

# An alternative data acquisition and evaluation strategy for improved isotope ratio precision using LA-MC-ICP-MS applied to stable and radiogenic strontium isotopes in carbonates

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Strontium isotopes in various marine carbonates were determined using an “AXIOM” MC-ICP-MS in combination with a NewWave UP193 laser ablation unit. Using a modified measurement and data reduction strategy, an external reproducibility of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in carbonates of about 19 ppm (RSD) was achieved. For recent and sub-recent marine carbonates a mean radiogenic strontium isotope ratio  $^{87}\text{Sr}/^{86}\text{Sr}$  of  $0.709170 \pm 0.000007$  (2SE) was determined, which agrees well with the value of  $0.7091741 \pm 0.0000024$  (2SE) reported for modern sea water (J. M. McArthur, D. Rio, F. Massari, D. Castrodi, T. R. Bailey, M. Thirlwall and S. Houghton, *Palaeogeogr. Palaeoclimatol. Palaeoeco.*, 2006, **242**(126), 2006). Compared to published laser-based methods, an improved accuracy and precision was achieved by applying a new data reduction protocol using the simultaneous responses of all isotopes measured. The latter is considered as a new principal approach for isotope ratio evaluation using LA-MC-ICP-MS. A major advantage of the presented method is the direct determination of the stable strontium isotope fractionation. Providing reproducible sample ablation, introduction into the plasma and stable plasma condition, this method excludes the efforts of a quantitative strontium recovery after ion chromatographic separation to avoid additional fractionation of the sample strontium due to chemical pre-treatment/separation (ion chromatography and solution preparation), and is therefore, together with the quicker sample preparation and spatially resolved analysis, advantageous when compared to published solution–nebulization bracketing-standard MC-ICP-MS methods for stable strontium isotope determination.

## Introduction

LA-ICP-MS is predominantly applied to determine spatially resolved element abundances in solid samples. Beside this application, only a few isotope geochemical applications, e.g. U/Pb zircon dating, are routinely measured.<sup>1</sup> This is mainly based on the fact that laser ablation prohibits any kind of matrix removal prior to isotope analysis, which significantly increases the risk of matrix related interferences superimposing the signals of the isotopes of interest.<sup>2</sup> This serious disadvantage for isotope applications is compensated by benefits such as the absence of any chemical pre-treatment of the sample, and thus, no procedure related additional blank and no isotope fractionation due to ion chromatography.

Over the last decade non-traditional stable isotopes have become a vitally growing field in geochemistry. Especially in marine geochemistry, carbonates are useful archives to reconstruct environmental parameters such as temperature, salinity or pH.<sup>3,4</sup> Divalent cations, their abundances and fractionated

isotopic ratios, contribute to the reconstruction of former parameters.<sup>5,6</sup> In particular, the fractionation of stable isotopes of calcium and strontium in carbonates have already been demonstrated to be temperature dependent.<sup>7,8</sup>

This recent development extended the application of strontium isotopes in environmental sciences, which was focusing on the radiogenic Sr isotope ratio  $^{87}\text{Sr}/^{86}\text{Sr}$  before, using the stable Sr isotope ratios  $^{86}\text{Sr}/^{88}\text{Sr}$  for normalization purposes. Sr isotopes stratigraphy (SIS), a tool to date marine carbonates, is a typical application of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in geochemistry.<sup>9,10</sup> Additionally, numerous authors used the radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  for provenance studies.

After publishing the temperature dependent strontium isotope fractionation, the question arose as to whether this would affect previous radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  results, in particular if the radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  of carbonates precipitated in the ocean and the ocean water itself would differ from each other. This is certainly not the case, as for both the same accepted value of  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$  is used to correct for any isotope fractionation, effectively erasing the mentioned temperature effect. Nevertheless, the stable strontium isotope fractionation was confirmed and further studied by different other authors.<sup>11–15</sup>

Starting with the study by Christensen *et al.* (1995) several authors published *in situ* determination of radiogenic Sr isotope ratios  $^{87}\text{Sr}/^{86}\text{Sr}$  and its application.<sup>16–20</sup> Analytical problems, such

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as appropriate correction for interferences, have already been studied and discussed in detail.<sup>18,20–22</sup> Therefore, occurring interferences and their influence will not be discussed within this study. However, they were considered and taken into account in our method development.

The Sr concentrations in this study range from about 1000 ppm (Cenozoic carbonates) and 3000 ppm (cod otolith) to about 12 000 ppm (cold seep carbonate), while Rb concentrations were close to zero. This is fairly common in biogenic marine carbonates, which form a huge group of interesting samples for marine biogeochemists *e.g.* as paleo-proxy archives. Thus, it is far more than just a rare special case and represents a major research focus in a number of research institutes.

The aim of this study was focused on strategies to improve precision. Therefore, a new data reduction protocol using the simultaneous response of all measured isotopes was developed. The proposed approach illustrated in this study on strontium isotopes is considered to be transferable to other isotope ratio systems analysed by LA-MC-ICP-MS.

## Experimental

### Instrumentation and data acquisition

The Sr isotope measurements were carried out using an AXIOM MC-ICP-MS coupled to a NewWave's UP193FX (FX – fast excimer) or UP193 solid state laser ablation unit, respectively. Typical operating conditions are summarized in Table 1.

Samples were cut to fit into the ablation chamber and fixated using Pattafix™. Prior to analysis, a 2 s pre ablation was carried out on all respective spots. Fine laminations in the carbonate samples were ablated in line scans. Broad laminations were ablated using a square raster of 100 × 100 μm. The target ion beam intensity for <sup>88</sup>Sr was 5 to 8 V. The laser spot sizes (typically 25–50 μm) and repetition rates (typically 10–20 Hz) were adjusted depending on the Sr intensity measured in the sample and the thickness of laminations.

For data collection, 7 of the 10 Faraday Cups of our AXIOM MC-ICP-MS were used, with amu86 at the axial cup and 3 more cups positioned 1 amu apart on both the low and high mass side, respectively.

Samples were ablated typically for 30 to 50 s followed by a 120 to 150 s post ablation period. During the latter, residual sample material was effectively washed out of the ablation cell by the He

carrier gas flow and the signals decreased to the respective baseline levels. An integration time of 6 s per data point was applied throughout the entire study.

No significant intensities of doubly charged ions and dimers were measured (<sup>48</sup>Ca<sub>2</sub><sup>+</sup>/<sup>48</sup>Ca<sup>+</sup> < 0.02%, <sup>87</sup>Sr<sup>2+</sup>/<sup>87</sup>Sr<sup>+</sup> < 0.4%).

The hydride generation was monitored at amu89. We found no statistically significant deviation of the amu89 signal from the baseline while ablating the samples. This implies both no detectable Y concentrations in the analysed carbonate samples and no significant variation in ArH during sample runs.

For this application we tuned our plasma to minimize polyatomic interferences because we considered them to be of higher importance than the doubly charged REE.

Changes of the Kr signal due to ablation were monitored at amu83. However, the Kr signal showed no statistically significant variation between solid sample introduction and the post ablation periods, which provides evidence for stable backgrounds of <sup>84</sup>Kr and <sup>86</sup>Kr.

For stable strontium determinations the well-known sample-standard bracketing approach was adopted, involving repeated switching between two distinct samples or sample areas, respectively.<sup>8</sup> The latter was chosen to correct for any drifts in the instrumental fractionation (mass bias) which, nevertheless, was found to be stable within 50 ppm h<sup>-1</sup> for <sup>88</sup>Sr/<sup>86</sup>Sr. The figures of merit using this approach will be discussed in the following chapter.

Elemental concentration profiles of the laminated non-skeletal precipitated carbonate samples were determined using LA-ICP-QMS at the ETH Zurich using a GeoLas M 193 nm excimer laser system (Lambda Physik, Göttingen Germany) in combination with a PerkinElmer Sciex Elan DRC II Quadrupol-ICP-MS (Perkin Elmer, Norwalk, USA)

The element concentrations were determined using a spot diameter of 80 μm, 5 Hz and a fluence of 17 J cm<sup>-2</sup>. A period of 30 s was used to measure background intensities and the samples were ablated for 60 s. The data reduction was carried out using the protocol described in Longerich *et al.* (1996).<sup>23</sup> External calibration was carried out using NIST610 glass standard and Ca was used as internal standard. A number of traverses were ablated across various growth zones of the carbonates by using single hole drilling.

### Data evaluation

The major difference in the data evaluation applied here compared to previously reported studies is the use of the dynamic response in the simultaneously collected isotope signals. We neither collect background data separately nor integrate just selected parts of the data collected for the data reduction. Prior to ablation, all cups collect baseline data as on-peak-zeros. Thus, we collect all data relative to a baseline that includes the Kr contributions from the Ar and He supply. When the ablation starts, all cups simultaneously envisage the signal increase with respect to the abundances of the isotopes (and interferences) and were measured. Therefore, all signal variations contribute evenly to the simultaneously collected data. After the ablation was stopped, the signal decrease to the baseline intensity was simultaneously recorded by all detectors. The isotope ratios can then be derived directly from the slope of a linear fit (using the

**Table 1** Instrumental parameters

<b>AXIOM MC-ICP-MS</b>	
Cool gas	14 l min <sup>-1</sup> (Ar)
Auxiliary gas	1.8 l min <sup>-1</sup> (Ar)
Nebulizer gas	0.8 l min <sup>-1</sup> (Ar)
RF power	1000 W
Reflected power	2 W
Ion energy	4968 V
Cones	R.A. Chilton RAC19/RAC705
Resolution	500 res
<b>UP193solid state/UP193FX</b>	
Ablation cell gas	0.7 l min <sup>-1</sup> (He)
Spot size	25–50 μm
Fluence	6 J cm <sup>-2</sup>
Repetition rate	10–20 Hz
Scan mode	Line/raster with 5 μm s <sup>-1</sup> scan speed

INDEX(LINEST(...)) function of MS EXCEL) of all data collected (with and without ablation running) by the particular pairs of cups, using the following consideration:

$86_{\text{gross}} = r_{\text{Sr}86} I_{\text{Sr}} + 86_{\text{back}}$ , where  $86_{\text{gross}}$  is the actual signal at amu 86,  $r_{\text{Sr}86}$  is the relative abundance of  $^{86}\text{Sr}$ ,  $I_{\text{Sr}}$  is the Sr intensity and  $86_{\text{back}}$  the background at amu 86, measured as baseline on top of the peak. The differential of the above equation (considering a constant background contribution) follows as:  $\partial 86_{\text{gross}} = r_{\text{Sr}86} \partial I_{\text{Sr}}$ . Similar equations can be used for the other isotopes.

Thus, the slope of the ideal signal responses on amu 86 and amu 88 is given by:  $m = \frac{\partial 86_{\text{gross}}}{\partial 88_{\text{gross}}} = \frac{r_{\text{Sr}86} \partial I_{\text{Sr}}}{r_{\text{Sr}88} \partial I_{\text{Sr}}} = \frac{r_{\text{Sr}86}}{r_{\text{Sr}88}} = \frac{\text{Sr}86}{\text{Sr}88}$ . The best approximation is thus the linear regression of the simultaneously measured intensities of the respective masses. This fit is better defined the higher the Sr signal departs from the baseline.

An example is presented in the results section of this paper. Using such a procedure avoids the splitting of a data set into a background and a data collection period. The advantages are:

(1) Subjective influence which may occur by setting the integration limits is avoided.

(2) All data are included and used for the evaluation.

(3) Each data point contributes to the fit depending on its signal intensity. This data treatment is not differentiating between periods with or without ablation and all data (including baseline values) are treated as equally valid.

(4) Deviations from the ideal linear fit (due to transient contributions of interferences or changing fractionation during the ablation) are detectable, e.g. in another method using a similar data reduction for stable chlorine isotope ratios this helped to identify interference contributions from ArH.<sup>24</sup>

The influence of such a data reduction method on precision and accuracy is demonstrated and discussed in the section below. One might argue that subjective decisions could be necessary to separate data from different phases of the sample (e.g. inclusions). This is in principle true, but:

(1) Inclusions would be visible while not following the dominant linear trend of the majority of data using our data reduction protocol.

(2) So far we could not find inclusions in all our biogenic marine carbonate samples.

Furthermore, we would have definitely found these inclusions in our multi-element measurements.

For all isotope ratio calculations the slopes of respective fits were used. Radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  data were normalized to a  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.1194 using the exponential law in the following form:

$\frac{R_{\text{meas}}}{R_{\text{true}}} = \left(\frac{m_1}{m_2}\right)^\beta$ , where  $R$  represents the measured, respectively true isotopic ratio of two isotopes with the masses  $m_1$  and  $m_2$ .

Prior to the normalization, the amu87 data were corrected for  $^{87}\text{Rb}$  contributions applying an  $^{87}\text{Rb}/^{85}\text{Rb}$  ratio of 0.385654 and the fractionation corrected 85/86 ratio (exponential law, using the  $\beta$  derived from the measured  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio for both Rb and Sr isotope normalization).

Stable Sr isotopes ( $\delta^{88/86}\text{Sr}$ ) were determined using a bracketing standard approach. Therefore, the ablation position was switched alternating between two distinct sample areas while continuously collecting data (30 s with and 120 s without ablation). We used aragonite to bracket aragonite, so this is supposed to be best possible matrix matching. Any fractionation from the

ablation itself would affect both in a similar way. After the measurement, the data of each distinct area were pooled for evaluation. This is advantageous because it largely compensates for instrumental drifts.

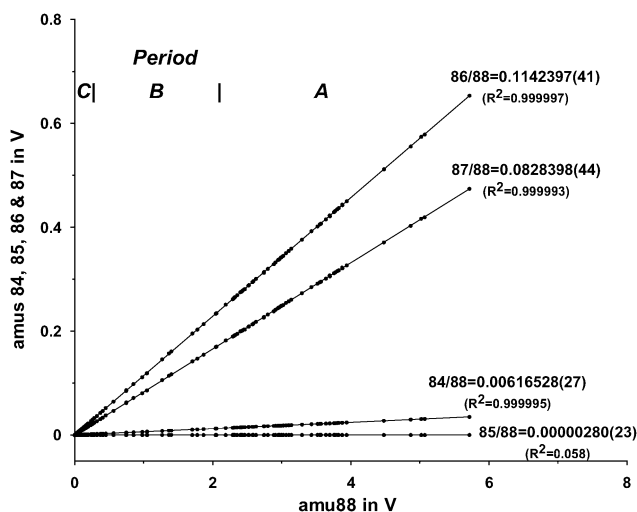
## Results and discussion

### Radiogenic Sr isotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) applications

To test and validate the measurement and calculation procedure, data were collected using a sample (SEK1) of cold seep related carbonate from South East Knoll/Hydrate Ridge (off Oregon) collected during RV "SONNE" cruise SO165. Before carrying out isotopes studies, elemental concentration profiles of the laminated non-skeletal precipitated carbonate samples were determined using LA-ICP-QMS at the ETH Zurich. In the sample region ablated in this study a mean Sr concentration of approx. 8000 ppm was determined.

For the here presented LA-MC-ICP-MS method, the dynamic responses of the signals on amu 84...88 are shown in Fig. 1 using raw data only. It can be seen that the signals follow a linear function between the on-peak-zero-baseline and the maximum intensity during ablation. The raw data ratios further used for isotope ratio calculations are given in Fig. 1 and were calculated from the best linear fit including their respective 2SE uncertainties (in brackets). We used the INDEX(LINEST(...)) function of MS EXCEL to calculate the parameters of a linear regression using our data. This function provides both the slope ( $m$ ) and the SE of  $m$ . No statistical weighting was applied.

Amu 83 (about 0.05 mV) representing the contribution of  $^{83}\text{Kr}$  indicated no significant changes of the krypton background



**Fig. 1** Simultaneous responses of the signals of amu 84–87 vs. amu 88 (exclusively raw data!). Numbers in the first brackets address the 2SE of the fitted slope. A, B and C refer to the periods of transient signal development discussed in the text. Note, even if 85/88 appears to be a straight line in this plot the amu 85 signals are too low to be correlated to amu 88 (low  $R^2$ ). Not displayed here is the 87/86 result for this data set being 0.725141(15) ( $R^2 = 0.999999$ ). Also not displayed is the 83/88 result of  $-0.0000004(15)$  and 89/88 result of  $0.0000012(14)$ , respectively, indicating no significant variations of the  $^{83}\text{Kr}$  background or influences of ArH or Y interferences.

during the ablation. Based on the amu 89 signal response, a measure for  $^{88}\text{SrH}^+$ , the hydride generation was determined to be negligible for our measurement.

This sample (SEK1) was used to test the method for both stable and radiogenic Sr isotope determination. We thus measured the selected sample regions 9 times using 30 s for each sampling of the material. Our data reduction result in an  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for this sample region of  $0.709178 \pm 0.000015$  (2SE) which is almost as good as conventional liquid-introduction MC-ICP-MS. The latter, which was performed with AXIOM/ARIDUS/APEX (technical details in Fietzke and Eisenhauer, 2006) provided an  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.709178 \pm 0.000010$  (2SE).<sup>8</sup>

For comparison, the same LA-MC-ICP-MS data set was evaluated using the conventional method using separate background reduction.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were calculated for each individual data point using the same corrections as described in the data evaluation paragraph. Finally, a  $2\sigma$ -outlier test was performed. Compared to the mean  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (Fig. 2) of  $0.709130 \pm 0.000076$  (2SE), the result using the data acquisition and calculation proposed in this study is approx. 4–5 times more precise and also more accurate.

To explain this improvement using the same data, a more detailed look into the 3 periods of transient signal development is necessary.

(A) During sample ablation the signal beam intensity of  $^{88}\text{Sr}$  varied between about 2.5 V and 6 V.

(B) After the ablation stopped residual material was transported from the ablation cell into the plasma contributing signal beam intensities decreasing from 2.5 V to

(C) the baseline level.

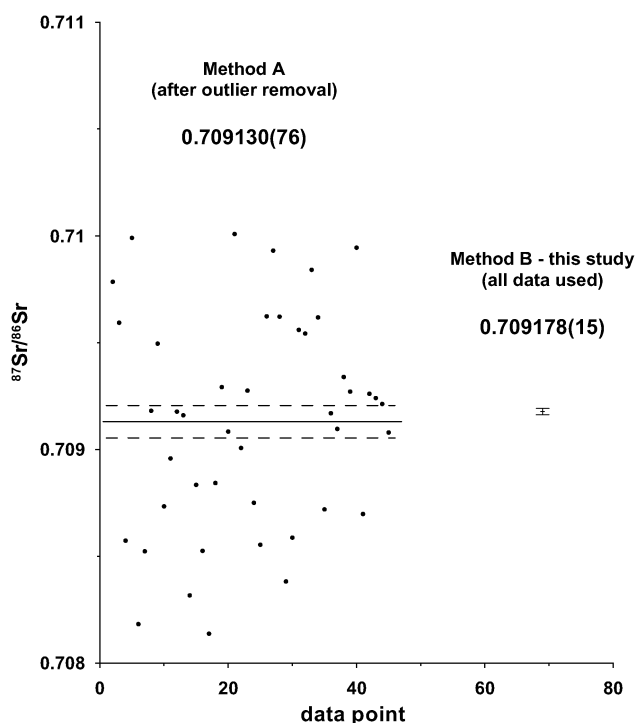
Conventionally, (B) is excluded from the data evaluation. From Fig. 1, it is visible that data from period (B) follow strictly the same trend (linear fit) as defined by the data of period (A) and (C). Thus, it appears to us these data are sample related (residual wash out from the ablation cell) and can be included into the data evaluation. This has the additional advantage that eventually occurring subjective influences by setting the integration limits for (A) and (C) are minimized and the entire data set is evaluated.

The data of period (A) are conventionally taken as statistically equal. Just from the point of counting statistics the uncertainties of individual data points of period (A) differ by a factor of 1.55 (square root of the ratio of maximal and minimal signal intensity: 360 Mcps/150 Mcps). Thus, it would be necessary to calculate an error-weighted mean of these data. Using the linear regression (INDEX(LINEST(...)) function of MS EXCEL), the fit is dominated by data points at its upper and lower end. Period B data also contribute but with a low significance to the fit and finally to the calculated isotope ratio.

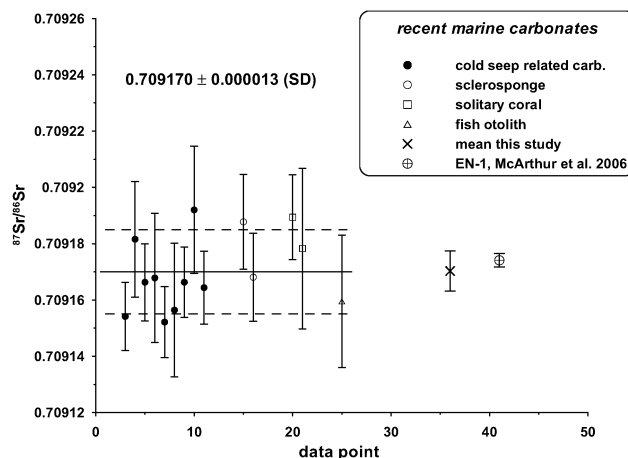
The same is true for the period (C). The background data are not separated from the rest of the data set and are treated in the same way as data from periods (A) and (B).

Based on the explanation given above, it can be seen that this method is a generally applicable concept for isotope ratio determinations using LA-MC-ICP-MS.

Fig. 3 contains a compilation of the radiogenic Sr isotope data of 4 different types of recent marine carbonates (gas hydrate carbonate, sclerosponge, solitary coral, fish otolith) determined by applying the described method. The mean of these data was calculated as  $0.709170 \pm 0.000013$  (SD), corresponding to an external reproducibility of 19 ppm. Our mean  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for recent marine carbonates of  $0.709170 \pm 0.000007$  (2SE) is in agreement with the EN-1 value of  $0.7091741 \pm 0.0000024$  (2SE) published by McArthur *et al.* (2006) and demonstrates the



**Fig. 2** Comparison between the conventional (Method A) and the new data evaluation (Method B) for the same data set as shown in Fig. 1. Errors of the resulting means are quoted in brackets as 2SE. Data evaluation for method A consisted of a separate background reduction. Only data points with an  $^{88}\text{Sr}$  beam intensity of more than 2.5 V were processed and a  $2\sigma$ -outlier removal was applied. In contrast for method B all data were used without any separate background reduction.



**Fig. 3** Radiogenic Sr isotope data of recent marine carbonates measured via LA-MC-ICP-MS. For comparison, the best available value for recent marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (determined on USGS standard EN-1, a recent marine carbonate) published by McArthur *et al.* (2006) is displayed.<sup>25</sup> For both means the uncertainty is quoted as 2SE.



potential of the described method for precise and accurate  $^{87}\text{Sr}/^{86}\text{Sr}$  determination using *in situ* ablation of the carbonates.<sup>25</sup>

In particular, the accuracy and reproducibility of our method compare well to the results published by Woodhead *et al.* (2005) who reported an accuracy of about 50 ppm (2SE) and external reproducibility of about 125 ppm (2SE) for otolith analyses using 60 s for ablation at 5–10 V total Sr intensity.<sup>20</sup>

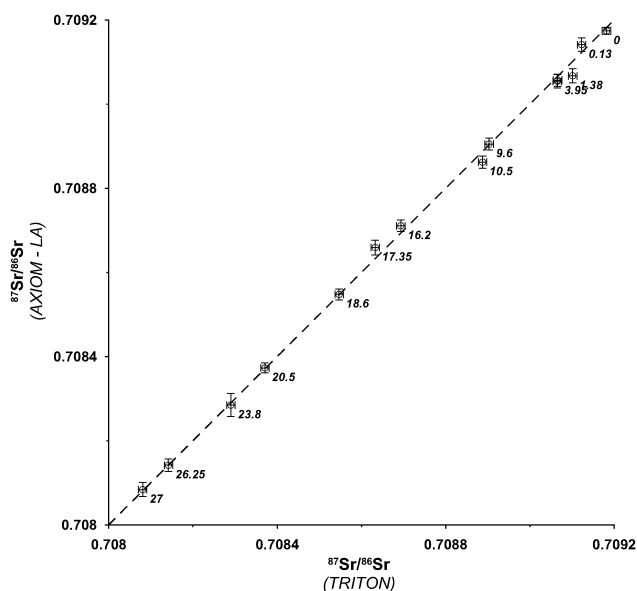
Sr isotopes stratigraphy (SIS), a tool to date marine carbonates, is a typical application of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in geochemistry.<sup>9,10</sup>

We tested our method (using a UP193solid state laser) for this particular application on a suite of Cenozoic marine carbonates covering an age interval of 0–27 Ma. Because of the lower Sr concentration ( $\sim 1000$  ppm Sr) these samples were ablated for 450 s followed by a 300 s intersite pause. During that time a square of  $100\ \mu\text{m} \times 100\ \mu\text{m}$  was continuously rastered 20 times using a  $35\ \mu\text{m}$  spot. Each measurement consumes about  $1\ \mu\text{g}$  carbonate corresponding to about 5 ng Sr and was repeated 3 times.

The same samples were prepared conventionally. Sr was separated from the carbonate matrix using EICHROM SrSpec resin, loaded (typically 400 ng Sr) onto Re filaments (plus Ta activator) and measured from single-filament by means of TIMS (TRITON). TIMS results were normalised using the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of NIST-987 measurements which are carried out regularly in our laboratory. A norm ratio of 0.710248 was applied.<sup>26</sup> The results of both methods are shown in Fig. 4. In general, these data agree well and are in good agreement with biostratigraphic ages and support the suitability of this LA-MC-ICP-MS method for further SIS applications.

### Stable Sr isotope ( $\delta^{88/86}\text{Sr}$ ) applications

The developed data acquisition and evaluation strategy was further applied to determine the stable Sr isotope ratio ( $\delta^{88/86}\text{Sr}$ )



**Fig. 4** Comparison of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of Cenozoic carbonates determined conventionally by TIMS (TRITON) and LA-MC-ICP-MS (AXIOM, this study). Samples cover an age range from 0 to approx. 27 Ma. Labels provide the biostratigraphic ages in Ma.

in carbonates. Details about notation, normalisation, liquid-introduction bracketing-standard MC-ICP-MS measurement protocols and application as temperature proxy in marine biogenic carbonates can be found elsewhere.<sup>8</sup>

In the already mentioned cold seep related carbonate sample SEK1 two distinct regions were measured *via* LA-MC-ICP-MS and conventionally *via* bracketing-standard MC-ICP-MS.

Both consist of pure aragonite (checked for calcite contaminations *via* XRD). One is translucent (SEK1-trans) and the other of white opaque appearance (SEK1-white). As mentioned above, this sample was analysed for elemental concentration profiles by LA-Q-ICP-MS at the ETH Zurich. The mean Sr concentrations in these sample regions were determined to be about 8000 ppm (SEK1-trans) and 12 000 ppm (SEK1-white), respectively.

Stable Sr isotope ratios ( $\delta^{88/86}\text{Sr}$ ) were determined in these samples using two different LA systems (NewWave UP193 solid state and UP193FX) and compared to the results obtained by conventional bracketing-standard MC-ICP-MS (including ion chromatographic Sr separation from the sample matrix).

The results are presented in Table 2. Both LA-MC-ICP-MS results agree with the value determined using conventional bracketing-standard MC-ICP-MS. LA data show no influence on variation of the Sr concentration (8000 ppm *vs.* 12 000 ppm). Both laser ablation systems seem to be equally suitable for this application.

To evaluate the potential of the method for typical  $\delta^{88/86}\text{Sr}$  applications on biogenic marine carbonates further tests were performed by LA-MC-ICP-MS (using UP193FX) on:

- (1) aragonitic sclerosponges (grown at  $16.2\ ^\circ\text{C}$  and  $27\ ^\circ\text{C}$ )
- (2) cod otolith (winter *vs.* summer growth section)

For (1) conventional bracketing MC-ICP-MS was applied. However, for cod otolith this was impossible due to the thin sample laminations.

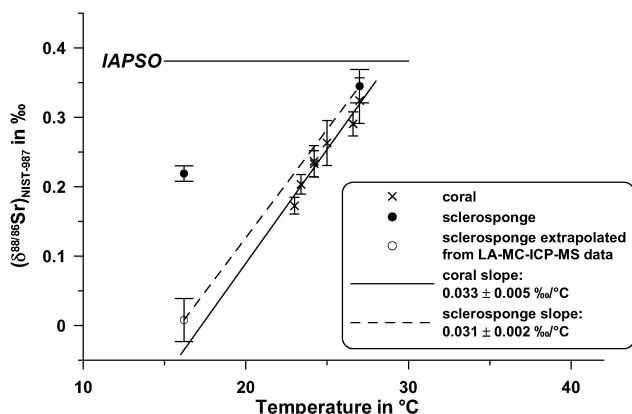
The results are shown in Table 3, and Fig. 5 contains a comparison of the sclerosponge data to previously reported data.<sup>8</sup> At the first impression, the sclerosponges follow a different temperature dependence. However, there is strong evidence that the conventionally determined low temperature ( $16.2\ ^\circ\text{C}$ ) sclerosponge data point is incorrect. This evidence is based on the fact that this particular sample was heavily coated, while the high temperature ( $27\ ^\circ\text{C}$ ) sample showed no coating. Thus, we assume the former data point was being affected by the contribution of this coating with unknown  $\delta^{88/86}\text{Sr}$  signature mixing of both

**Table 2** Results of stable Sr isotope ratio ( $\delta^{88/86}\text{Sr}$ ) determination on two sections of SEK1 *via* conventional bracketing standard MC-ICP-MS and LA-MC-ICP-MS using two different laser systems (NewWave UP193solid state and UP193FX), respectively. Note Sr concentration differences determined by LA-Q-ICP-MS. Uncertainties are quoted as 2SE

Sample	( $\delta^{88/86}\text{Sr}$ ) rel. NIST-987 in ‰ conv. MC-ICP-MS	( $\delta^{88/86}\text{Sr}$ ) in ‰ UP193solid state	( $\delta^{88/86}\text{Sr}$ ) in ‰ UP193FX
SEK1-trans (Sr: $\sim 8000$ ppm)	$0.169 \pm 0.010$		
SEK1-white (Sr: $\sim 12\ 000$ ppm)	$0.262 \pm 0.012$		
SEK1 white <i>vs.</i> trans	$0.093 \pm 0.016$	$0.104 \pm 0.026$	$0.086 \pm 0.025$

**Table 3**  $\delta^{88/86}\text{Sr}$  results of sclerosponge and cod otolith samples using bracketing standard MC-ICP-MS and LA-MC-ICP-MS (UP193FX). Uncertainties are quoted as 2SE

Sample	( $\delta^{88/86}\text{Sr}$ ) rel. NIST-987 in ‰ conv. MC-ICP-MS	( $\delta^{88/86}\text{Sr}$ ) in ‰ UP193FX
Sclerosponge (16.2 °C) <i>Vaceletia</i> sp.	0.219 ± 0.011	
Sclerosponge (27 °C) <i>Vaceletia</i> crypta	0.345 ± 0.024	
Sclerosponge 16.2 °C vs. 27 °C		0.339 ± 0.026
		0.328 ± 0.036
		0.344 ± 0.043
Mean	(0.126 ± 0.027)	0.337 ± 0.020
Cod otolith Summer vs. winter growth ring		0.031 ± 0.027



**Fig. 5** Comparison of the  $\delta^{88/86}\text{Sr}$  results of sclerosponge samples obtained by bracketing-standard MC-ICP-MS with published coral (*Pavona clavus*) data.<sup>8</sup> IAPSO sea water standard is displayed to represent global ocean  $\delta^{88/86}\text{Sr}$  composition. Using the LA-MC-ICP-MS data a similar temperature dependency for sclerosponges and corals is indicated.

carbonate phases during sample dissolution. The laser ablation analysis was performed on the pristine uncoated sample areas only. Calculating an extrapolated value for the low temperature data point using LA-MC-ICP-MS derived a  $\delta^{88/86}\text{Sr}$  difference for both samples and the conventionally determined  $\delta^{88/86}\text{Sr}$  value of the uncoated sample provides a more reasonable temperature systematic for the sclerosponges.

Assuming this to be correct, a temperature dependent  $\delta^{88/86}\text{Sr}$  fractionation of  $0.031(2)\text{‰ }^{\circ}\text{C}^{-1}$  can be predicted for sclerosponges, which is in agreement with the published values for corals of  $0.033(5)\text{‰ }^{\circ}\text{C}^{-1}$ .<sup>8</sup> It needs to be mentioned, however, that the latter result is preliminary and further detailed studies on this topic will be necessary.

Finally, the  $\delta^{88/86}\text{Sr}$  result for the cod otolith (consisting of layers of aragonite and organics) points to another interesting application: water temperature reconstructions from fish otoliths. Assuming a similar  $\delta^{88/86}\text{Sr}$ -temperature relation as found for other biogenic aragonite, the first result of a  $\delta^{88/86}\text{Sr}$  offset of  $0.031 \pm 0.027 \text{‰}$  between the summer and the winter growth section in this particular sample corresponds to a temperature difference of about  $1 \pm 1 \text{ }^{\circ}\text{C}$  between winter and summer. This temperature range of  $0\text{--}2 \text{ }^{\circ}\text{C}$  difference between both seasons appears reasonable, because cod can easily move between habitats to find preferred water conditions. Under the above mentioned assumption, temperature differences can only be estimated with  $1 \text{ }^{\circ}\text{C}$  precision. However, applying this method

to otoliths from species where the temperature difference is known to be higher between both seasons may show a distinct temperature sensitivity of  $\delta^{88/86}\text{Sr}$  for otolith aragonite when compared to other marine biogenic aragonite. To establish an absolute temperature calibration for any species, precise time-resolved temperature data would be necessary (e.g. from culturing experiments).

All presented applications underline the potential of more precise and accurate *in situ* determinations of both the radiogenic and stable Sr isotope ratios in carbonates.

Even if high precision data require a measurement time comparable to conventional methods (radiogenic Sr isotopes: TIMS, stable Sr isotopes: bracketing-standard MC-ICP-MS), the entire sample preparation procedure is drastically reduced in time. No chemical sample preparation is needed and, thus, sources of blank contributions are largely avoided. Furthermore, spatially resolved information can be obtained, which adds valuable information gained by *in situ* LA-MC-ICP-MS.

## Conclusions

The proposed and described method provides access to improved precision and accuracy for the *in situ* determination of radiogenic and stable Sr isotopes in carbonates. The use of the simultaneous dynamic responses of all isotopes of interest demonstrates the advantage for the evaluation of isotope ratio data determined using LA-MC-ICP-MS when compared to conventional data reduction protocols using separate integrations for background and data collection. The precision of the Sr isotopes ratio determination improved 5 times accompanied by an improved accuracy. The described strategies for data reduction demonstrated on carbonates with relatively high Sr concentration are considered to be transferable to other isotope ratio measurements using LA-MC-ICP-MS. The latter is supported by a recent study using similar calculation protocols for the determination of stable chlorine isotope ratios ( $\delta^{37}\text{Cl}$ ) via LA-MC-ICP-MS.<sup>24</sup>

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