mass | 84 | 85 | 86 | 87 | 88 |
| Element | Sr | Rb | Sr | Sr + Rb | Sr |

the Sr still remained in the resin after fair amount of 0.05M $HNO_3$ was passed through the column. This remaining Sr was only released from the resin by elution with 6M HCl. This phenomenon is not reported by the previous studies. From this observation, we estimated the total recovery yield of Sr as 94%. If we estimate the total recovery yield only from the $HNO_3$ elution, the apparent yield will be *ca.* 99%, which is comparable with the previous studies.

Prior to the Sr separation chemistry, an aliquot of the sample solution, containing *ca.* 200 ng Sr, was mixed with the double spike. The spike to sample ratio used in this study was $^{86}Sr_{spike}/^{86}Sr_{sample} = 47:53$, which was determined using error propagation simulations to obtain the smallest error propagation (Wakaki, 2012). The amount of double spike added to the sample was carefully controlled to match this ratio. The spiked sample solution was dried, dissolved in 0.5 mL of 3M $HNO_3$, and then passed through the Sr separation column in the same manner as described above. Strontium separation chemistry of the spiked sample was conducted in a separate laboratory using completely separated apparatus, such as columns, vials, and reagents, to avoid cross-contamination between the natural and spiked samples.

*Mass spectrometry and double-spike analysis*

Stable isotope analysis of Sr was carried out using the DS-TIMS method based on the combined internal normalization isotope ratio measurement and the iterative calculation protocol, similar to that described by Wakaki and Tanaka (2012). In the first step, Sr isotope ratios ($^{84}Sr/^{86}Sr$, $^{87}Sr/^{86}Sr$ and $^{88}Sr/^{86}Sr$) of both the natural and spiked samples were measured on a Thermo TRITON TIMS at Kochi Core Center. The isotope ratio measurement of the natural sample is necessary because the $^{87}Sr/^{86}Sr$ ratio is variable between the samples. A sample containing 100–300 ng Sr was loaded onto a tungsten single filament with

a tantalum oxide activator. The Sr isotopes were measured with the static multicollection mode using five faraday cups (Table 3). Ion beam intensity of $^{88}$Sr was kept at 12 V and 4 V ($12 \times 10^{-11}$ A and $4 \times 10^{-11}$ A) during the natural and spiked runs, respectively. A single measurement consisted of 400 cycles (20 cycles × 20 blocks) of 16 s integration of the ion signal. Peak centering was performed every 5 blocks. Faraday cup background noise was measured for a total of 6000 s during the measurement. Faraday cup gain was measured and corrected every day. The intensity of Rb$^+$ was monitored at mass 85, and isobaric interference of $^{87}$Rb$^+$ to $^{87}$Sr$^+$ was corrected using $^{87}$Rb/$^{85}$Rb = 0.3856 (Berglund and Wieser, 2011). It is well known that the "raw" isotope ratios change systematically during TIMS analysis due to instrumental isotope fractionation, and thus use of the internal normalization with the exponential law to correct for this instrumental isotope fractionation is essential in obtaining high-precision isotope ratio data (e.g., Russell *et al.*, 1978). In this study, Sr isotope ratios ($^{84}$Sr/$^{86}$Sr and $^{87}$Sr/$^{86}$Sr) were measured by internal normalization with exponential law using $^{86}$Sr/$^{88}$Sr as the normalizing ratio. As a first step of the data analysis, the natural run was normalized with $^{86}$Sr/$^{88}$Sr = 0.1194 (Steiger and Jäger, 1977), and the spiked run was normalized with the average value of the measured $^{86}$Sr/$^{88}$Sr ratio. The $^{86}$Sr/$^{88}$Sr ratios used in this initial normalization step need not to be the "true" value. The measured $^{84}$Sr/$^{86}$Sr and $^{87}$Sr/$^{86}$Sr ratios as well as the $^{86}$Sr/$^{88}$Sr ratio used for normalization for both the natural and the spiked run were treated as the input data for the following double spike data processing step.

The conventional $^{87}$Sr/$^{86}$Sr ratio for the sample was obtained from this initial normalization step of the natural sample measurement. The small systematic bias of $^{87}$Sr/$^{86}$Sr between different mass spectrometry sessions was corrected to $^{87}$Sr/$^{86}$Sr$_{SRM-987}$ = 0.710248 (McArthur *et al.*, 2001) on a session-by-session basis. Here, uncertainty of the $^{87}$Sr/$^{86}$Sr ratio for the single run is reported as the 2 SE internal error. Six to ten measurements of SRM-987 were carried out during a single session, which typically gave repeatability of 7 ppm (2SD).

The second step was data processing for the double-spike run. The tentatively normalized measured isotope ratio of the natural sample $R_{in}$ (i = 84, 87, and 88) deviates from its true isotope ratio $R_{iN}$. This can be expressed in a linear-style isotope fractionation law as

$$R_{iN} = R_{in} (1 + \beta_n \Delta_i), \qquad (1)$$

where $\beta_n$ is the remaining instrumental isotope fractionation factor (per atomic mass unit) and $\Delta_i$ is the mass difference factor of the exponential approximation law (Johnson and Beard, 1999) calculated from the atomic mass of $^i$Sr ($m_i$) as $\Delta_i = (m_i - m_{86}) - (m_i - m_{86})^2/2m_{86}$. A

similar equation can be defined relating the measured isotope ratio of the spiked sample, $R_{im}$, and its true isotope ratio $R_{iM}$ using the remaining instrumental isotope fractionation factor $\beta_m$:

$$R_{iM} = R_{im} (1 + \beta_m \Delta_i). \qquad (2)$$

Since the spiked sample is a mixture of the sample and the double spike, the mixing equation can be defined using a mixing parameter q and the isotope ratio of the double spike ($R_{iS}$) as

$$R_{iN} - R_{iS} = q (R_{iM} - R_{iS}). \qquad (3)$$

Substituting Eqs. (1) and (2) into Eq. (3) gives

$$R_{iS} - R_{in} = q (R_{iS} - R_{im}) - q \beta_m (\Delta_i R_{im}) + \beta_n (\Delta_i R_{in}). \, (4)$$

Three independent isotope ratios of Sr give three independent equations of this form with three unknown parameters. We took the 3-by-3-matrix approach (Hamelin *et al.*, 1985; Wakaki and Tanaka, 2012) to solve this equation for q, $\beta_n$ and $\beta_m$. Then, using these parameters, the fractionation-corrected $^{88}$Sr/$^{86}$Sr ratios of the natural and spiked samples, $R_{88N}$ and $R_{88M}$, are calculated from Eqs. (1) and (2). Sr concentration of the sample can be obtained from the measured q value using the isotope dilution method.

The isotope fractionation behavior during the TIMS measurement is best described by the exponential isotope fractionation law (Russell *et al.*, 1978). The linear-style isotope fractionation law used in Eqs. (1) and (2) generates a systematic bias when the $\beta$ vales are far from 0. However, this potential systematic bias can be minimized by introducing an iterative approach, as follows. The raw data of both the natural and spiked sample measurements are reprocessed through internal normalization using the calculated $R_{88N}$ and $R_{88M}$ values for the normalization. This gives a new set of the measured isotope ratios, $R_{in2}$ and $R_{im2}$. The data processing described above was repeated with this new set of measured isotope ratios, and a new set of fractionation-corrected $^{88}$Sr/$^{86}$Sr ratios was calculated. This iterative calculation procedure was repeated several times until the $\beta_n$ and $\beta_m$ values become reasonably small. Finally, the fractionation-corrected $^{84}$Sr/$^{86}$Sr and $^{88}$Sr/$^{86}$Sr ratios of the sample are calculated by Eq. (1) using the final $\beta_n$ value.

The stable Sr isotopic results were expressed in delta notation with reference to the average of the measured SRM-987 on a session-by-session basis as

$$\delta^i\text{Sr} (‰) = [(^i\text{Sr}/^{86}\text{Sr})_{sample}/(^i\text{Sr}/^{86}\text{Sr})_{NBS987} - 1] \times 10^3$$
$$(i = 84 \text{ and } 88).$$

*Table 4. Radiogenic and stable Sr isotopic compositions of the reference samples*

| Sample | Session# | Run | $^{87}Sr/^{86}Sr$ *1 | $\delta^{84}Sr$ (‰) *2 | $\delta^{88}Sr$ (‰) *2 | n |
|--------|----------|-----|---------------------|------------------------|------------------------|---|
| SRM-987 | Average | | 0.710248 (5) *3 | ≡0.00 (3) *3 | ≡0.00 (2) *3 | 65 |
| Wako-9999 | #1 | run 1 | 0.708388 (2) | −0.32 (4) | 0.32 (2) | |
| | #2 | run 1 | 0.708391 (2) | −0.36 (4) | 0.33 (2) | |
| | #2 | run 2 | 0.708393 (2) | −0.37 (4) | 0.32 (2) | |
| | #2 | run 3 | 0.708387 (2) | −0.35 (4) | 0.33 (2) | |
| | #3 | run 1 | 0.708390 (2) | −0.34 (4) | 0.32 (2) | |
| | #3 | run 2 | 0.708392 (2) | −0.34 (4) | 0.33 (2) | |
| | #3 | run 3 | 0.708391 (2) | −0.30 (4) | 0.30 (2) | |
| | #4 | run 1 | 0.708391 (2) | −0.36 (5) | 0.34 (2) | |
| | #5 | run 1 | 0.708391 (2) | −0.37 (3) | 0.35 (2) | |
| | #5 | run 2 | 0.708391 (2) | −0.32 (3) | 0.31 (2) | |
| | #5 | run 3 | 0.708392 (2) | −0.31 (3) | 0.32 (2) | |
| | #6 | run 1 | 0.708395 (2) | −0.36 (5) | 0.31 (2) | |
| | #6 | run 2 | 0.708388 (2) | −0.34 (5) | 0.33 (2) | |
| | #7 | run 1 | 0.708388 (2) | −0.30 (2) | 0.32 (2) | |
| | #7 | run 2 | 0.708395 (2) | −0.35 (2) | 0.32 (2) | |
| | Average | | 0.708391 (5) *3 | −0.34 (5) *3 | 0.32 (2) *3 | 15 |

*1 Errors of the $^{87}Sr/^{86}Sr$ ratios are expressed as 2 SE internal errors.
*2 Errors of the $\delta^{84}Sr$ and $\delta^{88}Sr$ values are expressed as 2σ errors, estimated from both the internal and external errors.
*3 Errors of the average are expressed as 2 SD.

Using the measured SRM-987 as a reference is important for reducing the possible systematic bias between sessions, because the Sr isotope ratio measurement by TIMS may be affected by long-term aging effects (decrease in ion detection efficiency) of the faraday-cup detectors.

## RESULTS AND DISCUSSION

*Precision of Sr stable isotope analysis by DS-TIMS*

The stable Sr isotopic results for the isotopic reference materials SRM-987 and Wako-9999 are summarized in Table 4 and Fig. 1. The results for the conventional $^{87}Sr/^{86}Sr$ ratio are also presented. Repeated analysis of SRM-987 during this study gave average 2 SD external precisions of the $\delta^{84}Sr$ and $\delta^{88}Sr$ values as 0.03‰ and 0.02‰, respectively. Repeated analyses of the in-house isotopic reference Wako-9999 during seven analytical sessions gave consistent results within analytical errors, with average $\delta^{84}Sr$ and $\delta^{88}Sr$ values of −0.34 ± 0.05‰ and 0.32 ± 0.02‰, respectively. These results show that our $\delta^{88}Sr$ analysis is reproducible within ±0.02‰ over a long-term period.

The typical 2 SE internal errors calculated from the 2 SE internal errors of two isotope ratio measurements (natural and spiked runs) by error propagation were 0.016‰ and 0.006‰ for $\delta^{84}Sr$ and $\delta^{88}Sr$, respectively.

The internal error is significantly small compared with the external errors; thus, it is not appropriate for representing the analytical uncertainty. Therefore, we report here the analytical uncertainty of $\delta^{84}Sr$ and $\delta^{88}Sr$ by taking the root-sum square of both the internal and external errors. The external error was estimated for each analytical session from the 2 SD of multiple SRM-987 analyses.

Sample to spike ratio is one of the factor that may affect the precision and accuracy of the double-spike method. To check the acceptable range of sample to spike ratios, six SRM-987 samples were analyzed with different sample to spike ratios ($^{86}Sr_{spike}$:$^{86}Sr_{sample}$ ranging from 31:69 to 61:39). The stable Sr isotopic results of the six analyses were indistinguishable with 0 and the analytical errors are comparable with each other (Table 5). Therefore, we conclude that the precision and accuracy of the DS analysis is not degraded for sample to spike ratios within this range.

*Sr isotope fractionation during Sr separation chemistry*

The isotope fractionation behavior of Sr during extraction chromatography was investigated in detail by DS-TIMS. A 1 mL 3M $HNO_3$ solution of SRM-987, containing 90.95 $\mu$g of Sr, was loaded onto the column and successively eluted with 2 mL of 6M $HNO_3$, 0.5 mL of 3M $HNO_3$, and 2.6 mL of 0.05M $HNO_3$. All the eluent, in-
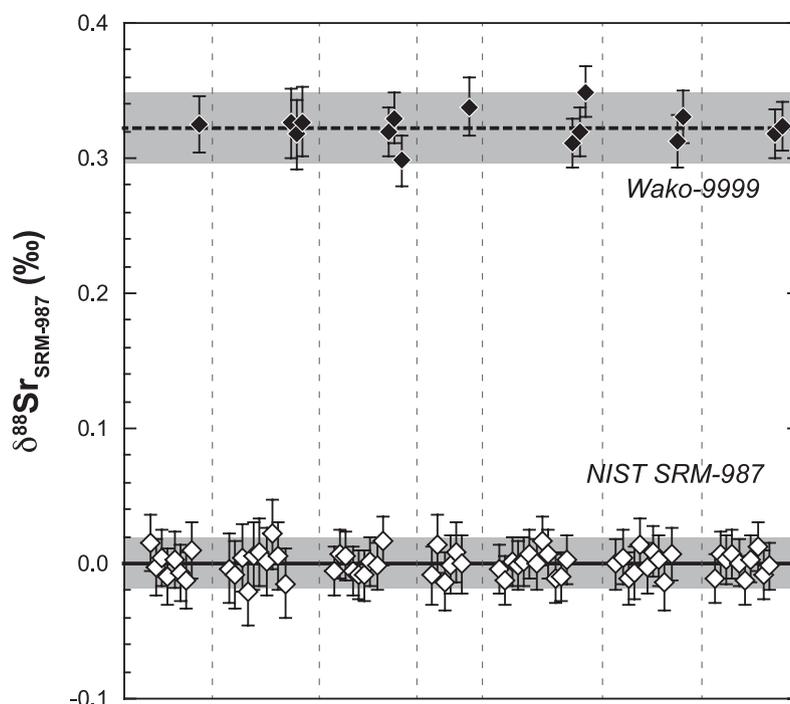
Fig. 1. Long-term analyses of SRM-987 (white diamonds) and Wako-9999 (black diamonds) reagents during seven analytical sessions over 16 months. Black and dashed horizontal lines represent the average $\delta^{88}$Sr of SRM-987 and Wako-9999, respectively. The gray area represents the 2 SD errors. Note that the average $\delta^{88}$Sr of SRM-987 analyses within an analytical session is defined as 0. The vertical line separates the data from different analytical sessions.

cluding the sample loads and the washouts, were collected as eight continuous fractions.

The Sr elution data are shown in Table 6 and Fig. 2a. In column chromatography, the most important parameter controlling the elution curve is the number of theoretical plates, N, which is described by the maximum peak height in $\%_{Sr}$/mL, $C_{max}$, and peak elution volume, $v'$, as

$$N = 2\pi \, (C_{max} \, v'/100)^2 \quad \text{(Glueckauf, 1955).} \quad (5)$$

An acceptable range for these two parameters, $C_{max}$ and $v'$, was estimated from the experimental data by comparing the elution data and the theoretical elution curves, similar to that described by Wakaki and Tanaka (2012), as $C_{max} = 915 \pm 30 \, \%_{Sr}$/mL and $v' = 3.790 \pm 0.005$ mL. This gives the theoretical number of plates for this experiment as N = 44.5 ± 4.5, which results in the best-fit elution curve shown in Fig. 2a.

After the elution, part of the each eluted fractions were spiked and analyzed for the stable Sr isotopic compositions. The $\delta^{88}$Sr values of the eluted fractions vary from +1.05‰ to –0.64‰ and change systematically from heavy isotope enrichment to light isotope enrichment during the elution (Table 6 and Fig. 2b). This observation is consistent with the previous reports on Sr isotope fractionation during extraction chromatography (Ohno and Hirata,

Table 5. Radiogenic and stable Sr isotopic compositions of the reference sample SRM 987 analyzed with different sample to spike ratios

| $^{86}Sr_{spike}/(^{86}Sr_{spike}+^{86}Sr_{sample})$ | $^{87}Sr/^{86}Sr$ *1 | $\delta^{84}Sr$ (‰) *2 | $\delta^{88}Sr$ (‰) *2 |
|---|---|---|---|
| 0.306 | 0.710249 (4) | –0.04 (11) | 0.01 (3) |
| 0.367 | 0.710256 (4) | –0.03 (11) | 0.01 (3) |
| 0.408 | 0.710253 (4) | 0.07 (11) | –0.01 (2) |
| 0.506 | 0.710245 (4) | 0.02 (11) | –0.01 (2) |
| 0.561 | 0.710254 (5) | 0.02 (11) | 0.01 (2) |
| 0.612 | 0.710252 (4) | 0.01 (11) | 0.01 (2) |

*1 Errors of the $^{87}Sr/^{86}Sr$ ratios are expressed as 2 SE internal errors.
*2 Errors of the $\delta^{84}Sr$ and $\delta^{88}Sr$ values are expressed as 2σ errors, estimated from both the internal and external errors.

2007; Charlier et al., 2012). An exception to this isotopic trend is the final fraction, which has a higher $\delta^{88}$Sr value than that expected from the trend. The reason for this higher value is not clear, but a similar tendency can be seen in the data of Ohno and Hirata (2007).

The $\delta^{88}$Sr in seven out of the eight eluted fractions shows a linear correlation with the accumulated weight fraction of Sr in a probability plot (Fig. 3). This linear correlation is consistent with the theoretical isotope fractionation behavior (Glueckauf, 1958). The theory

*Table 6. Radiogenic and stable Sr isotopic compositions of the fractions obtained from the elution experiment*

| Sample | Eluted section [mL] | Eluent | Volume [mL] | Sr [μg] | Run | $^{87}Sr/^{86}Sr$ *1 | $\delta^{84}Sr$ [‰] *2 | $\delta^{88}Sr$ [‰] *2 | n |
|---|---|---|---|---|---|---|---|---|---|
| Fraction 1 | 0–3.5 | 3M + 6M HNO$_3$ *4 | 3.5 | 0.342 (1) | | 0.710251 (4) | −1.15 (11) | 1.05 (2) | |
| Fraction 2 | 3.5–3.6 | 0.05M HNO$_3$ | 0.1 | 0.133 (1) | | 0.710246 (7) | −0.98 (14) | 0.98 (6) | |
| Fraction 3 | 3.6–3.7 | 0.05M HNO$_3$ | 0.1 | 0.785 (2) | | 0.710258 (7) | −0.82 (12) | 0.83 (3) | |
| Fraction 4 | 3.7–3.75 | 0.05M HNO$_3$ | 0.05 | 11.65 (2) | | 0.710254 (4) | −0.57 (11) | 0.47 (2) | |
| Fraction 5 | 3.75–3.8 | 0.05M HNO$_3$ | 0.05 | 37.14 (6) | | 0.710250 (5) | −0.30 (11) | 0.20 (2) | |
| Fraction 6 | 3.8–3.9 | 0.05M HNO$_3$ | 0.1 | 35.08 (4) | #1 | 0.710252 (5) | 0.32 (11) | −0.32 (2) | |
| | | | | | #2 | 0.710252 (5) | 0.26 (11) | −0.30 (2) | |
| | | | | | #3 | 0.710255 (4) | 0.40 (11) | −0.34 (2) | |
| | | | | | Average | 0.710253 (4) *3 | 0.33 (14) *3 | −0.32 (4) *3 | 3 |
| Fraction 7 | 3.9–4.1 | 0.05M HNO$_3$ | 0.1 | 4.422 (8) | | 0.710247 (5) | 0.62 (11) | −0.64 (2) | |
| Fraction 8 | 4.1–6.1 | 0.05M HNO$_3$ | 2.0 | 0.817 (1) | | 0.710249 (5) | 0.24 (11) | −0.24 (2) | |

*1 Errors of the $^{87}Sr/^{86}Sr$ ratios are expressed as 2 SE internal errors.
*2 Errors of the $\delta^{84}Sr$ and $\delta^{88}Sr$ values are expressed as 2σ errors, estimated from both the internal and external errors.
*3 Errors of the average are expressed as 2 SD.
*4 The first fraction contains the sample loading with 1 mL 3M HNO$_3$, and elution with 2 mL of 6M HNO$_3$ and 0.5 mL of 3M HNO$_3$ in successive order.

describes the slope of this correlation line as $(\alpha - 1)\sqrt{N}$, where $\alpha$ is the Sr isotope fractionation factor between the Sr extraction resin and 0.05M HNO$_3$ (Glueckauf, 1958). The best fit to the experimental data in Fig. 3 gives the Sr isotope fractionation factor between the Sr extraction resin and 0.05M HNO$_3$ as $\alpha^{88}Sr_{Sr\,resin} = (^{88}Sr/^{86}Sr)_{Sr\,resin}/(^{88}Sr/^{86}Sr)_{nitric\,acid} = 0.999947 \pm 0.000001$. The temperature during this experiment was not strictly controlled but was likely around 25°C.

The most important observation in this experiment is that a very small amount of Sr (about 0.4% of the total Sr) is eluted in the early washout fraction (which includes the sample loading, 6M HNO$_3$, and 3M HNO$_3$) prior to Sr collection by 0.05M HNO$_3$. This observation is consistent with the theoretical behavior since the Sr distribution factor between the Sr spec resin and 6M (and 3M) HNO$_3$ is large but finite (Horwitz et al., 1992). The loss of a small amount of Sr during column chromatography is inevitable; therefore, 100% recovery of Sr is not possible using Sr spec resin. This early washout fraction has a highly fractionated stable Sr isotopic composition enriched in heavy isotopes. Therefore, eliminating this fraction will bias the stable Sr isotopic composition of the remaining Sr fraction to slightly negative $\delta^{88}Sr$ values (our column setting yields a 0.005‰ shift) even if the amount of Sr in the early washout fraction is small. This small potential bias may not be negligible for analytical uncertainties as small as 0.01–0.02‰ and may become a significant error source for non-DS analysis. Therefore, a combined evaluation of the accuracy of both chemical separation and mass spectrometry is important for high-precision analyses.

The isotope fractionation occurring in column separation is due to equilibrium reaction between the resin and the eluent and thus is an equilibrium isotopic fractionation. On the other hand, the isotope fractionation occurring in the mass spectrometer is a kinetic isotope fractionation. The mass dependence of the equilibrium isotopic fractionation is slightly different from that of that of kinetic isotope fractionation (Young et al., 2002). However, the difference between equilibrium fractionation and kinetic fractionation is negligibly small for Sr, if the degree of fractionation is small as 0.005‰. Therefore, the small column-induced fractionation can be accurately corrected by the double spike technique.

*Sr stable isotopic composition of modern seawater*

The Sr isotopic results of the seven surface seawater samples from the Pacific and Atlantic oceans, as well as four deep seawater samples from the North Pacific, are summarized in Table 7. Most of the samples were analyzed several times with independent spiking and Sr separation chemistry. All the seawater samples analyzed showed indistinguishable $\delta^{88}Sr$ values within analytical errors (Fig. 4). The average $\delta^{88}Sr$ of the 11 seawater samples was 0.407 ± 0.012‰ (2 SD).

Among the seawater samples analyzed, four deep seawater samples showed $\delta^{88}Sr$ values indistinguishable from the surface seawater samples. The $\delta^{88}Sr$ values of the deep seawater samples were also consistent with the published deep seawater data of 0.39 ± 0.02‰ (deep Pacific seawater, depth not mentioned; de Souza et al., 2010) and 0.38 ± 0.05‰ (deep BATS, 2000 m; Scher et al., 2013). The deep seawater samples of the North Pacific
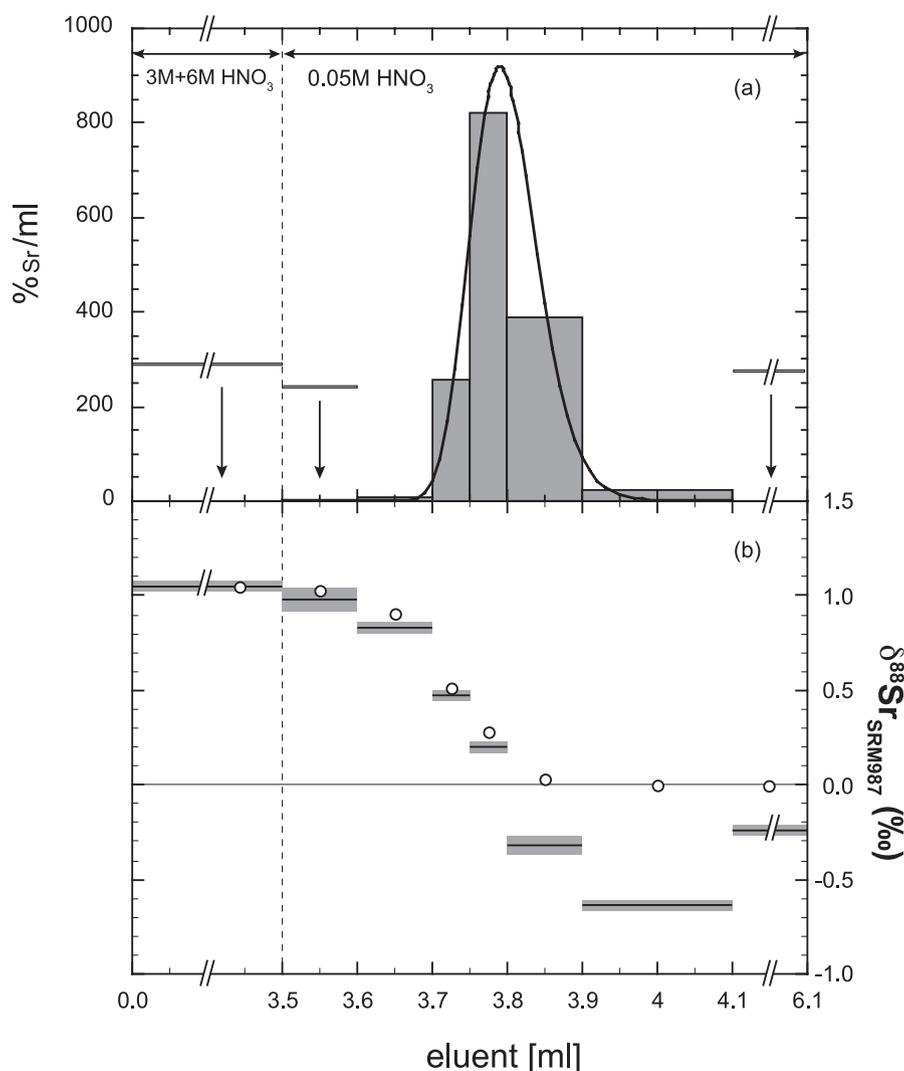
*Fig. 2. (a) Elution profile of Sr during extraction column chromatography using Sr spec resin. The eluted Sr of the Sr collection phase, as well as the early washout phase, was divided into eight samples with different eluent volumes. The y-axis represents the fraction of Sr per unit volume. The fraction of Sr in each sample is represented by the area of the gray box. The solid curve represents the best-fit elution curve calculated with a peak elution volume of 3.79 mL and a maximum peak height of 915 %$_{Sr}$/mL (corresponding to a number of theoretical plates of 44.5). (b) Isotope fractionation profile of Sr during extraction column chromatography. Black lines and gray boxes represent $\delta^{88}Sr$ values and 2-sigma error ranges of the samples, respectively. White circles represent the accumulated $\delta^{88}Sr$ values throughout the elution. The $\delta^{88}Sr$ value of the starting material (SRM-987) is defined as 0 and represented with a horizontal line.*

analyzed in this study were taken from 4000 and 5000 m depths at a latitude of 47°N (Table 1). The CCD of the North Pacific at latitudes between 40 and 50°N was *ca.* 3500–4000 m (Berger *et al.*, 1976); therefore, the four samples analyzed in this study represent deep seawater below the CCD. Our data clearly show that deep seawater below the CCD has a stable Sr isotopic composition indistinguishable from that of surface seawater.

Calcium carbonates are the primary sink for marine Sr, and thus, play an important role in marine Sr cycling (Krabbenhöft *et al.*, 2010). Formation of both biogenic

and inorganic calcium carbonates accompanies temperature-dependent Sr stable isotope fractionation on the sub-permil order; moreover, $\delta^{88}Sr$ values of marine carbonates are systematically lighter than those of seawater, at about 0.1–0.3‰ (Fietzke and Eisenhauer, 2006; Rüggeberg *et al.*, 2008; Böhm *et al.*, 2012). The $\delta^{88}Sr$ value of seawater is *ca.* 0.1‰ heavier than that of the Sr input sources to the modern ocean, such as river water and hydrothermal fluids, and this stable Sr isotopic difference is attributed to the precipitation of isotopically light carbonates (Krabbenhöft *et al.*, 2010). These obser-
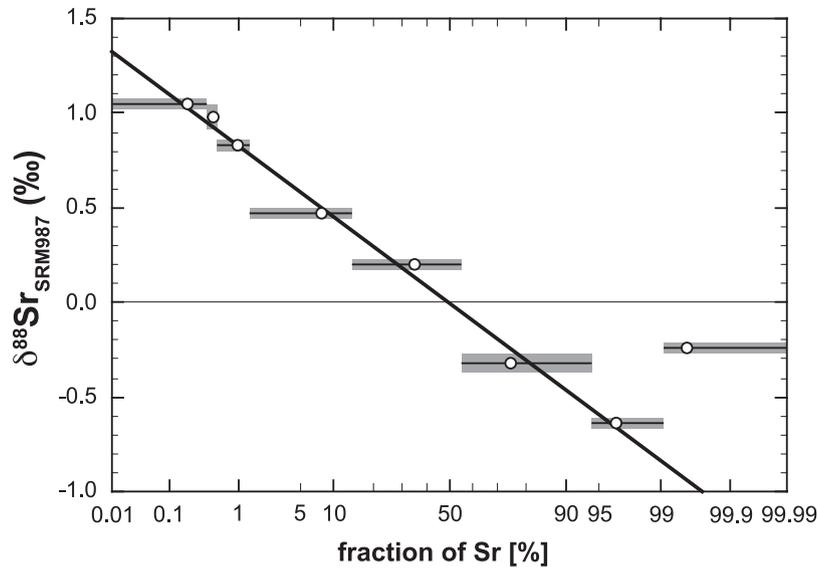
Fig. 3. The $\delta^{88}Sr$ values of the isotopically fractionated samples during extraction column chromatography are plotted against the accumulated weight fraction of Sr on a probability scale. Black lines and gray boxes are $\delta^{88}Sr$ values and 2-sigma error ranges, respectively. The median value of the accumulated weight fraction of Sr is indicated by white circles (note that x axis is not on a linear scale). The $\delta^{88}Sr$ value of the starting material (SRM-987) is represented by a horizontal line. The solid line represents linear regression through the seven median data points. The last sample was excluded from this regression.
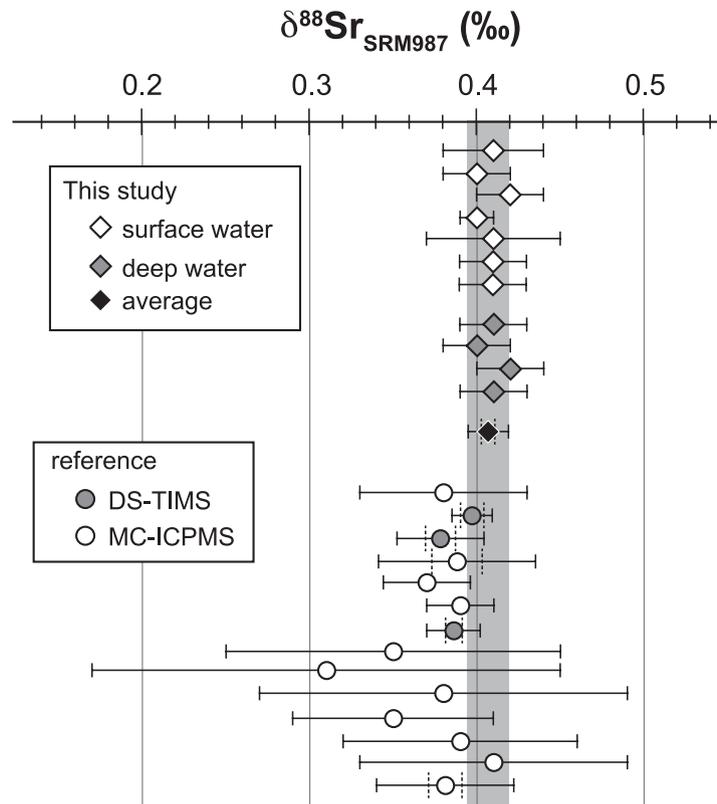


Fig. 4. $\delta^{88}Sr$ values of the seawater samples are plotted with data compiled from the literature. White and gray diamonds represent surface and deep waters, respectively. The black diamond shows the average seawater $\delta^{88}Sr$ value analyzed in this study. White and gray circles represent literature data analyzed by MC-ICPMS and DS-TIMS techniques, respectively. Solid and dashed error bars represent 2SD and 2SE error ranges, respectively.

Sr stable isotopic composition of deep seawater    235

*Table 7. Radiogenic and stable Sr isotopic compositions of seawater samples*

| Sample | Run | Sr [ppm] *1 | $^{87}Sr/^{86}Sr$ *2 | $\delta^{84}Sr$ [‰] *3 | $\delta^{88}Sr$ [‰] *3 | n |
|---|---|---|---|---|---|---|
| Pacific (nearshore) | | | | | | |
| 130316-2 | #1 | 8.10 | 0.709177 (2) | −0.39 (4) | 0.39 (2) | |
| | #2 | 8.10 | 0.709172 (2) | −0.47 (5) | 0.42 (2) | |
| | #3 | 8.12 | 0.709172 (2) | −0.43 (3) | 0.42 (2) | |
| | Av. *4 | 8.11 | 0.709174 (6) | −0.43 (8) | 0.41 (3) | 3 |
| 130316-3 | #1 | 8.13 | 0.709172 (2) | −0.38 (4) | 0.39 (2) | |
| | #2 | 7.94 | 0.709175 (2) | −0.42 (4) | 0.39 (3) | |
| | #3 | 8.12 | 0.709168 (2) | −0.41 (4) | 0.41 (3) | |
| | Av. *4 | 8.06 | 0.709172 (7) | −0.40 (4) | 0.40 (2) | 3 |
| 130316-4 | #1 | 8.20 | 0.709171 (2) | −0.39 (4) | 0.41 (2) | |
| | #2 | 8.13 | 0.709172 (2) | −0.42 (4) | 0.42 (3) | |
| | #3 | 8.12 | 0.709168 (2) | −0.43 (4) | 0.42 (3) | |
| | Av. *4 | 8.15 | 0.709170 (5) | −0.41 (5) | 0.42 (2) | 3 |
| | | | | | | |
| Atlantic (nearshore) | | | | | | |
| CASS-5 | #1 | 7.40 | 0.709176 (2) | −0.41 (4) | 0.40 (3) | |
| | #2 | 7.65 | 0.709174 (2) | −0.42 (4) | 0.40 (2) | |
| | #3 | 7.42 | 0.709173 (2) | −0.40 (4) | 0.41 (2) | |
| | Av. *4 | 7.49 | 0.709174 (3) | −0.41 (1) | 0.40 (1) | 3 |
| | | | | | | |
| Atlantic (surface) | | | | | | |
| BCR-403 | #1 | 8.25 | 0.709173 (2) | −0.47 (4) | 0.43 (3) | |
| | #2 | 8.22 | 0.709169 (2) | −0.40 (4) | 0.40 (3) | |
| | #3 | 8.31 | 0.709170 (2) | −0.41 (4) | 0.40 (2) | |
| | Av. *4 | 8.26 | 0.709170 (4) | −0.43 (8) | 0.41 (4) | 3 |
| IAPSO (P147) | #1 | 8.11 | 0.709171 (2) | −0.42 (4) | 0.41 (3) | |
| | #2 | 8.33 | 0.709170 (2) | −0.50 (4) | 0.41 (3) | |
| | #3 | 8.32 | 0.709171 (2) | −0.43 (4) | 0.41 (2) | |
| | #4 | 8.33 | 0.709172 (2) | −0.46 (4) | 0.42 (2) | |
| (P152) | #1 | 8.32 | 0.709173 (2) | −0.43 (4) | 0.41 (3) | |
| | #2 | 8.33 | 0.709173 (2) | −0.41 (4) | 0.40 (2) | |
| | #3 | 8.79 | 0.709176 (2) | −0.40 (3) | 0.39 (2) | |
| (P153) | #1 | 8.32 | 0.709170 (2) | −0.40 (4) | 0.41 (3) | |
| | #2 | 8.35 | 0.709172 (2) | −0.40 (4) | 0.41 (2) | |
| | #3 | 8.34 | 0.709172 (2) | −0.41 (3) | 0.40 (2) | |
| | Av. *4 | 8.35 | 0.709172 (4) | −0.42 (4) | 0.41 (2) | 10 |
| NASS-6 | #1 | 7.46 | 0.709173 (2) | −0.44 (4) | 0.40 (3) | |
| | #2 | 7.49 | 0.709171 (2) | −0.44 (4) | 0.42 (3) | |
| | #3 | 7.49 | 0.709173 (2) | −0.39 (4) | 0.40 (2) | |
| | Av. *4 | 7.48 | 0.709172 (3) | −0.42 (6) | 0.41 (2) | 3 |
| | | | | | | |
| Pacific (deep) | | | | | | |
| BD-7 4000 m | | 8.43 | 0.709172 (2) | −0.40 (5) | 0.41 (2) | |
| BD-7 5000 m | #1 | 8.40 | 0.709173 (2) | −0.42 (4) | 0.41 (2) | |
| | #2 | 8.43 | 0.709172 (2) | −0.41 (3) | 0.39 (2) | |
| | #3 | 8.46 | 0.709170 (2) | −0.41 (3) | 0.40 (2) | |
| | Av. *4 | 8.43 | 0.709171 (3) | −0.41 (1) | 0.40 (2) | 3 |
| BD-14 4000 m | | 8.44 | 0.709168 (2) | −0.44 (5) | 0.42 (2) | |
| BD-14 5000 m | | 8.40 | 0.709172 (2) | −0.43 (5) | 0.41(2) | |
| | | | | | | |
| Average seawater | Av. *4 | | 0.709172 (3) | −0.42 (3) | 0.407 (12) | 11 |

*1 Sr concentrations are expressed in parts per million of mass fraction (g/g); *2 Errors of the $^{87}Sr/^{86}Sr$ ratios are expressed as 2 SE internal errors; *3 Errors of the $\delta^{84}Sr$ and $\delta^{88}Sr$ values are expressed as $2\sigma$ errors, estimated from both the internal and external errors; *4 Errors of the average are expressed as 2 SD.

*Table 8. Compilation of stable Sr isotopic compositions of seawater*

| Reference | Sample | Method | $\delta^{88}$Sr (‰) | 2SD | 2SE | n |
|---|---|---|---|---|---|---|
| This study | average | DS-TIMS | 0.407 | 0.012 | 0.004 | 11 |
| Stevenson *et al.* (2014) | IAPSO | DS-TIMS | 0.397 | 0.012 *[1] | 0.007 | 3 |
| Neymark *et al.* (2014) | NASS-6 | DS-TIMS | 0.378 | 0.026 *[1] | 0.009 | 8 |
| Scher *et al.* (2013) | BATS | MC-ICPMS | 0.38 | 0.05 | | 14 |
| Kramchaninov *et al.* (2012) | IAPSO | MC-ICPMS | 0.388 | 0.047 *[1] | 0.015 | 10 |
| Liu *et al.* (2012) | IAPSO | MC-ICPMS | 0.370 | 0.026 | | 7 |
| de Souza *et al.* (2010) | Deep Pacific seawater | MC-ICPMS | 0.39 | 0.02 | | 102 |
| Krabbenhöft *et al.* (2009) | IAPSO | DS-TIMS | 0.386 | 0.016 *[1] | 0.005 | 10 |
| Halicz *et al.* (2008) | IAPSO | MC-ICPMS | 0.35 | 0.10 | | 15 |
| Halicz *et al.* (2008) | GOA-1 *[2] | MC-ICPMS | 0.31 | 0.14 | | 8 |
| Halicz *et al.* (2008) | NASS-4 | MC-ICPMS | 0.38 | 0.11 | | 8 |
| Halicz *et al.* (2008) | average | MC-ICPMS | 0.35 | 0.06 | | 3 |
| Ohno and Hirata (2007) | 63S170E | MC-ICPMS | 0.39 | 0.07 | | 3 |
| Ohno and Hirata (2007) | 63S170E | MC-ICPMS | 0.41 | 0.08 | | 3 |
| Fietzke and Eisenhauer (2006) | IAPSO | MC-ICPMS | 0.381 | 0.041 *[1] | 0.010 | 17 |
| Average DS-TIMS *[3] | | | | 0.392 | 0.025 | 0.013 | 4 |

*[1] Calculated from the 2SE and n values reported in the reference.
*[2] High salinity value of 41 was reported for GOA-1, an Indian Ocean sample from Gulf of Aqaba (Halicz et al., 2008).
*[3] Calculated from Krabbenhöft et al. (2009), Neymark et al. (2014), Stevenson et al. (2014), and this study.

vations suggest that the Sr stable isotopic composition of seawater is strongly affected by carbonate production. Besides the role of the primary output from the ocean, biogenic carbonates provide a vertical transport of Sr into deep sea. Biogenic carbonates are formed predominantly in shallow ocean and settle down the water column upon death to be re-dissolved at depths below the CCD. Since biogenic carbonates contain isotopically light Sr at significantly high concentrations, this process should transport isotopically light Sr into deep sea. Dissolution of the carbonates discharges the light Sr and may affect the Sr stable isotopic composition of deep seawater. However, the indistinguishable $\delta^{88}$Sr values between the deep seawater and surface seawater analyzed in this study indicate that the mass of Sr released by carbonate transportation and dissolution processes was not sufficiently large to change the Sr stable isotopic composition of deep seawater to a measurable degree. This is consistent with the conservative behavior of Sr in the ocean.

The results of the seawater analyses in this study demonstrate the high precision and reproducibility of our DS-TIMS technique (Fig. 4). Compared with the published seawater $\delta^{88}$Sr values, our results plot at a slightly higher end of the data distribution, but overlap with most of the data within analytical errors (Fig. 4 and Table 8). Although our results show slightly higher $\delta^{88}$Sr values than the other DS-TIMS data, all DS-TIMS data agrees within 2SD analytical error ranges. Therefore, we conclude that our results are essentially consistent with the published datasets. Among the published data, some of the non-DS MC-ICP-MS data seem to have low values compared with the DS-TIMS data. As shown in the previous section, Sr separa-

tion chemistry using Sr spec resin can cause an artificial isotope fractionation of Sr; i.e., loss of heavy isotope-enriched Sr in the early washout phase will shift the Sr isotopic composition of the recovered Sr toward light isotope enrichment. Since DS-TIMS analysis can correct for this possible column-induced isotope fractionation, DS-TIMS data are likely to be more accurate. Using the DS-TIMS data reported in this study and three previous reports (Krabbenhöft *et al.*, 2009; Neymark *et al.*, 2014; Stevenson *et al.*, 2014), we estimate the average $\delta^{88}$Sr value of seawater to be 0.392 ± 0.013‰ (2 SE, n = 4).

### CONCLUSIONS

The DS-TIMS technique described in this study allows high-precision and high-accuracy analysis of stable Sr isotopic composition, with a long-term external reproducibility of ±0.02‰ for $\delta^{88}$Sr. Detailed examination of the Sr isotope fractionation behavior during column chromatography using Sr spec resin showed that a very small amount of Sr with a highly fractionated isotopic composition was lost in the sample loading and purification procedures prior to Sr collection. This Sr loss yields a slight systematic bias in the $\delta^{88}$Sr value toward the negative side. The advantage of the double-spike technique is that the mass bias correction is applied not only to the instrumental mass bias but also to the mass bias incurred in the chemical separation process. Therefore, the possible systematic bias during column chromatography does not affect the accuracy of the DS-TIMS data. The $\delta^{88}$Sr values of all the 11 seawater samples analyzed agreed with the literature values, demonstrating the accuracy of the $\delta^{88}$Sr

analysis in this study. The stable Sr isotopic composition of deep seawater taken below the CCD in the North Pacific Ocean also agreed with that of the surface waters. This observation indicates that the seawater stable Sr isotopic composition is homogeneous down to depths below the CCD.

## REFERENCES

Berger, W. H., Adelseck, C. G., Jr. and Mayer, L. A. (1976) Distribution of carbonate in surface sediments of the Pacific Ocean. *J. Geophys. Res.* **81**, 2617–2627.

Berglund, M. and Wieser, M. E. (2011) Isotopic compositions of the elements 2009 (IUPAC Technical Report). *Pure Appl. Chem.* **83**, 397–410.

Böhm, F., Eisenhauer, A., Tang, J., Dietzel, M., Krabbenhöft, A., Kisakürek, B. and Horn, C. (2012) Strontium isotope fractionation of planktic foraminifera and inorganic calcite. *Geochim. Cosmochim. Acta* **93**, 173–182.

Charlier, B. L. A., Nowell, G. M., Parkinson, I. J., Kelley, S. P., Pearson, D. G. and Burton, K. W. (2012) High temperature strontium stable isotope behavior in the early solar system and planetary bodies. *Earth Planet. Sci. Lett.* **329–330**, 31–40.

de Souza, G. F., Reynolds, B. C., Kiczka, M. and Bourdon, B. (2010) Evidence for mass-dependent isotopic fractionation of strontium in a glaciated granitic watershed. *Geochim. Cosmochim. Acta* **74**, 2596–2614.

Fietzke, J. and Eisenhauer, A. (2006) Determination of temperature-dependent stable strontium isotope ($^{88}Sr/^{86}Sr$) fractionation via bracketing standard MC-ICP-MS. *Geochem. Geophys. Geosyst.* **7**, Q08009, doi:10.1029/2006GC001243.

Gamo, T. and The Scientific Members of the Expedition (2012) Preliminary Report of the Hakuho Maru Cruise KH-12-4 "BIG DIPPER Expedition": Zonal studies on biogeochemistry of trace elements and isotopes in the sub-arctic North Pacific Ocean (GEOTRACES). Atmosphere and Ocean Research Institute, The University of Tokyo, Chiba, Japan.

Glueckauf, E. (1955) Theory of chromatography part 9. The "theoretical plate" concept in column separations. *Trans. Faraday Soc.* **51**, 34–44.

Glueckauf, E. (1958) Theory of chromatography part 11. enrichment of isotopes by chromatography. *Trans. Faraday Soc.* **54**, 1203–1205.

Halicz, L., Segal, I., Fruchter, N., Stein, M. and Lazar, B. (2008) Strontium stable isotopes fractionate in the soil environments? *Earth Planet. Sci. Lett.* **272**, 406–411.

Hamelin, B., Manhes, G., Albarede, F. and Allegre, C. J. (1985) Precise lead isotope measurements by the double spike technique: a reconsideration. *Geochim. Cosmochim. Acta* **49**, 173–182.

Horwitz, E. P., Chiarizia, R. and Dietz, M. L. (1992) A novel strontium-selective extraction chromatographic resin. *Solvent Extr. Ion Exch.* **10**, 313–336.

Johnson, C. M. and Beard, B. L. (1999) Correction of instrumentally produced mass fractionation during isotopic analysis of Fe by thermal ionization mass spectrometry. *Int. J. Mass Spectrom.* **193**, 87–99.

Kim, T., Obata, H., Gamo, T. and Nishioka, J. (2015) Sampling and onboard analytical methods for determining subnanomolar concentrations of zinc in seawater. *Limnol. Oceanogr.: Methods* **13**, 30–39.

Krabbenhöft, A., Fietzke, J., Eisenhauer, A., Liebetrau, V., Böhm, F. and Vollstaedt, H. (2009) Determination of radiogenic and stable strontium isotope ratios ($^{87}Sr/^{86}Sr$; $\delta^{88/86}Sr$) by thermal ionization mass spectrometry applying an $^{87}Sr/^{84}Sr$ double spike. *J. Anal. At. Spectrom.* **24**, 1267–1271.

Krabbenhöft, A., Eisenhauer, A., Böhm, F., Vollstaedt, H., Fietzke, J., Liebetrau, V., Augustin, N., Peucker-Ehrenbrink, B., Müller, M. N., Horn, C., Hansen, B. T., Nolte, N. and Wallmann, K. (2010) Constraining the marine strontium budget with natural strontium isotope fractionations ($^{87}Sr/^{86}Sr*$, $\delta^{88/86}Sr$) of carbonates, hydrothermal solutions and river waters. *Geochim. Cosmochim. Acta* **74**, 4097–4109.

Kramchaninov, A. Y., Chernyshev, I. V. and Shatagin, K. N. (2012) Isotope analysis of strontium by multicollector inductively-coupled plasma mass spectrometry: high-precision combined measurement of $^{88}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$ isotope ratios. *J. Anal. Chem.* **67**, 1084–1092.

Liu, H. C., You, C. F., Huang, K. F. and Chung, C. H. (2012) Precise determination of triple Sr isotopes ($\delta^{87}Sr$ and $\delta^{88}Sr$) using MC-ICP-MS. *Talanta* **88**, 338–344.

McArthur, J. M., Howarth, R. J. and Bailey, T. R. (2001) Strontium isotope stratigraphy: LOWESS version 3: best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age. *J. Geol.* **109**, 155–169.

Moynier, F., Agranier, A., Hezel, D. C. and Bouvier A. (2010) Sr stable isotope composition of Earth, the Moon, Mars, Vesta and meteorites. *Earth Planet. Sci. Lett.* **300**, 359–366.

Neymark, L. A., Premo, W. R., Mel'nikov, N. N. and Emsbo, P. (2014) Precise determination of $\delta^{88}Sr$ in rocks, minerals, and waters by double-spike TIMS: a powerful tool in the study of geological, hydrological and biological processes. *J. Anal. At. Spectrom.* **29**, 65–75.

Ohno, T. and Hirata, T. (2007) Simultaneous determination of mass-dependent isotopic fractionation and radiogenic isotope variation of strontium in geochemical samples by multiple collector-ICP-mass spectrometry. *Anal. Sci.* **23**, 1275–1280.

Ohno, T., Komiya, T., Ueno, Y., Hirata, T. and Maruyama, S. (2008) Determination of $^{88}Sr/^{86}Sr$ mass-dependent isotopic fractionation and radiogenic isotope variation of $^{87}Sr/^{86}Sr$ in the Neoproterozoic Doushantuo Formation. *Gondwana Res.* **14**, 126–133.

Patchett, P. J. (1980a) Sr isotopic fractionation in Ca-Al inclusions from the Allende meteorite. *Nature* **283**, 438–441.

Patchett, P. J. (1980b) Sr isotopic fractionation in Allende

chondrules: a reflection of solar nebular processes. *Earth Planet. Sci. Lett.* **50**, 181–188.

Rüggeberg, A., Fietzke, J., Liebetrau, V., Eisenhauer, A., Dullo, W.-C. and Freiwald, A. (2008) Stable strontium isotopes ($\delta^{88/86}$Sr) in cold-water corals—A new proxy for reconstruction of intermediate ocean water temperatures. *Earth Planet. Sci. Lett.* **269**, 570–575.

Russell, W. A. and Papanastassiou, D. A. (1978) Calcium isotope fractionation in ion-exchange chromatography. *Anal. Chem.* **50**, 1151–1154.

Russell, W. A., Papanastassiou, D. A. and Tombrello, T. A. (1978) Ca isotope fractionation on the earth and other solar system materials. *Geochim. Cosmochim. Acta* **42**, 1075–1090.

Scher, H. D., Griffith, E. M. and Buckley, W. P., Jr. (2013) Accuracy and precision of $^{88}$Sr/$^{86}$Sr and $^{87}$Sr/$^{86}$Sr measurements by MC-ICPMS compromised by high barium concentrations. *Geochem. Geophys. Geosyst.* **15**, 499–508.

Steiger, R. H. and Jäger, E. (1977) Subcommission on geochronology: convention on the use of decay constants in geo- and cosmochronology. *Earth Planet. Sci. Lett.* **36**, 359–362.

Stevenson, E. I., Hermoso, M., Rickaby, R. E. M., Tyler, J. J., Minoletti, F., Parkinson, I. J., Mokadem, F. and Burton, K. W. (2014) Controls on stable strontium isotope fractionation in coccolithophores with implications for the marine Sr cycle. *Geochim. Cosmochim. Acta* **128**, 225–235.

Veizer, J. (1989) Strontium isotopes in seawater through time. *Annu. Rev. Earth Planet. Sci.* **17**, 141–167.

Wakaki, S. (2012) Estimation of optimal isotopic compositions of Sr, Ba, Nd and Sm spikes for double spike thermal ionization mass spectrometry by error propagation simulation. *J. Earth Planet. Sci. Nagoya Univ.* **59**, 17–37.

Wakaki, S. and Tanaka, T. (2012) Stable isotope analysis of Nd by double spike thermal ionization mass spectrometry. *Int. J. Mass Spectrom.* **323–324**, 45–54.

Wei, G., Ma, J., Liu, Y., Xie, L., Ku, W., Deng, W. and Ren, Z. (2013) Seasonal changes in the radiogenic and stable strontium isotopic composition of Xijiang River water: Implications for chemical weathering. *Chem. Geol.* **343**, 67–75.

Young, E. D., Galy, A. and Nagahara, H. (2002) Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. *Geochim. Cosmochim. Acta* **66**, 1095–1104.