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

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Recent findings of natural strontium isotope fractionation have opened a new field of research in non-traditional stable isotope geochemistry. While previous studies were based on data obtained by MC-ICP-MS we here present a novel approach combining thermal ionization mass spectrometry (TIMS) with the use of an $^{87}Sr/^{84}Sr$ double spike (DS). Our results for the IAPSO sea water and JCp-1 coral standards, respectively, are in accord with previously published data. Strontium isotope composition of IAPSO sea water standard was determined as $\delta^{88/86}Sr$ = 0.386(5) ‰ (δ values relative to the SRM987), $^{87}Sr/^{86}Sr^*$ = 0.709312(9) n=10 and a corresponding conventionally normalized $^{87}Sr/^{86}Sr$ = 0.709168(7) (all uncertainties 2SEM). For JCp-1 coral standard we obtained $\delta^{88/86}Sr$ = 0.197(8) ‰, $^{87}Sr/^{86}Sr^*$=0.709237(2) and $^{87}Sr/^{86}Sr$ = 0.709164(5) n=3. We show that applying this DS-TIMS method the precision is improved by at least a factor of 2-3 when compared to MC-ICP-MS.

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1. Introduction

The Rubidium/Strontium (Rb/Sr) radiogenic isotope system is one of the oldest isotopic applications measured by mass-spectrometry [1, 2] and probably the most frequently applied one for absolute and stratigraphic age dating as well as for provenance studies [3, 4]. Thermal ionization mass spectrometry (TIMS) or alternatively multi-collector-inductively-coupled-plasma-mass-spectrometry (MC-ICP-MS) are the common methods in order to determine the radiogenic ingrowths and variations of $^{87}Sr/^{86}Sr$ from the radioactive beta minus decay of ^{87}Rb to ^{87}Sr via a half-live of about 48 billion years. TIMS and MC-ICP-MS based Sr isotope measurements usually provide an external reproducibility of ~10 to ~15 ppm because during the mass-spectrometer runs any fluctuation of the $^{87}Sr/^{86}Sr$-ratio due to mass and temperature dependent isotope fractionation is normalized and corrected relative to the commonly accepted $^{86}Sr/^{88}Sr$-ratio of 0.1194 [5]. Following this procedure only the radiogenic ingrowth of the $^{87}Sr/^{86}Sr$ can be determined whereas any other variation due to equilibrium or kinetic isotope fractionation is invisible and cannot be used to constrain additional geochemical information.

Recent studies applying the MC-ICP-MS combined with the bracketing standard method [6, 7] showed that the $^{88}Sr/^{86}Sr$-ratio of seawater ($\delta^{88/86}Sr$~0.381‰) significantly deviates from the $^{88}Sr/^{86}Sr$-ratio of SRM987 (per definition $\delta^{88/86}Sr$=0). In the same study [6] it was also found that $\delta^{88/86}Sr$ values of marine and artificially precipitated calcium carbonates show a temperature controlled isotopic difference of 0.17 to 0.36 ‰ between the carbonate precipitates and the bulk solution, with the carbonates isotopically lighter than the seawater. Either one or both major sources for Sr to the ocean (hydrothermal sources and continental weathering) must be fractionated relative to the SRM987.

Although bracketing standard is a suitable method to determine simultaneous natural fractionation of $^{87}Sr/^{86}Sr$ and $\delta^{88/86}Sr$, it can be assumed that TIMS in combination with a double-spike (DS-TIMS) may provide even higher precision and accuracy. So far MC-ICP-MS methods were burdened with the problem of potential fractionation during ion chromatographic Sr separation and the sensitivity for matrix effects during the ICP-MS measurements [6-10]. Both problems can be overcome by the use of an appropriate double spike.

Sr double spikes have already successfully been used in order to determine Sr isotope values for the early solar system [11, 12]. The application of a Sr double spike follows earlier attempts in the Pb-isotope analytic where double spikes have been used in the sixties of the last century [13] with recent progress in application induced by the pioneering work of Galer [14]. In order to use a DS for Sr isotope analysis at least two isotope measurements have to be performed. One unspiked run (ic-run, isotope composition) and one run with the double spike added to the sample solution (id-run, isotope dilution). Data reduction and the simultaneous calculation of $^{87}Sr/^{86}Sr^*$- ($^{87}Sr/^{86}Sr^*$ = fractionated $^{87}Sr/^{86}Sr$ ratio from our spike correction algorithm) and $\delta^{88/86}Sr$ can be performed following certain numerical procedures previously designed for Pb [13, 15-17] and Ca isotope analysis [18].

Here we present the application of a $^{87}Sr/^{84}Sr$ double spike for the simultaneous determination of $^{87}Sr/^{86}Sr^*$ and $\delta^{88/86}Sr$, respectively. The results of earlier studies could be reproduced with higher external precision [6, 7].

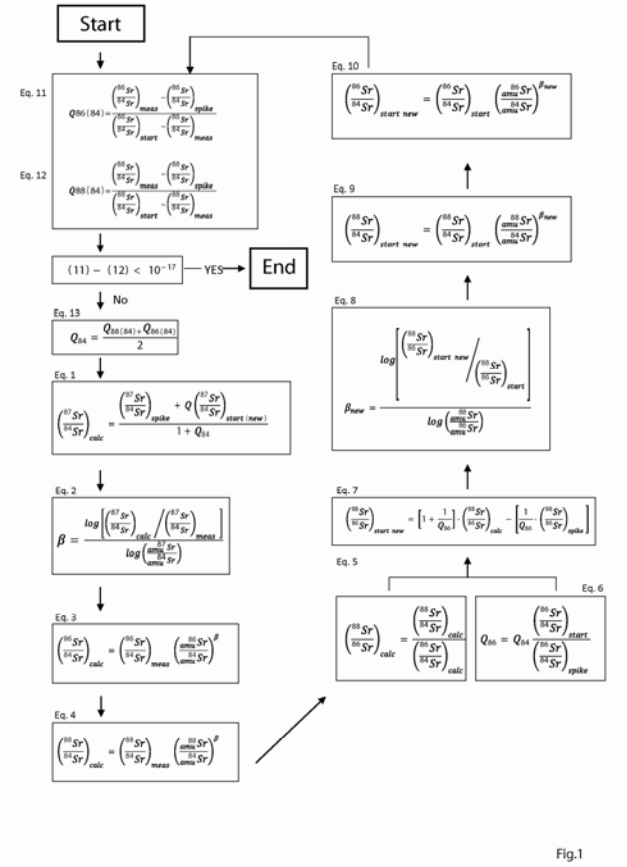


Fig.1

2. Experimental methods and TIMS measurement

2.1 $^{87}Sr/^{84}Sr$-double spike preparation

In order to prepare an $^{87}Sr/^{84}Sr$ spike solution we purchased two Sr-cabonates enriched in ^{84}Sr and in ^{87}Sr, respectively, from Oak Ridge National Laboratory, USA with a certified isotopic compositions given in Tab.1. The abundance of interfering ^{87}Rb was reported to be less than 1 ppm in the ^{84}Sr solution and less than 56 ppm in the ^{87}Sr solution. In order to reach the anticipated $^{87}Sr/^{84}Sr$-ratio of ~1 we mixed the two solutions in a way that the mixture consists of 48% of the ^{87}Sr-solution and 52% of the ^{84}Sr-solution, respectively. With the given abundances of Sr isotopes in the two solutions we calculated theoretical values for $^{86}Sr/^{84}Sr$-, $^{87}Sr/^{84}Sr$- and $^{88}Sr/^{84}Sr$-ratios of the desired $^{87}Sr/^{84}Sr$ spike solution. These values were used as start values for the calibration of the spike relative to the SRM987 $SrCO_3$ standard from the National Institute of Standards and Technology (NIST) as described below.

2.2 TIMS multicollector measurement procedure

Sr was extracted from all samples by using standard ion chromatographic procedure (Tab.2). Prior to the TIMS measurements the solutions were evaporated to dryness and redissolved in 2 µL H_3PO_4. For TIMS measurements rhenium ribbon single filaments are used in combination with a Ta_2O_5-activator which stabilizes the signal and enhances the ionization rate. About 2 µL of the Ta_2O_5-activator solution is first added on the filament and heated to near dryness at a current of about 0.5 A. Then 2 µL of the sample solution containing 250 to 500 ng Strontium were added to the activator solution and heated to dryness at a current of 1 A. Finally we increased the current to a value of 1.6 A and kept it there for about one minute until the sample color turned into a light brown. The last step in this procedure was to heat up the filament until a light red glow was visible. The current was kept at this setting for about 20 to 30 seconds. For the measurements of the SRM987 no column chemistry was necessary because of the negligible amounts of interfering ^{87}Rb in the standard material. Nevertheless aliquots of SRM987 standard material were also separated by the above mentioned ion exchange method showing no significant deviation from the untreated material.

Sr isotope measurements were carried out at the IFM-GEOMAR mass spectrometer facilities in Kiel, Germany, using a TRITON mass spectrometer (ThermoFisher, Bremen, Germany) which operates in positive ionization mode with a 10 kV

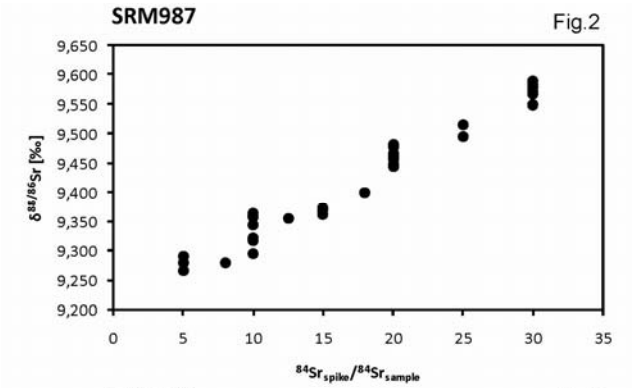
acceleration voltage and 10^{11} Ω resistors for the Faraday cups. The instrument is equipped with nine moveable Faraday cups as detection system which account for the dispersion of the whole Sr isotope mass range from ~84 to 88 amu, respectively.

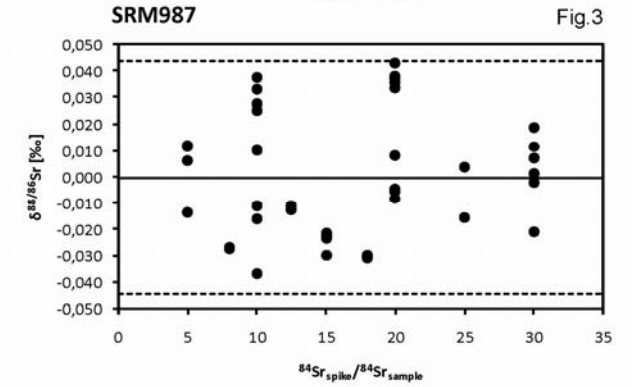
Mass 85 is measured in order to monitor the interfering ^{87}Rb. Prior to each measurement session a gain calibration of all amplifiers was carried out. Measurement started with a heatup-sequence (pyrometer controlled) heating up the filament by increasing the current to 2.6 A (ramping velocity of 0.5 A/min). The final current usually corresponds to a temperature of ~1380 °C. The ion beam was then automatically focused (including wheel focus) and peak centering was performed. Then the filament was slowly (0.05 A/min) heated up to ~3.2 A corresponding to a temperature of ~1430 to 1490 °C. When the signal intensity reached 6 V on mass 88, data acquisition was started. 14 scans with 17 seconds integration time and 3 seconds idle time eachare summarized to one block. For each sample 9 blocks corresponding to 126 scans were measured. Before each block the baseline (deflected beam) was recorded and the amplifier rotation was performed.

Applying the double spike technique at least two separate runs for one measurement are necessary: one ic-run and one id-run where the ^{86}Sr/^{84}Sr-, ^{87}Sr/^{84}Sr- and ^{88}Sr/^{84}Sr-ratios are determined. To correct for isotope fractionation during TIMS measurement the ^{86}Sr/^{84}Sr, ^{87}Sr/^{84}Sr and the ^{88}Sr/^{84}Sr-ratios are normalized to the mean of the first block of the ^{87}Sr/^{84}Sr isotope ratio.

2.3 Double spike algorithm

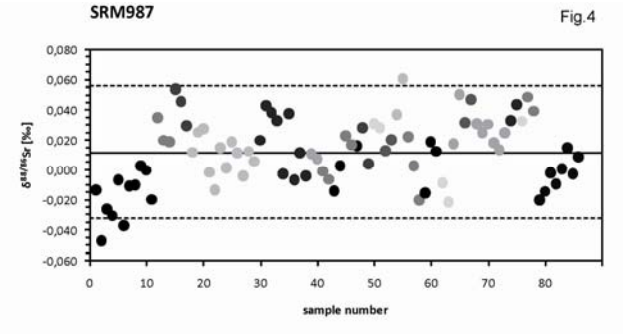
The mean of the measured and normalized ^{86}Sr/^{84}Sr-, ^{87}Sr/^{84}Sr- and ^{88}Sr/^{84}Sr-ratio of the two ic-runs are taken as start values for the spike correction algorithm (Fig.1). The results of the id-runs need to be denormalized and corrected for the added DS. In order to decompose the sample/spike mixture we used an iterative routine closely following the one presented earlier for Ca-isotopes [18] based on the classical isotope dilution equation and on an similar algorithm presented earlier for Pb isotopes [13].





Our algorithm (Fig.1) starts with the calculation of the sample to spike ratio (Q86(84)=Q88(84)=$^{84}Sr_{sample}/^{84}Sr_{spike}$) from the measured ^{86}Sr/^{84}Sr (Q86(84)) and ^{88}Sr/^{84}Sr (Q88(84)) ratios and their corresponding values of the id- and ic-run (eqs.11 and 12 in Fig.1). Although the approximation of $^{84}Sr_{sample}/^{84}Sr_{spike}$ from Q86(84) and Q88(84) are supposed to be identical they differ to a certain extend prior to the denormalization procedure. The $^{87}Sr/^{84}Sr_{calc}$ (eq.1) can be calculated from the ^{87}Sr/^{84}Sr-ratio of the ic-run and the ^{87}Sr/^{84}Sr-ratio of the spike as well as from the mean of Q86(84) and Q88(84) in eq.13, respectively. Comparison of $^{87}Sr/^{84}Sr_{calc}$ and $^{87}Sr/^{84}Sr_{meas}$ in eq.2 then allows the calculation of a fractionation factor ß which is used to denormalize the ^{86}Sr/^{84}Sr and ^{88}Sr/^{84}Sr-ratios in eq.3 and 4, respectively. A first approximate ^{88}Sr/^{86}Sr-ratio can then be determined by a comparison of $^{88}Sr/^{84}Sr_{calc}$ and $^{86}Sr/^{84}Sr_{calc}$ (eq.5), respectively. From Q86 (eq.6) and $^{88}Sr/^{86}Sr_{calc}$ a new ^{88}Sr/^{86}Sr is determined (eq.7) which is then used for iterative calculation of an improved Sr isotope fractionation factor ($ß_{new}$). This $ß_{new}$ allows us to calculate new start values for the algorithm (eq.9 and 10). They again are used to simultaneously calculate Q86(84) and Q88(84). The algorithm usually needs ~20 iterative steps in order to meet the stop criteria being the difference of Q86(84) and Q88(84) smaller than $1 \cdot 10^{-17}$. Latter stop criteria guarantees that $ß_{new}$ becomes zero.

The $^{88}Sr/^{86}Sr$-ratios are reported in the common δ-notation. The session offset corrected $^{88}Sr/^{86}Sr$-ratios are normalized to the accepted value $^{88}Sr/^{86}Sr=8.375209$ and reported in the usual δ-notation (Eq.1) as defined earlier [6].

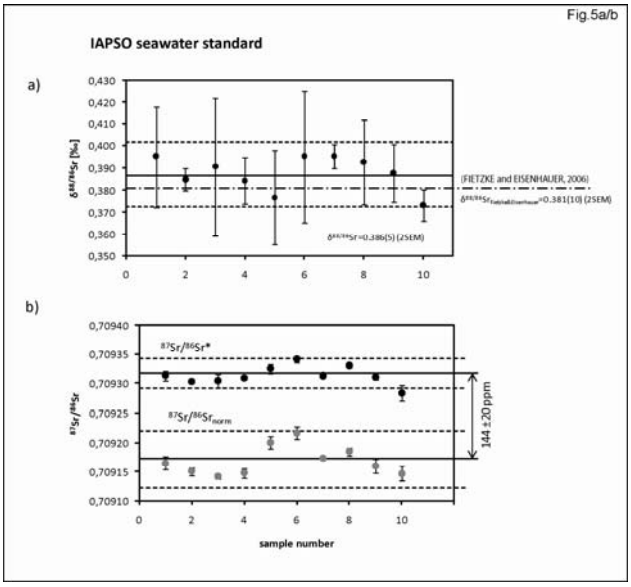


Eq.1 $$\delta^{88/86}Sr = \left(\frac{\left(\frac{^{88}Sr}{^{86}Sr}\right)_{sample}}{\left(\frac{^{88}Sr}{^{86}Sr}\right)_{SRM987}} - 1 \right) \cdot 1000$$

3. Results

3.1 Spike calibration

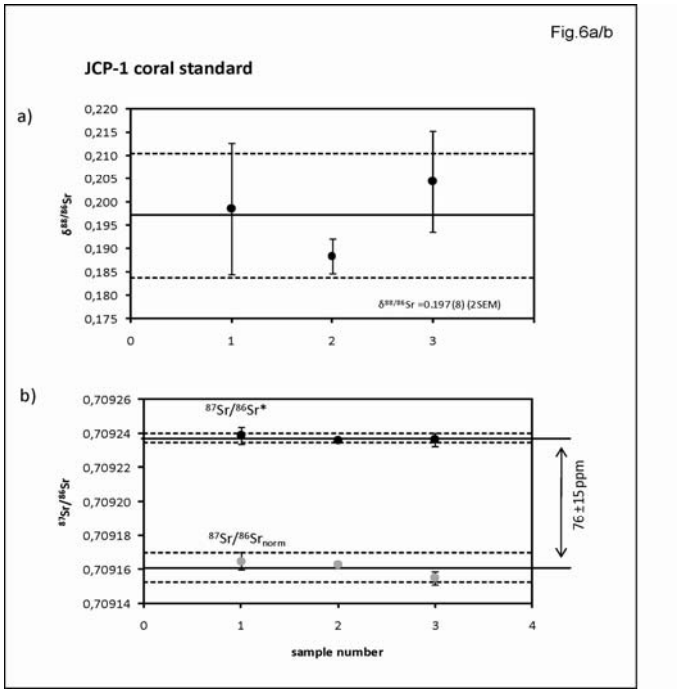
In order to perform double spike calibration measurements we used two different Sr standards: (1) NIST SRM987 and (2) the international seawater standard IAPSO. The first one was needed to calibrate the double spike and worked as a general reference standard for all of our measurements. The second standard has a known offset to the SRM987 in its $\delta^{88/86}Sr$-value of ~0.381(10) ‰ and serves as an independent control point [6].



For calibration and spike optimization the SRM987 standard solutions were spiked with different amounts in order to produce solutions with $^{84}Sr_{spike}/^{84}Sr_{sample}$ ratios in a range from 5 to 30. The calculated spike isotope ratios using the certified isotope compositions of the enriched solutions (Tab.1) produced results showing that the $\delta^{88/86}Sr$ values vary with the $^{84}Sr_{spike}/^{84}Sr_{sample}$-ratio (Fig.2). This is a consequence of the deviation of the calculated spike values from the real composition. In order to extract the real composition and for an optimization procedure we generated the least square sum of all measured $\delta^{88/86}Sr$ values of SRM987 and minimized it by slightly varying the spike isotope ratios using a least square fit which was performed with the solver function of Microsoft Excel®. After this optimization procedure no further dependency of the $\delta^{88/86}Sr$ on the $^{84}Sr_{spike}/^{84}Sr_{sample}$

ratio could be found (Fig.3). Latter values are then assumed to be the best approximation of the "true" Sr double spike composition as presented in Tab.3.

During the course of the double spike calibration ~40 measurements of SRM987 standard with varying $^{84}Sr_{spike}/^{84}Sr_{sample}$ ratios have been performed. The typical internal precision of the single measurements was 7 ppm (RSD) for the $^{86}Sr/^{84}Sr$-ratio and 9 ppm for the $^{88}Sr/^{84}Sr$-ratio in the ic-runs. We measured 11 ppm (RSD) for the $^{86}Sr/^{84}Sr$-ratio and 21 ppm for the $^{88}Sr/^{84}Sr$-ratio in the id-run. The internal precision correlates with the $^{84}Sr_{spike}/^{84}Sr_{sample}$-ratio.
Concerning error propagation we found that a $^{84}Sr_{spike}/^{84}Sr_{sample}$ ratio of ~20 provide the optimal composition for sample measurements.



3.2 Results of standard measurements

Our measurements show that there are significant session-to-session variations in the isotopic ratios of the standard SRM987 measurements (Fig.4). This behavior is also known for other isotope measurements using TIMS. The reasons for this phenomena are not entirely known. Potential sources could be e.g. the Faraday Cup degradation or differing source vacuum conditions due to the use of two distinct cryo traps. In order to account for this observation we calculated the mean of the fractionation corrected isotope $\delta^{88/86}Sr$- and $^{87}Sr/^{86}Sr$*-ratios of SRM987 and determined its offset to the accepted value for $^{88}Sr/^{86}Sr = 8.375209$ ($\delta^{88/86}Sr=0$) and $^{87}Sr/^{86}Sr = 0.710240$, respectively [5]. This offset was then used to correct the corresponding values of every single sample and resulted in the session corrected $\delta^{88/86}Sr$- and $^{87}Sr/^{86}Sr$*-values.

During the course of this project the $\delta^{88/86}Sr$- and $^{87}Sr/^{86}Sr$*-values of the IAPSO seawater standard (Fig.5a/b) were found to be 0.386(5)‰ and 0.709312(9) (2SEM, n=10), respectively. The $\delta^{88/86}Sr$ value for the IAPSO is in general accord with the value determined earlier [6]. The $^{87}Sr/^{86}Sr$* value is significantly different from the accepted $^{87}Sr/^{86}Sr_{norm}$ seawater ratio of 0.709168(7). Latter difference of 144 ppm (Fig.5a/b) is due to the conventional normalization procedure where the measured $^{87}Sr/^{86}Sr$ ratio is normalized to a constant $^{88}Sr/^{86}Sr$-ratio of 8.375209 ($\delta^{88/86}Sr=0$) neglecting any kind of Sr isotope fractionation. Renormalization of our measured $^{87}Sr/^{86}Sr$* value of 0.709312(9) to a $\delta^{88/86}Sr$ value of zero results in an average value of $^{87}Sr/^{86}Sr_{norm}$ 0.709166(9) which is in accord with the generally accepted radiogenic $^{87}Sr/^{86}Sr$-ratio for seawater [19, 20]. This is not a contradiction to the above stated value of $^{87}Sr/^{86}Sr$=0.709168(7) of seawater but a consequence of two different ways of calculating the $^{87}Sr/^{86}Sr_{norm}$ and $^{87}Sr/^{86}Sr$*, respectively. The first value is purely the result of the conventional Sr measurement (ic-run) while the latter uses both measurements (ic-/ id-run) for the calculation.

The values for the modern coral standard JCp-1 are plotted in the same way as for the IAPSO above (Fig.6a/b). The measurements show a value of 0.197(8) ‰ (2SEM) for $\delta^{88/86}Sr$ and of 0.709237(2) for the $^{87}Sr/^{86}Sr$* ratio. There is a significant difference of the $\delta^{88/86}Sr$ values for JCp-1 and IAPSO in the order of 189±9 ppm. Similar to this observation there is also a significant 75±15 ppm difference between our measured $^{87}Sr/^{86}Sr$* ratio for JCp-1 and seawater (0.709312(9)). The ~80 ppm difference of the JCp-1 carbonate standard to the IAPSO seawater standard in the $^{87}Sr/^{86}Sr$* and the ~2 times larger difference in the $\delta^{88/86}Sr$-value indicate mass- and probably temperature dependent Sr isotope fractionation during the precipitation of $CaCO_3$ from seawater. This results are in accord with earlier studys [6-8].

Comparison of our data with previous studies show that the here presented DS-TIMS method produces accurate results. The major advantage of our method is the 2-3 times better external precision. Additionally the use of a double spike solves the problems inherent in published MC-ICP-MS methods like fractionation during chemical sample pretreatment and matrix related mass bias fluctuations.

The analytical blank was determined to 0.3 ng of Sr which was considered to be neglectable.

4. Conclusions

With our DS-TIMS method we are able to determine the stable $\delta^{88/86}Sr$ and the radiogenic $^{87}Sr/^{86}Sr^*$ simultanously. The use of a double spike overcomes the problem of any uncontrolled fractionation during sample pretreatment in particular ion chromatographic separation of Strontium from the sample matrix. The external precision could be improved by a factor of 2-3 compared to established MC-ICP-MS methods. Finally this DS-TIMS method is not burdened by mass bias fluctuations known from MC-ICP-MS bracketing standard approaches.

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Notes and references

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Figure captions:

Fig. 1: Flow Chart of the Sr-double spike algorithm applied in order to denormalize measured $^{88}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$ data and to calculate paired $^{87}Sr/^{86}Sr^*$-$\delta^{88/86}Sr$ values. Usually about 20 cycles are necessary in order to achieve the desired precision.
Fig. 2: The SRM987 standard solutions were spiked with different amounts of spike in order to produce solutions with $^{84}Sr_{sample}/^{84}Sr_{spike}$ ratios in a range from 5 to 30. We observed that the measured $\delta^{88/86}Sr$ values are positively correlated with the $^{84}Sr_{spike}/^{84}Sr_{sample}$-ratio when using the spike isotope ratios for $^{86}Sr/^{84}Sr$, $^{87}Sr/^{84}Sr$ and $^{88}Sr/^{84}Sr$ as calculated from the reported certified values.
Fig. 3: After optimization of the spike ratios there is no further dependency of the $\delta^{88/86}Sr$ from the $^{84}Sr_{spike}/^{84}Sr_{sample}$ -ratio. The black line marks the average value of ~0 and the broken line the 2SD standard deviation from the defined value.

Fig. 4: Longterm session-to-session variations for the SRM987 standard result in a $\delta^{88/86}Sr_{mean}$ of ~0.012±0.044 (2sd). Different color mark different measurement sessions of SRM987. Black line marks the average value and the broken lines mark the 2sd-standard deviation.

Fig. 5a: Longterm measurements of the IAPSO seawater standard. Every data point represents the mean of up to 5 single measurements of the same solution. The determined value of $\delta^{88/86}Sr_{mean}$=0.386±0.005 (2SEM) of the measurements (black linke) are in agreement with previous data. The error bars are 2SD (broken lines).

Fig. 5b: $^{87}Sr/^{86}Sr^*$ (black points) and $^{87}Sr/^{86}Sr_{norm}$-values (grey points) of the IAPSO seawater standard are signifcanty different ($^{87}Sr/^{86}Sr^*$=0.709312(9); $^{87}Sr/^{86}Sr_{norm}$=0.709173(18)) corresponding to a value of ~144±20 ppm.

Fig. 6a: The $\delta^{88/86}Sr_{JCp\text{-}1\text{-}mean}$=0.197(8) (2SEM, black line) of the coral standard JCp-1 measurements. Every data point represents the mean of up to 3 single measurements of the same solution. Note, that the $\delta^{88/86}Sr_{JCp\text{-}1\text{-}mean}$ is about a factor of 2 isotopically lighter than $\delta^{88/86}Sr_{Seawater}$ due to mass dependent isotope fractionation. The error bars are 2SD (broken lines).

Fig. 6b: $^{87}Sr/^{86}Sr^*$- (black points; 0.709237(2)) and $^{87}Sr/^{86}Sr_{norm}$ -values (grey; 0.709164(15)) of coral standard JCp-1 are significantly different. Note that the $^{87}Sr/^{86}Sr^*$ of JCp-1 is isotopically lighter than $^{87}Sr^{86}Sr^*$ of seawater by ~80 ppm.

Tables:

Tab. 1: Original isotope composition of the two Oak Ridge National Laboratory Sr carbonate standards:

	^{84}Sr (%)	^{86}Sr (%)	^{87}Sr (%)	^{88}Sr (%)	Solution
1.	~0.01	0.82(2)	91.26(10)	7.91(10)	^{87}Sr-Solution
2.	99.64(1)	0.14(1)	0.03(1)	0.19(1)	^{84}Sr-Solution

Tab. 2: Sample treatment

step	description
1	Addition of 2 ml 4.5 N HNO_3 to the weighed and grinded sample
2	Splitting the samples into two fractions
3	Addition of the spike solution to one fraction
4	Drying the samples at ~90°C
5	Column separation of the spiked and unspiked sample. BIO-RAD 650 µl columns with Eichrom Sr-SPS resin (mesh size 50-100 µm). To perform this separation we filled the columns to one third with the resin followed by a washing procedure
6	Drying the separated samples at ~90°C
7	Addition of 200 µl 4.5 N HNO_3 and 50 µl 30 % H_2O_2 and heating the solution in a closed beaker at least 5 hours at ~80°C
8	Drying the sample at ~80°C
9	Loading the sample with 2µL H_3PO_4 solution onto Re filaments
10	Measuring the samples

Tab. 3: Sr double spike composition:

$^{86}Sr/^{84}Sr$	$^{87}Sr/^{84}Sr$	$^{88}Sr/^{84}Sr$
0.009898	0.925937	0.083292