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**Sr-isotope analysis of speleothems by LA-MC-ICP-MS: high temporal  
resolution and fast data acquisition**

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28 **Abstract**

29 Speleothems are well established climate archives. A wide array of geochemical proxies,  
30 including stable isotopes and trace elements are present within speleothems to reconstruct past  
31 climate variability. However, each proxy is influenced by multiple factors, often hampering  
32 robust interpretation. Sr isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) can provide useful information about water  
33 residence time and water mixing in the host rock, as they are not fractionated during calcite  
34 precipitation. Laser ablation multi-collector-inductively coupled plasma mass spectrometry  
35 (LA-MC-ICP-MS) has rarely been used for determination of Sr isotope signatures in  
36 speleothems, as speleothems often do not possess appropriately high concentrations of Sr to  
37 facilitate this analysis. Yet the advantages of this approach include rapid data acquisition, higher  
38 spatial resolution, larger sample throughput and the absence of chemical treatment prior to  
39 analysis. We present LA-MC-ICP-MS Sr isotope data from two speleothems from Morocco  
40 (Grotte de Piste) and India (Mawmluh Cave), and we compare linescan and spot analysis  
41 ablation techniques along speleothem growth axes. The analytical uncertainty of our LA-MC-  
42 ICP-MS Sr data is comparable to studies conducted on other carbonate materials. The results  
43 of both ablation techniques are reproducible within analytical error, implying that this technique  
44 yields robust results when applied to speleothems. In addition, several comparative  
45 measurements of different carbonate reference materials (i.e. MACS-3, Jct-1, JCp-1), including  
46 tests with standard bracketing and comparison of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios with a nanosecond laser  
47 ablation system and a state-of-the-art femtosecond laser ablation system, highlight the  
48 robustness of the method.

49

50 **Keywords:** Speleothem; Strontium isotopes; Laser ablation, Multi-collector inductively  
51 coupled plasma mass spectrometry, Femtosecond

## 52 **1. Introduction**

53 Speleothems (cave CaCO<sub>3</sub> deposits) are well established climate archives and are found  
54 worldwide in karst environments (Asmerom et al., 2010; Cheng et al., 2016; Cruz et al., 2005;  
55 Genty et al., 2003; Hoffmann et al., 2016; Kennett et al., 2012; Luetscher et al., 2015; Wang et  
56 al., 2001). They can be dated with unprecedented precision using the <sup>230</sup>Th/U-dating method  
57 (Richards and Dorale, 2003; Scholz and Hoffmann, 2008), and provide a range of climate  
58 proxies that record a number of environmental processes and can be analysed at up to sub-  
59 annual resolution.

60 Oxygen isotopes in speleothems ( $\delta^{18}\text{O}$  values) depend on paleo-temperature and rainfall  
61 properties, such as amount, seasonality and moisture sources (e.g., Fairchild et al., 2006;  
62 McDermott, 2004), whereas carbon isotopes can provide information on soil productivity,  
63 vegetation characteristics and effective rainfall (McDermott, 2004). In addition, trace elements  
64 (e.g., Sr, Mg, P, Ba) may be interpreted in terms of effective infiltration, prior calcite  
65 precipitation, water residence time, source and reservoir effects, weathering processes in the  
66 epikarst zone and soil composition (Ayalon et al., 1999; Fairchild et al., 2000; Fairchild and  
67 Treble, 2009; Verheyden et al., 2000; Wassenburg et al., 2016a; Wassenburg et al., 2016b).  
68 Within the epikarst and soil zone, different sources of trace elements (for example aeolian dust  
69 vs. host rock) may be present and display varying compositions. A change in the dripwater  
70 pathway or in the relative contribution of different sources, may thus affect the dripwater trace  
71 element composition, which often renders their interpretation a challenging task (Banner et al.,  
72 1994).

73 Important information on the influence of different sources of trace elements in dripwaters may  
74 be provided by Sr isotopes, which have been shown to provide additional insights on  
75 precipitation and water residence time in the host rock (Banner et al., 1996; Oster et al., 2010).  
76 In CaCO<sub>3</sub>, the Sr<sup>2+</sup> ion substitutes at the Ca<sup>2+</sup> ion sites in the mineral lattices due to their similar

77 properties and ionic radii (Banner, 2004). No isotopic fractionation of Sr isotopes is observed  
78 during precipitation of CaCO<sub>3</sub> and the incorporation of Sr into the crystal lattice. Thus, the  
79 <sup>87</sup>Sr/<sup>86</sup>Sr ratio of carbonates is identical to that of the parent solution (Banner and Kaufman,  
80 1994).

81 Although the first Sr isotope analyses on speleothems were conducted in 1990 (Avigour et al.,  
82 1990), relatively few studies have focused on this topic so far. The main source for Sr in  
83 speleothems is the host rock, but several factors have been proposed to affect Sr isotope ratios:  
84 varying water residence time in the epikarst (Banner et al., 1996); (Oster et al., 2010; Oster et  
85 al., 2014; Verheyden et al., 2000), changes in aeolian input in response to sea-level changes or  
86 atmospheric circulation (Goede et al. 1998; Ayalon et al. (1999); Bar-Matthews et al. (1999);  
87 Li et al. (2005); Zhou et al. 2009), changes in weathering intensity of soil and host rock in  
88 response to rainfall (Avigour et al., 1990), changes in the distance to the shoreline and  
89 incorporation of sea-salt signals (Fisher et al., 2010), as well as mixing of the Sr signals of  
90 different rock types and soils (Frumkin and Stein (2004); Hori et al. (2013)). All these studies  
91 either used Thermal Ionization Mass Spectrometry (TIMS, Avigour et al. (1990); Goede et al.  
92 (1998); Frumkin and Stein (2004); Li et al. (2005); Zhou et al. (2009); Hori et al. (2013)), or  
93 solution MC-ICP-MS (multi-collector inductively coupled plasma mass spectrometry, Ayalon  
94 et al. (1999); Bar-Matthews et al. (1999); Verheyden et al. (2000); Fisher et al. (2010); (Oster  
95 et al., 2010; Oster et al., 2014). For both techniques samples need to be drilled/milled, and  
96 require chemical separation prior to mass spectrometric analysis. This is time-consuming, and  
97 limits the achievable spatial resolution of <sup>87</sup>Sr/<sup>86</sup>Sr records. Strontium isotope analysis by laser  
98 ablation (LA-) MC-ICP-MS offers the opportunity to measure the <sup>87</sup>Sr/<sup>86</sup>Sr ratio *in-situ* at high  
99 spatial resolution and without any prior chemical treatment. Although this technique has been  
100 widely applied to petrological samples (e.g. Christensen et al. (1995); Davidson et al. (2001);  
101 Waight et al. (2002); Bizzarro et al. (2003); Ramos et al. (2004); Jackson and Hart (2006), and

102 carbonate and phosphate materials, such as gastropods, otoliths, teeth, clam shells, fine- and  
103 coarse-grained carbonates and corals (Christensen et al. (1995), Ehrlich et al., 2001, Outridge  
104 et al. (2002), Bizzarro et al., 2003, Ramos et al., 2004, Woodhead et al. (2005), Copeland et al.  
105 (2008), it has only recently been used for measuring  $^{87}\text{Sr}/^{86}\text{Sr}$  in speleothems (Wortham et al.,  
106 2017).

107 Here we present a LA-MC-ICP-MS method for measuring Sr isotopes on speleothems, based  
108 on previously mentioned studies on different sample materials. We show results from two  
109 speleothem samples and compare different sampling techniques. Both samples consist of  
110 aragonite and have a rather high Sr concentration  $>300 \mu\text{g/g}$ , which makes them highly suitable  
111 to apply LA-MC-ICP-MS. We also discuss the effects of different tuning parameters and  
112 compare results obtained by two different laser systems (a New Wave UP 213 nm laser and a  
113 NWR Femto200 laser ablation system).

114

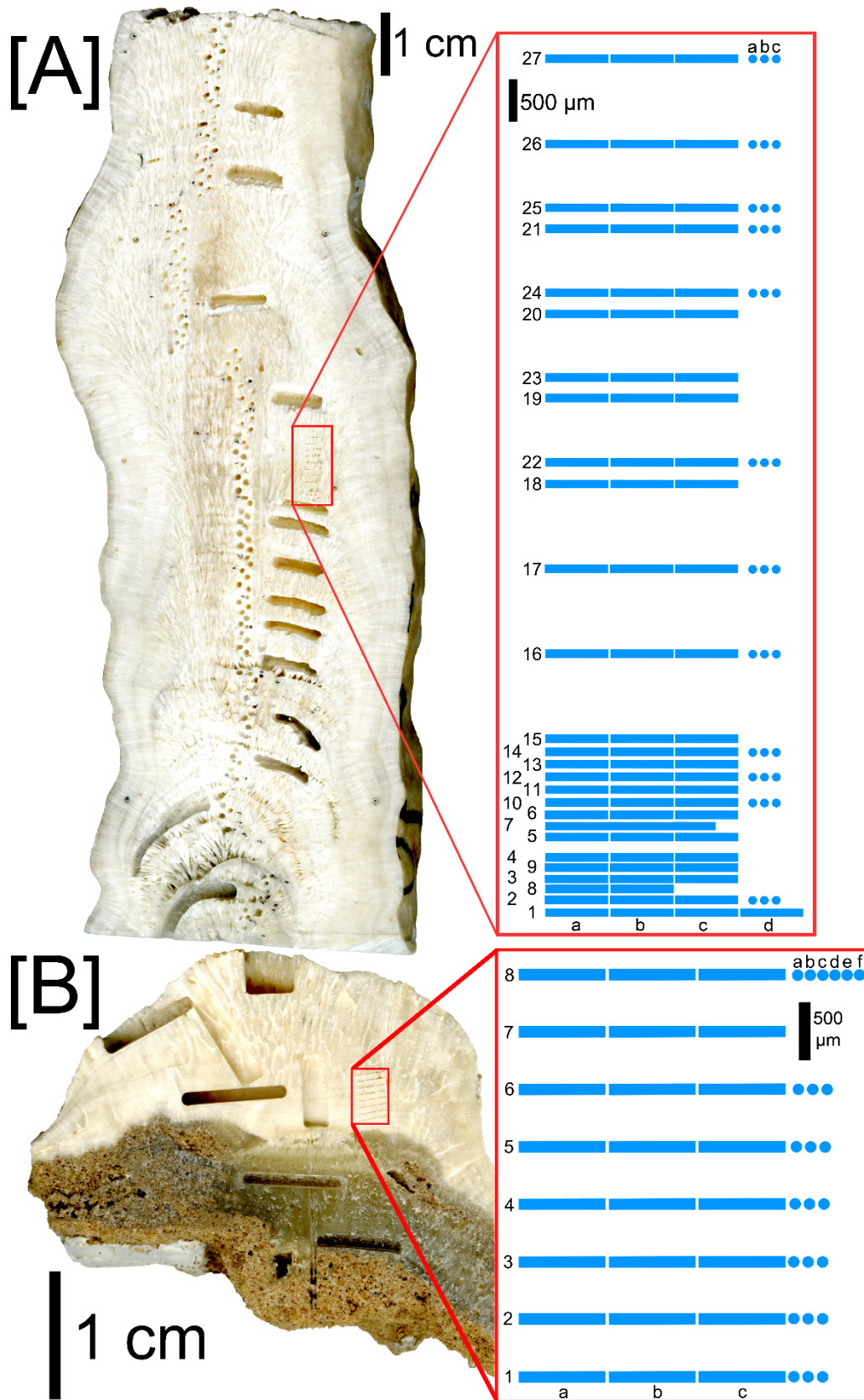
## 115 **2. Speleothem samples**

116 The investigated speleothem samples stem from two different caves. Stalagmite GP5 was  
117 sampled at Grotte de Piste (Morocco), and stalagmite MAW-4 stems from Mawmluh Cave  
118 (Meghalaya, India). Stalagmite GP5 has a total length of 78 cm. A detailed description of the  
119 cave and the sample is given in Wassenburg et al. (2012) and Wassenburg et al. (2013). In this  
120 study, an approximately 15 cm long part of the sample (Fig. 1) was studied which corresponds  
121 to the time span from ca. 800 to 1760 AD. Previous data is published in Wassenburg et al.  
122 (2013) and only briefly summarised here. GP5 was precisely dated by the  $^{230}\text{Th}/\text{U}$ -method.  
123 Furthermore, the mineralogy of the sample was investigated by XRD and showed that GP5 is  
124 mainly aragonitic, with minor calcitic parts ( $<2\%$ ). Strontium concentrations range from 200 to

125 500  $\mu\text{g/g}$ , with an average concentration of 426 ( $\pm 49$ )  $\mu\text{g/g}$ . In some parts, the sample is  
126 characterized by mm-scale layering of porous and less porous layers.

127 Stalagmite MAW-4 (Fig. 1) from Mawmluh cave is a small sample with a total length of 3 cm.  
128 The upper part of the sample ( $\sim 15$  mm), consists of aragonite, and covers the time span from  
129 1950 to 2006 AD (Wassenburg et al., 2016b). It has an average growth rate of  $\sim 293$   $\mu\text{m/a}$ , and  
130 can thus provide very high resolution. The stalagmite was actively growing at the time of  
131 collection (March 2006). The lower part of the sample consists of calcite, the base is dated 395  
132  $\pm 55$  a BP. The calcite-to-aragonite transition is clearly visible by a change in colour from  
133 greyish (calcite) to white/beige (aragonite). In the upper aragonitic part, this stalagmite has a  
134 relatively high Sr concentration (1458–1729  $\mu\text{g/g}$ , (Wassenburg et al., 2016b), and is thus  
135 extremely suitable for Sr isotope measurements by LA-MC-ICP-MS. The calcite section has a  
136 Sr concentration of a few hundred  $\mu\text{g/g}$ , and was not investigated in this study. For more  
137 information about the cave setting and microclimatic conditions, see Breitenbach et al. (2010)  
138 and Breitenbach et al. (2015).





139

140 **Figure 1:** [A] Sampling approach for speleothem GP5. The red rectangle indicates the sampling  
 141 section, blue lines show the LA-MC-ICP-MS linescan positions. The spot analyses were

142 performed near the right end of the third linescan as indicated by the blue spots. [B] Sampling  
143 approach for speleothem MAW-4. The red rectangle indicates the sampling section. Linescan  
144 and spot analyses are similarly indicated as in [A]. All line lengths, widths and distances are on  
145 scale.

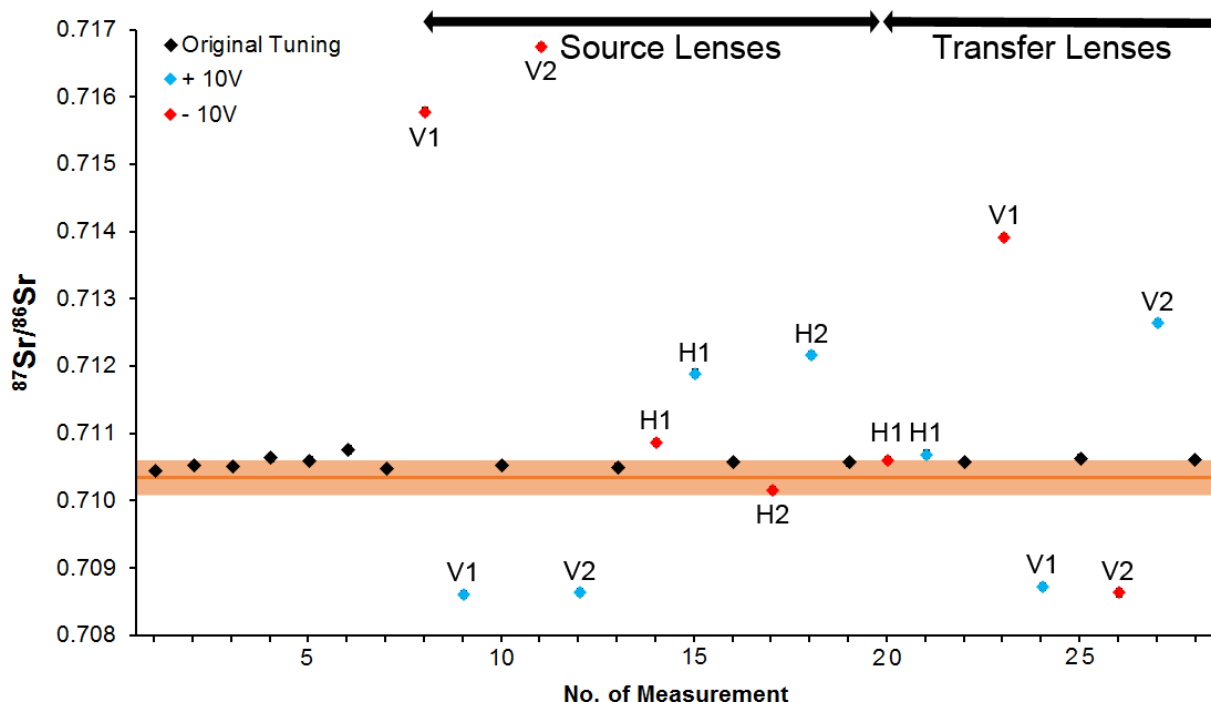
146

### 147 **3. Materials and methods**

#### 148 **3.1 Analytical setups**

149 The measurement routine was developed with a NU Plasma MC-ICP-MS (see Table 1 for cup-  
150 configuration) coupled with a New Wave UP213 nm Nd:YAG laser ablation system at the Max  
151 Planck Institute for Chemistry, Mainz. Measurements were also performed with the MC-ICP-  
152 MS coupled to a NWR Femto200 laser ablation system to compare results obtained with two  
153 laser ablation systems. The femtosecond laser is less sensitive to matrix effects that may cause  
154 isotope fractionation (Poitrasson et al., 2003; Vanhaecke et al., 2010). Prior to laser ablation,  
155 the MC-ICP-MS was coupled to a CETAC Aridus II Desolvating Nebulizer system for tuning.  
156 The Sr reference solution NIST SRM 987 was used for optimizing the peak shape and  
157 coincidence of the individual Sr isotopes ( $^{88}\text{Sr}$ ,  $^{87}\text{Sr}$ ,  $^{86}\text{Sr}$ ,  $^{84}\text{Sr}$ ) and to test the influence of  
158 different tuning parameters on ion beam intensity and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. Several tuning  
159 parameters were changed systematically. Tests showed that the gas flows of the Aridus  
160 introduction system have a significant effect on the Sr isotope ratios. Furthermore, the torch  
161 position and the tuning of the high voltage lenses are important, since they affect the sample  
162 introduction into the system and the ion beam inside the mass spectrometer. Finally, the source  
163 lenses have been shown to have a significant effect on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. In order to test the  
164 effects of changes in the lens settings, we started with seven measurements of NIST SRM 987  
165 to test the stability of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio over time. In a first step, the lens settings were tuned

166 for maximum  $^{88}\text{Sr}$  intensity. Subsequently, the different source and transfer lens settings were  
 167 changed systematically. For each lens, three measurements were performed: First, the voltage  
 168 of the lens was decreased by 10 V, then increased by 20 V, and finally decreased by 10 V to  
 169 return to the original value. This procedure was performed for all seven source and transfer  
 170 lenses. Results are presented in Fig. 2 and Supplement A1.



171  
 172 **Figure 2:**  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios obtained on reference solution NIST SRM 987. The orange line  
 173 represents the literature value of  $^{87}\text{Sr}/^{86}\text{Sr} = 0.71034 \pm 0.00026$  (GeoReM, (Jochum et al., 2005),  
 174 the shading in bright orange shows the  $2\sigma$  standard error. The large fluctuations in the Sr isotope  
 175 ratio are caused by changes in the settings of the source and transfer lenses of the NU Plasma  
 176 MC-ICP-MS, marked by the black arrows. Black diamonds represent measurements with the  
 177 original lens settings, while blue (red) diamonds represent measurements with a 10 V increase  
 178 (decrease) in lens voltage in comparison to the original lens setting.

179

180 Settings were then further optimised with the NU MC-ICP-MS coupled to the LA system. Since  
181 the UP213 nm laser ablation system offers higher fluence values (20 – 30 J/cm<sup>2</sup>) and count rates  
182 than the femtosecond laser (0.7 – 0.8 J/cm<sup>2</sup>), this system allows measurement of samples with  
183 comparably low Sr concentrations (>200 µg/g). Potential matrix effects are assessed by  
184 comparison with the femtosecond laser. All samples and reference materials have a low Rb  
185 content (Table 2). The operating parameters for the MC-ICP-MS and the laser ablation systems  
186 are given in Table 3.

187

### 188 **3.2. Reference materials**

189 The reference material (RM) Jct-1 was measured to determine the accuracy and precision of  
190 the method. This modern marine carbonate sample originates from a recent giant clam and has  
191 a <sup>87</sup>Sr/<sup>86</sup>Sr-ratio comparable to modern sea water (<sup>87</sup>Sr/<sup>86</sup>Sr of 0.70918 ± 0.00001, 2σ, Faure and  
192 Mensing (2005)), as confirmed by solution MC-ICP-MS measurements (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.70915 ±  
193 0.00005, Ohno and Hirata (2007)). Recently, a more precise <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.70917 ± 0.00001  
194 has been obtained for Jct-1 by MC-ICP-MS (Weber et al., In Revision). Due to its comparable  
195 Sr content of 1400 µg/g (Aizawa, 2008), Jct-1 was chosen as RM for the measurements of  
196 samples GP5 and MAW-4. Furthermore, the RMs Jcp-1, a modern coral with <sup>87</sup>Sr/<sup>86</sup>Sr =  
197 0.70916 ± 0.00002 (Ohno and Hirata (2007)) and MACS-3, a synthetic carbonate pellet  
198 (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.7075532 ± 0.0000037; Jochum et al. (2011)), were also tested. Both of these RM  
199 samples have a very high Sr concentration (7500 µg/g for Jcp-1, (Aizawa, 2008), and  
200 6760 µg/g for MACS-3, (Jochum et al., 2012) and are well suited for femtosecond laser  
201 analysis. For tuning and test measurements, we used a modern day bivalve shell of *Glycymeris*  
202 sp., which has two distinct areas of different Sr concentrations of ca. 1000 and 5000 µg/g.

203

### 204 3.3. Laser ablation sampling method

205 Multiple LA-MC-ICP-MS measurements were performed perpendicular to the growth axis of  
206 the speleothem samples, parallel to and within the same distinct growth layers to check for  
207 reproducibility. In order to identify the best method for analysing Sr-isotope ratios in  
208 speleothems by LA-MC-ICP-MS, we applied two different sampling methods. First, we used  
209 the linescan technique, which has the advantage that a high signal intensity can be maintained  
210 for a relatively long measurement interval, improving counting statistics. In contrast, for spot  
211 analyses, the signal intensity slowly decreases with ablation depth. However, for spot analyses,  
212 mixing of material from different growth layers is excluded. The linescans followed individual  
213 growth bands and each of usually three linescans per growth layer had a circular spot size of 80  
214 – 100  $\mu\text{m}$  and a length of 750  $\mu\text{m}$  (except linescan GP5-7, which was 2000  $\mu\text{m}$ ). They were  
215 scanned with a scan-speed of 5  $\mu\text{m}/\text{s}$ , providing about 150 s per linescan measurement. This  
216 sampling approach enables us to identify potential changes in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio at a very high  
217 spatial resolution. Prior to each analysis, a pre-ablation was performed with a spot size of  
218 110  $\mu\text{m}$  and a scan-speed of 80  $\mu\text{m}/\text{s}$  (Table 3). The first 5 s are discarded due to high intensities  
219 when the laser starts, which is typical for laser ablation analyses. Spots were analysed with a  
220 circular spot size of 100  $\mu\text{m}$  and a dwell time of 120 s. To test the reproducibility of the method,  
221 three line scans were placed parallel to each other within the same growth band with less than  
222 50  $\mu\text{m}$  between the end and start of each linescan (Fig. 1). The distance between the measured  
223 layers varied between 150  $\mu\text{m}$  and 850  $\mu\text{m}$  for GP5 and 500  $\mu\text{m}$  for MAW-4. The spot analyses  
224 of GP5 were performed for a few layers only. Each spot analysis is located near the end of the  
225 respective line scan. For correction purposes, RM JcT-1 was measured three times before and  
226 after each set of samples (usually six measurements in total).

227 To compare both laser ablation systems, we performed measurements with different RMs.  
228 Since the Sr concentration of JcP-1 is almost six times that of JcT-1, the laser settings for the

229 UP213 laser ablation system were adjusted to prevent the  $^{88}\text{Sr}$  intensity from reaching critical  
230 values. We used a laser energy of 60 %, a repetition rate of 5 Hz and a spot size of 55  $\mu\text{m}$ . All  
231 measurements were performed as spot analyses. To test the robustness of the results, we also  
232 applied our standard bracketing approach on JCp-1 by measuring samples of JcT-1 before and  
233 after JCp-1. The laser settings for JcT-1 were chosen as described in Table 3.

234 Our NWR Femto200 laser ablation system only allows spot sizes up to 65  $\mu\text{m}$ , therefore we  
235 only measured RMs with high Sr concentrations, such as JCp-1 and MACS-3. The laser  
236 parameters for these measurements are presented in Table 3. Spot measurements with the  
237 femtosecond laser ablation system suffer from a rapid decrease in signal intensity. Thus, all  
238 measurements were performed as linescans. We measured three samples of JCp-1, followed by  
239 six measurements of MACS-3 and again three samples of JCp-1.

240

#### 241 **4. Correction procedure for LA-MC-ICP-MS**

242 Strontium isotopes were measured on cups H4 ( $^{88}\text{Sr}$ ), H2 ( $^{87}\text{Sr}$ ), Ax ( $^{86}\text{Sr}$ ) and L3 ( $^{84}\text{Sr}$ )  
243 (Table 1). The major advantage of Sr-isotope analysis with LA-MC-ICP-MS is that Sr-isotopes  
244 are measured *in-situ*, without the need of chemical separation. This means, however, that the  
245 matrix contains several other isotopes that potentially affect the Sr isotope signal (i.e.,  $^{87}\text{Rb}$ , but  
246 also doubly charged ions, such as  $^{176}\text{Yb}$ ,  $^{174}\text{Yb}$ ,  $^{172}\text{Yb}$ ,  $^{168}\text{Yb}$ ,  $^{168}\text{Er}$ , and molecular interferences,  
247 such as Ca-argides and/or -dimers, Table 1). In addition, the Ar gas may contain impurities of  
248 Kr, with interfering isotopes of  $^{86}\text{Kr}$  and  $^{84}\text{Kr}$  (Table 1). Some masses are affected by several  
249 interferences. For example, the  $^{84}\text{Sr}$  signal on mass 84 may be affected by  $^{84}\text{Kr}^+$ ,  $^{168}\text{Er}^{2+}$   $^{168}\text{Yb}^{2+}$   
250 and Ca argides/dimers. Therefore, it is necessary to find another mass that is not affected by  
251 other interferences, which can be used to correct for other masses of the same ion using known  
252 isotopic abundances. For example, we used mass number 86.5 that is mostly unaffected by other

253 signals to correct for the Yb-interference by monitoring  $^{173}\text{Yb}^{2+}$ . Thus, the order of the  
254 corrections is important. The correction procedure is outlined in detail below. Fig. 3 shows the  
255 magnitude of the individual correction steps on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for measurements on samples  
256 JcT, GP5 and MAW-4.

257

#### 258 **4.1 Background correction**

259 Potential interferences of  $^{86}\text{Kr}$ ,  $^{84}\text{Kr}$ ,  $^{83}\text{Kr}$  and  $^{82}\text{Kr}$  from minor contaminations in the Ar gas  
260 supply are corrected by a blank measurement. For this reason, prior to each analysis an on-peak  
261 background correction is performed for 45 s during the laser warm-up time. Then, the median  
262 for each signal intensity is calculated and subtracted from the measured signal. This removes  
263 all Kr interferences as well as potential remains of Sr from previous measurements.

264

#### 265 **4.2 Rare-earth elements (REE)**

266 After background correction, different interferences must be eliminated. Doubly-charged  
267 isotopes of Er and Yb can be detected on half masses (Table 1).  $^{173}\text{Yb}$  is the only isotope  
268 measured on cup H1 on half-mass 87.5, and  $^{171}\text{Yb}$  is the only one measured on cup L1 on half  
269 mass 85.5. Thus,  $^{173}\text{Yb}$  and  $^{171}\text{Yb}$  can be measured without any interferences. By assuming  
270 constant isotope ratios for Yb (Berglund and Wieser (2011)), the signal for all Yb isotopes can  
271 be calculated. Although Yb is quite rare in speleothem samples (Table 2), this correction may  
272 have a minor influence on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios.

273 The second step is to correct for Er.  $^{167}\text{Er}$  is the only isotope measured on ion counter IC-1 on  
274 half mass 83.5, and other Er isotopes can be calculated assuming constant isotope ratios in the  
275 same way as Yb (Berglund and Wieser (2011)). Erbium is uncommon in speleothem samples  
276 (Table 2) and this correction is only of minor importance. Several laser ablation studies on other

277 sample materials did not even correct for rare earth elements (REE) during Sr isotope analysis  
278 (e.g. Christensen et al. (1995); Barnett-Johnson et al. (2005); Jochum et al. (2009); Copeland et  
279 al. (2010)).

280

### 281 **4.3 Molecular interferences**

282 The next step is to correct for molecular interferences of Ca dimers and argides. Since it is  
283 impossible to differentiate between the signals resulting from argides and dimers, the relative  
284 amounts of each signal are taken into account to correct for those interferences in relation to  
285 the signal on mass 82. This mass is used as a reference since it has **no** other interferences and a  
286 potentially higher signal of argides and dimers than mass 83, which is also free of significant  
287 interferences (Table 1). As an example, we briefly describe the correction of mass 84 for Ca  
288 argides and dimers.

289 After correcting for background and REEs, the correction for Ca argides is performed by the  
290 following relationship:

$$291 \quad 84_{ArCorr} = 84_{uncorr} - 82_{uncorr} * \left( \frac{\sum CaAr_{84}}{\sum CaAr_{82}} \right) \text{(Eq. 1)}$$

292 where  $84_{ArCorr}$  is the corrected signal on mass 84,  $84_{uncorr}$  is the uncorrected signal (besides  
293 background and REE correction) on mass 84 and  $82_{uncorr}$  is the signal on mass 82.  $\sum CaAr_{84}$  is  
294 the sum of the relative portion of Ca argides on mass 84, and  $\sum CaAr_{82}$  is the sum of the relative  
295 portion of Ca argides on mass 82, based on their natural occurrence (Berglund and Wieser,  
296 2011). This correction is performed for masses 88, 86, 84 and 83. For the interferences from  
297 Ca dimers, the correction is done in a similar way, again using the signal on mass 82 as a  
298 reference:

$$299 \quad 84_{Corr} = 84_{ArCorr} - 82_{uncorr} * \left( \frac{\sum CaCa_{84}}{\sum CaCa_{82}} \right) \quad \text{(Eq. 2)}$$



300 where  $84_{\text{corr}}$  is the corrected signal on mass 84,  $84_{\text{Arccorr}}$  is the background corrected intensity on  
 301 mass 84, REEs and Ca argides, and  $82_{\text{uncorr}}$  is the uncorrected signal (besides background and  
 302 REE correction) on mass 82.  $\Sigma\text{CaCa}_{84}$  is the sum of the relative portion of Ca dimers on mass  
 303 84 and  $\Sigma\text{CaCa}_{82}$  is the sum of the relative portion of Ca dimers on mass 82. This correction is  
 304 performed for masses 88, 87, 86, 85, 84 and 83 and only applied for signals  $> 0$  V. All other  
 305 signals remain uncorrected because the intensity of Ca argides and dimers is too small to detect  
 306 and does not affect the results.

307

#### 308 4.4 Mass bias

309 After correcting the raw signals for interferences, the mass bias needs to be corrected. This  
 310 correction is performed prior to the correction for the interference of Rb, because the mass bias  
 311 obtained from the  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio is subsequently used to obtain the mass bias corrected  
 312  $^{85}\text{Rb}/^{87}\text{Rb}$  ratio (section 4.5). Based on the signals corrected for background, REEs, Ca argides  
 313 and dimers, raw values for the ratios of  $^{86}\text{Sr}/^{88}\text{Sr}$ ,  $^{84}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  are calculated. Then, a  
 314 mass fractionation factor  $\alpha$  is calculated to correct for the instrumental mass fractionation based  
 315 on the  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio and the exponential law described in Ingle et al. (2003):

$$316 \quad R_{\text{corr}} = R_{\text{meas}} * \left( m_{87\text{Sr}} / m_{86\text{Sr}} \right)^\alpha \quad (\text{Eq. 3})$$

317 where  $m_{87}$  and  $m_{86}$  are the masses of  $^{87}\text{Sr}$  and  $^{86}\text{Sr}$ . The mass fractionation factor  $\alpha$  is calculated  
 318 as described in Ehrlich et al. (2001):

$$319 \quad \alpha = \left( \ln \left( \frac{\left( \frac{^{86}\text{Sr}}{^{88}\text{Sr}} \right)_{\text{true}}}{\left( \frac{^{86}\text{Sr}}{^{88}\text{Sr}} \right)_{\text{meas}}} \right) \right) / \ln(m_{86} / m_{88}) \quad (\text{Eq. 4})$$

320 where  $(^{86}\text{Sr}/^{88}\text{Sr})_{\text{true}}$  is the accepted value of 0.1194 (Steiger and Jäger, 1977) and  $m_{88}$  is the  
 321 mass of  $^{88}\text{Sr}$ .

322

#### 323 **4.5 Interference of rubidium**

324 The final step in the correction procedure is to correct the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for the interference of  
325  $^{87}\text{Rb}$ . Due to the previous corrections, mass 85 only consists of  $^{85}\text{Rb}$  (Table 1), which can be  
326 used to calculate the fraction of  $^{87}\text{Rb}$  by using the constant ratio of  $^{87}\text{Rb}/^{85}\text{Rb} = 0.3857$   
327 (Berglund and Wieser (2011)) This was done following equation 5:

$$328 \quad {}^{87}\text{Rb} = \left( \frac{{}^{87}\text{Rb}}{{}^{85}\text{Rb}_{\text{Lit}}} * {}^{85}\text{Rb}_{\text{meas}} \right) * \left( \frac{m_{87}}{m_{85}} \right)^\alpha \quad (\text{Eq. 5})$$

329 where  $^{87}\text{Rb}/^{85}\text{Rb}_{\text{Lit}}$  is the literature value (Berglund and Wieser, 2011)(Berglund and Wieser,  
330 2011)(Berglund and Wieser, 2011),  $^{85}\text{Rb}_{\text{meas}}$  is the Rb signal on mass 85, corrected for  
331 background, REEs and Ca argides/dimers,  $m_{87}$  is the mass of  $^{87}\text{Rb}$ ,  $m_{85}$  is the mass of  $^{85}\text{Rb}$ , and  
332  $\alpha$  is the mass fractionation factor. The correction on  $^{87}\text{Sr}/^{86}\text{Sr}$  is then performed using the  
333 following equation:

$$334 \quad \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}_{\text{RbCorr}}} = \left[ \frac{({}^{87}\text{Sr}_{\text{uncorr}} - {}^{87}\text{Rb})}{{}^{86}\text{Sr}} \right] * \left( \frac{m_{87}}{m_{86}} \right)^\alpha \quad (\text{Eq. 6})$$

335 where  $^{87}\text{Sr}_{\text{uncorr}}$  is the Sr signal on mass 87 corrected for background, REEs and argides/dimers  
336 (not for Rb),  $^{87}\text{Rb}$  and  $^{86}\text{Sr}$  are the corrected signals for Rb on mass 87 and Sr on mass 86,  
337 respectively,  $m_{87}$  and  $m_{86}$  are the masses for Sr and  $\alpha$  is the mass fractionation factor. This Rb  
338 correction is only considered robust for samples with a Rb/Sr ratio  $<0.02$  (Irrgeher et al., 2016).  
339 For samples with higher Rb content, an alternative Rb-correction is necessary (Müller and  
340 Anczkiewicz, 2016). All speleothem samples and RMs analysed in this study are below this  
341 threshold (Table 2).

342

#### 343 **4.6 Data processing**

344 After calculating the interference-free  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, the results are calibrated by standard-  
 345 bracketing using RMs with well-known  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, as has been recommended for Sr-  
 346 isotope analysis (Irrgeher et al., 2016). Furthermore, to avoid effects of individual large peak  
 347 values, we performed a  $2\sigma$  outlier test for the median of all  $^{87}\text{Sr}/^{86}\text{Sr}$  values, removing all values  
 348 deviating  $>2\sigma$  from the median.

349 Usually, the final  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios obtained for the RMs deviate slightly from the reference  
 350 values, necessitating an additional correction step. Each sample is therefore bracketed by a set  
 351 of three individual measurements of a suitable RM. The mean value of the three RMs is  
 352 calculated, and a correction factor for the sample is calculated according to the following  
 353 equation:

$$354 \quad Sr_{Corr} = \frac{{}^{87}\text{Sr}/{}^{86}\text{Sr}_{true}}{{}^{87}\text{Sr}/{}^{86}\text{Sr}_{meas}} \quad (\text{Eq. 7})$$

355 where  $^{87}\text{Sr}/^{86}\text{Sr}_{true}$  is the literature value of the RM and  $^{87}\text{Sr}/^{86}\text{Sr}_{meas}$  is the measured ratio of the  
 356 RM. We then use the mean value of the two correction factors from the two sets of RMs  
 357 (measured prior and subsequent to the sample) and apply it to the measured sample  $^{87}\text{Sr}/^{86}\text{Sr}$   
 358 ratio. Since the measurements of the RMs are associated with an uncertainty, error propagation  
 359 is performed by adding the relative  $2\sigma$  standard error for the measurement of the RM ( $2\sigma$  Std  
 360  $\text{Err}_{Ref}$ ) to the relative  $2\sigma$  standard error of the measured sample ( $2\sigma$  Std  $\text{Err}_{Spl}$ ):

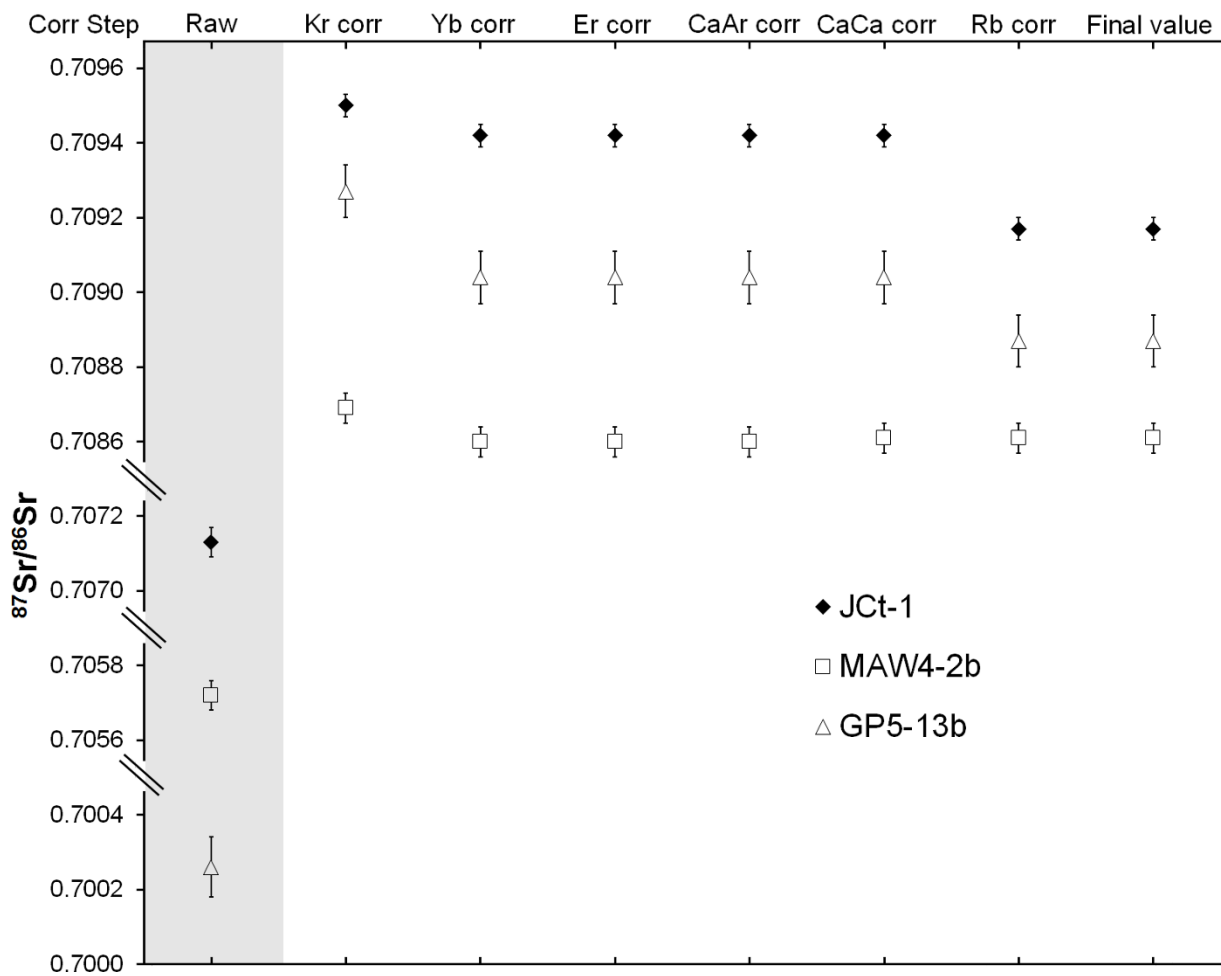
$$361 \quad 2\sigma \text{ Std Err}_{SampleCorr} [\%] = \sqrt{(2\sigma \text{ Std Err}_{Ref} [\%])^2 + (2\sigma \text{ Std Err}_{Spl} [\%])^2} \quad (\text{Eq. 8})$$

362 The  $2\sigma$  Std  $\text{Err}_{Ref}$  value is calculated from the mean of the relative  $2\sigma$  standard errors of all  
 363 RMs, while the  $2\sigma$  Std  $\text{Err}_{Spl}$  is calculated from the mean of the linescans or spot measurements  
 364 for each sample layer. By applying the error propagation, the  $2\sigma$  standard error of each sample  
 365 usually increases by  $\pm 0.00001 - 0.00002$  (0.01 – 0.03 ‰).

366

367 **5. Results**

368 The results from the speleothem samples obtained with the two sampling methods (linescans  
369 and spot analyses, respectively) are presented in Table 2. Due to the extensive correction  
370 procedure, we show the effect of each correction step on the  $^{87}\text{Sr}/^{86}\text{Sr}$  value for one LA-MC-  
371 ICP-MS measurement of JcT-1, MAW-4 and GP5, respectively. The results are presented in  
372 Fig. 3. The correction step associated with the largest effect is the background correction and,  
373 depending on the sample, the corrections for interferences of Yb and Rb. Corrections for Ca  
374 argides and dimers are insignificant for our results.



375

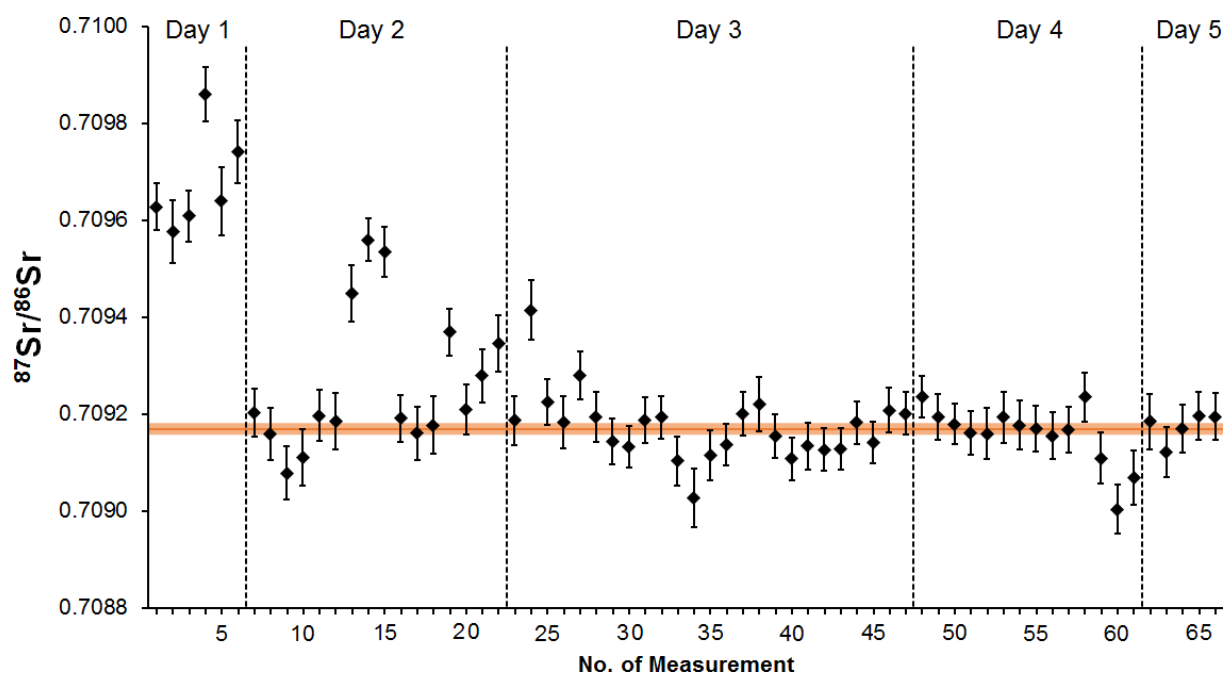
376 **Figure 3:** Influence of the different correction steps on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of JcT-1 (black  
377 diamonds), MAW-4 (squares) and GP5 (triangles). Note that all results are mass bias corrected.

378

379 **5.1. Influence of tuning parameters on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio**

380 Our solution MC-ICP-MS measurements show that tuning for maximum Sr intensity does not  
381 necessarily lead to a “true”  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, but may deviate from the accepted value of the  
382 reference solution NIST SRM 987 ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.71034 \pm 0.00026$ , GeoReM, Jochum et al.  
383 (2005)) on the third or fourth decimal. This can be avoided by tuning the mass spectrometer to  
384 obtain the Sr isotope ratio known from the literature (at the expense of signal intensity). The  
385 procedure is described in chapter 3.1. While some changes have a large influence on the isotope  
386 ratio (e.g. the decrease by 10 V for source lenses V1 and V2), others only have a minor  
387 influence, such as the changes at transfer lens H1 (Fig. 2). We note that this might be a specific  
388 pattern for our mass spectrometer and may differ in other laboratories. After restoring to the  
389 original setting, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio was comparable to the starting value (Fig. 2).

390 Figure 4 (data in Supplement A1) shows the evolution of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio during consecutive  
391 days of LA-MC-ICP-MS measurements of RM Jct-1. While the Sr isotope ratio increased  
392 during the first measurements, source lens adjustments brought the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio back towards  
393 the reference value.



394

395 **Figure 4:**  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of reference material Jct-1 obtained during different days, showing  
 396 the tuning influence during the first measurements. The orange line represents the reference  
 397 value of Jct-1 of  $^{87}\text{Sr}/^{86}\text{Sr} = 0.70917 \pm 0.00001$  (Weber et al., In Revision), the shading in bright  
 398 orange corresponds to its  $2\sigma$  standard error. Dashed vertical lines separate different days of  
 399 measurements. (For interpretation of the references to colour in this figure legend, the reader is  
 400 referred to the web version of this article.)

401

402 These results highlight the necessity of the standard-bracketing approach, which corrects the  
 403 described effects. Nevertheless, we minimised the influence of these effects by tuning the  
 404  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio towards the reference value prior to the measurement, or, if necessary, again  
 405 afterwards.

406

## 407 5.2 Tests with reference materials

### 408 5.2.1 Nanosecond LA-MC-ICP-MS

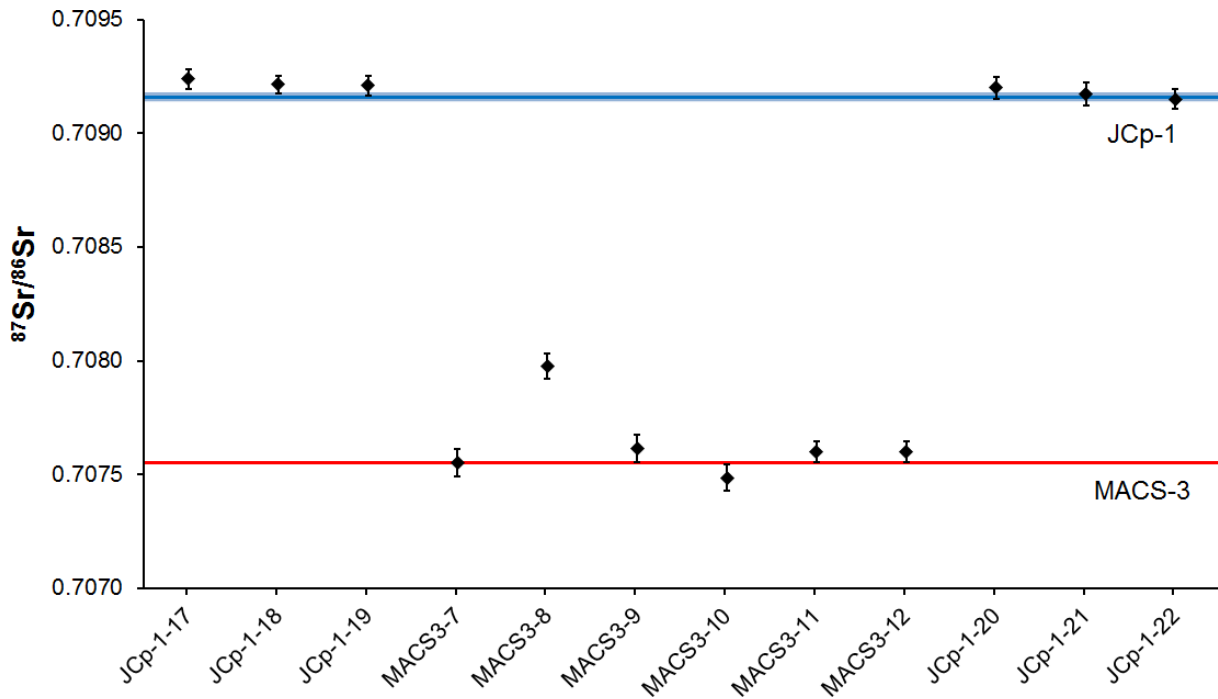
409 For the nanosecond laser ablation system, we chose the carbonate RMs JcT-1, JcP-1 and  
410 MACS-3 and applied the method described above (section 3.3). These RM's have a large range  
411 of Sr concentrations, and we are aware that changes of the laser parameters between different  
412 samples can affect the measurements. Nevertheless, all measurements showed sufficient  
413 fluence ( $\sim 10 \text{ J/cm}^2$  for JcP-1 and MACS-3 and  $> 22 \text{ J/cm}^2$  for JcT-1) and the obtained  $^{87}\text{Sr}/^{86}\text{Sr}$   
414 ratios showed the expected results within error. The mean value of the JcP-1 measurements  
415 was  $^{87}\text{Sr}/^{86}\text{Sr} = 0.70913 \pm 0.00008$  ( $n = 3$ ) and agree with the literature value of  $0.70916 \pm$   
416  $0.00002$  (Ohno and Hirata, 2007). In addition, the uncorrected JcP-1  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is  $0.70914$   
417  $\pm 0.00007$  ( $n = 3$ ) and the uncorrected  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of JcT-1 is  $0.70917 \pm 0.00005$  ( $n = 5$ ), thus  
418 both are indistinguishable from the literature values. The results for MACS-3 provide an  
419 average  $^{87}\text{Sr}/^{86}\text{Sr}$  value of  $0.70753 \pm 0.00005$  ( $n = 16$ ), which is in agreement with the literature  
420 value of  $0.7075532 \pm 0.0000037$  (Jochum et al., 2011).

421

## 422 5.2.2 Femtosecond LA-MC-ICP-MS

423 In order to further test our methodology, we used a femtosecond laser ablation system on  
424 carbonate RM's with high Sr concentrations (JcP-1 and MACS3) following the method as  
425 described in chapter 3.3. All measurements were corrected by the standard bracketing approach  
426 yielding  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in agreement with the reference values (Fig. 5). An exception is  
427 measurement MACS-3-8, which shows a strongly elevated  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. This sample may  
428 have been affected by changes in the Kr signal intensity because unusual peak intensities in  
429  $^{84}\text{Kr}$  were observed during the blank measurement. It is thus likely that similar fluctuations  
430 occurred during the measurement which affected the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. The measured raw  $^{87}\text{Sr}/^{86}\text{Sr}$   
431 ratios before the standard bracketing correction for JcP-1 are  $0.70920 \pm 0.00004$  ( $n = 6$ ) and  
432  $0.70757 \pm 0.00005$  for MACS-3 (without MACS3-8,  $n = 5$ ), in agreement with the literature  
433 values. After performing the standard bracketing approach, the average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is

434  $0.70917 \pm 0.00006$  for JCp-1 (n = 6) and  $0.70752 \pm 0.00006$  for MACS-3 (without MACS3-8,  
 435 n = 5).



436

437 **Figure 5:**  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of reference materials JCp-1 and MACS-3 obtained by fs-LA-MC-  
 438 ICP-MS. The red line represents the literature value of MACS-3 of  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7075532 \pm$   
 439  $0.0000037$  (Jochum et al., 2011), the blue line shows the literature value of JCp-1 of  $^{87}\text{Sr}/^{86}\text{Sr}$   
 440  $= 0.70916 \pm 0.00002$  (Ohno and Hirata, 2007), with its  $2\sigma$  standard error shown as bright blue  
 441 shading. The error range for the reference value of MACS-3 is too small to be visible in the  
 442 figure. Note that sample MACS-3-8 was strongly affected by very variable  $^{84}\text{Kr}$  intensities  
 443 during the blank measurement and probably during the sample measurement as well.

444

### 445 5.3 Speleothem GP5

446 On sample GP5, a total number of 27 different layers were measured (Fig. 6 [A]). In the area  
 447 between  $\sim 116$  to  $118.5$  mm distance from top (DFT) the resolution is high (i.e. less than  $100 \mu\text{m}$   
 448 between linescans). Further measurements were performed with a distance of  $\sim 1000 \mu\text{m}$



449 between each other. Some measurements suffer from changing mass bias and low intensities  
450 ( $^{88}\text{Sr} < 1 \text{ V}$ ), resulting in decreasing values of  $^{87}\text{Sr}/^{86}\text{Sr}$  (in particular linescans GP5-17-21,  
451 Table 2). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios generally show only minor variations, ranging from  $0.70856 \pm$   
452  $0.00017$  to  $0.70920 \pm 0.00007$ . The low-resolution measurements from 108.3 to 115.3 mm DFT  
453 show a relatively stable Sr isotope composition with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between  $0.70890 \pm 0.00011$   
454 and  $0.70913 \pm 0.00008$ . The average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of all linescans is  $0.70892 \pm 0.00006$  ( $n =$   
455 79).

456 36 spot analyses were performed on stalagmite GP5. These were placed near the right end of  
457 the third linescan within the same growth layer (Fig. 1). At signal intensities lower than ca.  
458 0.6 V on  $^{88}\text{Sr}$ , we found a significant decrease of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. Corresponding  
459 measurements are marked with double diamonds  $\blacklozenge\blacklozenge$  in Table 2. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the spot  
460 measurements from GP5 are presented as circles in Fig. 6 [A]. The results show a similar pattern  
461 as the linescans, even though the  $2\sigma$  standard errors are slightly larger. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio varies  
462 between  $0.70872 \pm 0.00024$  and  $0.70907 \pm 0.00011$ . The mean of all spot measurements is  
463  $^{87}\text{Sr}/^{86}\text{Sr} = 0.70897 \pm 0.00005$  ( $n = 32$ ) and in good agreement with the linescan data.

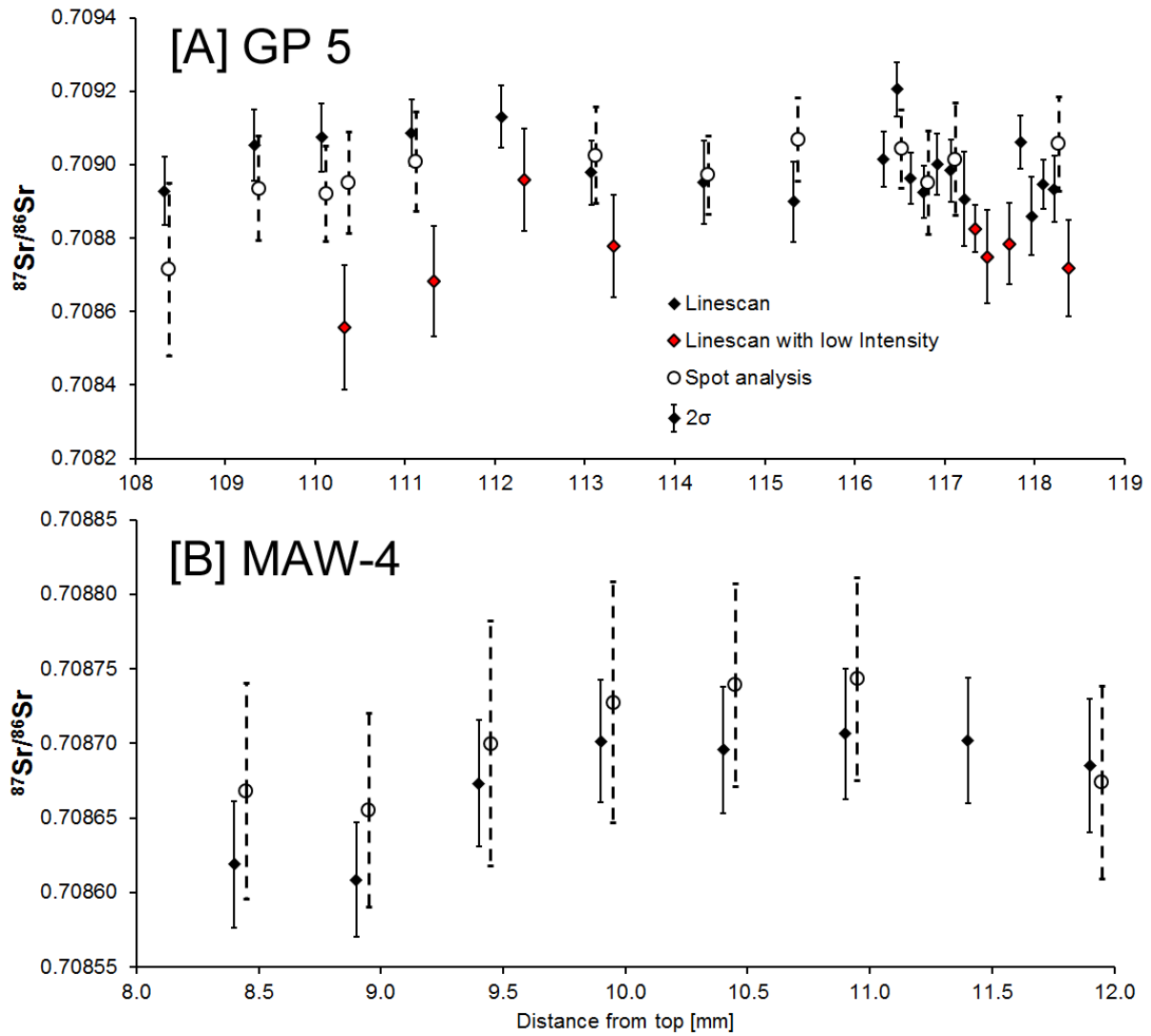
464

#### 465 **5.4 Speleothem MAW-4**

466 On MAW-4, 24 linescans were performed at a sampling resolution of 500  $\mu\text{m}$  (Fig. 1). The  
467  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are presented in Fig. 6 [B]. While the first two measurements at 8.4 and 8.9 mm  
468 DFT are similar, the following measurements show a slightly increasing trend towards higher  
469 values, reaching a maximum of  $0.70871 \pm 0.00004$ . The  $2\sigma$  standard error of all measurements  
470 is  $\pm 0.00004$  with an average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio over all linescans of  $0.70867 \pm 0.00003$  ( $n = 24$ ).

471 24 spot analyses were performed on stalagmite MAW-4, placed near the right end of the third  
472 linescan within the same growth layer (Fig. 1). Note that layer MAW-4-7 was not measured.

473 For layer MAW-4-8, a total number of six spot measurements were performed to test the  
474 reproducibility. The mean of MAW-4-Spot-8a-c is within error of the mean of MAW-4-Spot-  
475 8d-f. Since MAW-4-Spot-8a-f are in perfect agreement, they were combined as a single  
476 measurement (MAW-4-Spot-8). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the spot measurements of MAW-4 are  
477 presented as circles in Fig. 6 [B]. A pattern, similar to the linescans can be observed with two  
478 measurements at 8.4 and 8.9 mm DFT showing lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios compared to the other  
479 values. In contrast to the linescan measurements, this increase is not significant due to larger  
480 errors. Nevertheless, an increase and a plateau at the same distance from top is visible for the  
481 spot analyses. The  $2\sigma$  standard error of all measurements is in the range of  $\pm 0.00006$  to  
482  $\pm 0.00008$  and therefore higher than for the linescans. The average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio over all spot  
483 measurements is  $0.70870 \pm 0.00002$  ( $n = 24$ ), in agreement with the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio derived from  
484 the linescans.



485

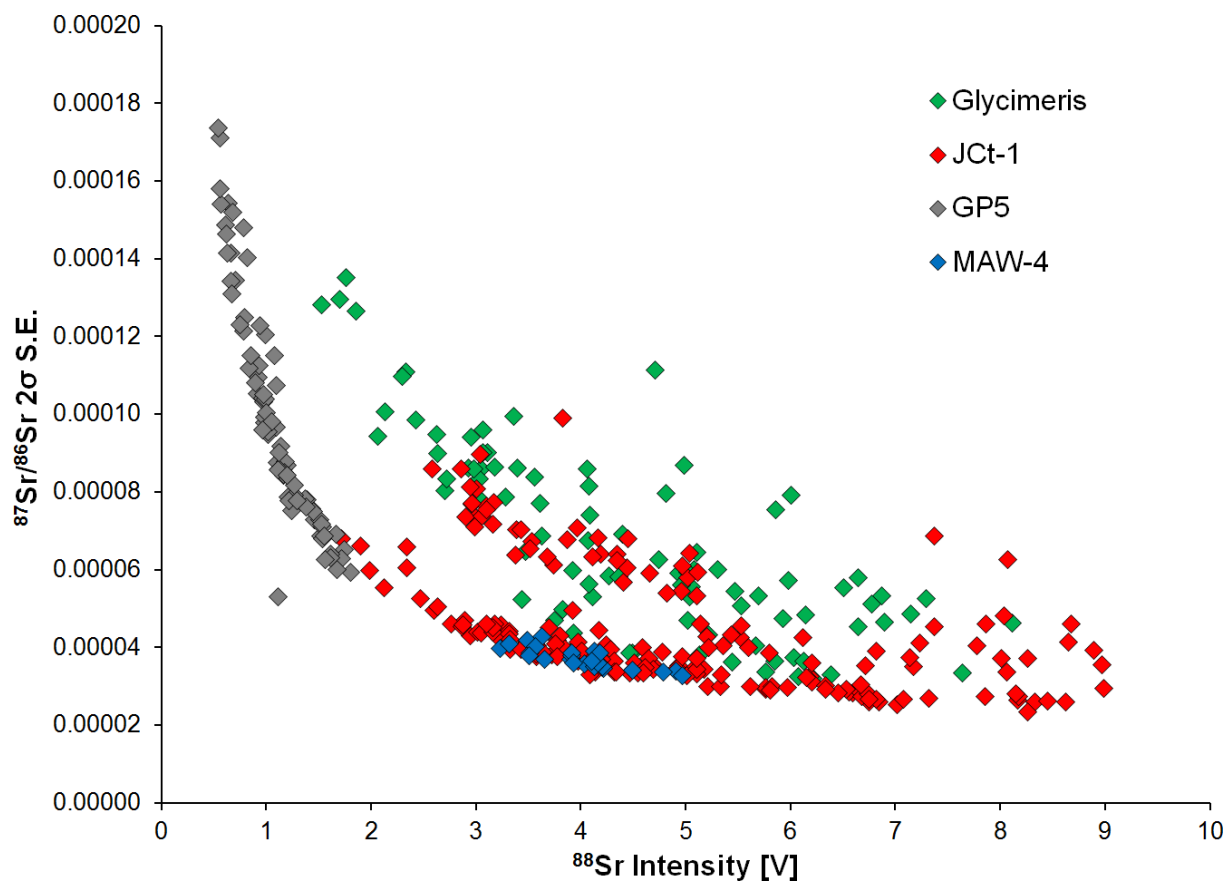
486 **Figure 6:** [A]  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are plotted against the distance from top of speleothem GP5.  
 487 Linescan measurements affected by low signal intensities are marked red. [B]  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios  
 488 of speleothem MAW-4 against distance from top [mm] for the linescan as well as the spot  
 489 analyses. For better visualization of the error bars, spot analyses data were shifted to the right  
 490 by 0.05 mm.

491

492 **6. Discussion**

493 **6.1 Linescan versus spot analysis**

494 We used two different laser ablation methods for this study, i.e., linescans along growth bands  
495 and spots, to test which is the best approach. In general, the linescan method provides much  
496 smaller  $2\sigma$  standard errors than the spot analysis. For RM JCt-1, the final  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio usually  
497 has a  $2\sigma$  standard error in the range of  $\pm 0.00002 - 0.00005$  for linescan measurements,  
498 representing a total error in the range of  $0.003 - 0.01\%$ . For spot analyses, the  $2\sigma$  standard error  
499 was in the range of  $\pm 0.00005 - 0.00007$ . The  $2\sigma$  standard error is highly dependent on the Sr  
500 concentration of the sample (Fig. 7). The different precision in spot and linescan analyses is  
501 caused by: 1) the longer integration time for the linescan approach, and 2) decreasing signal  
502 intensity during spot analysis caused by deepening of the laser crater. Therefore, the spot  
503 analysis approach might be insufficiently precise to resolve small scale changes in the  $^{87}\text{Sr}/^{86}\text{Sr}$   
504 ratio. This is exemplified in MAW-4, where an increase in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio was significant  
505 for the linescan approach, but not for the spot analyses due to larger errors. A disadvantage of  
506 the linescan approach, however, is that unwanted sampling of material from different growth  
507 layers (with a different  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio) may occur. Furthermore, linescans require a larger  
508 sample surface compared to spot analysis. We recommend using the linescan approach only for  
509 speleothems with a regular (parallel) layering that provides a relatively large sample surface  
510 (ca. 3 mm width and length). For speleothems with irregular layering, spot analysis may be the  
511 preferable option. Tests with spot analyses showed that higher repetition rates ( $> 10$  Hz) result  
512 in a higher signal intensity and precision, which is desirable for samples with relatively low Sr  
513 concentration (200-500  $\mu\text{g/g}$ ), such as GP5. However, the sample material should be dense and  
514 stable enough to resist such a high ablation efficiency. Higher repetition rates also result in  
515 deeper laser craters and thus potentially in ablating into different layers. However, for repetition  
516 rates in the range of  $5 - 10$  Hz the depth of the crater should be  $\leq 12\ \mu\text{m}$  and even less for  
517 linescan measurements ( $\leq 2\ \mu\text{m}$ ). Thus, this effect should only be important for very slowly  
518 growing speleothems.



519  
 520 **Figure 7:** Scatter plot of  $^{88}\text{Sr}$  intensity vs.  $^{87}\text{Sr}/^{86}\text{Sr}$   $2\sigma$  standard error. The dependency of the  
 521  $^{87}\text{Sr}/^{86}\text{Sr}$   $2\sigma$  standard error on the  $^{88}\text{Sr}$  intensity is shown for the linescan measurements of Jct-  
 522 1, *Glycimeris* sp., GP5 and MAW-4.

523  
 524 **6.2 Nanosecond versus femtosecond laser systems**

525 Ablating RMs JcP-1 and MACS-3 with either a nanosecond or a femtosecond laser gives  
 526 similar results. While the nanosecond laser provides the advantage of measuring lower  
 527 concentration samples with higher precision, the femtosecond laser is less vulnerable to  
 528 fractionation effects and offers better control on the ablation process (Glaus et al., 2010; Koch  
 529 and Gunther, 2007). In addition, the refractory Sr is generally less affected by matrix, elemental  
 530 and isotopic fractionation effects in comparison to the volatile Rb (Horn and von Blanckenburg,  
 531 2007). However, with our setup, the femtosecond laser approach requires much higher Sr

532 concentrations ( $> 1400 \mu\text{g/g}$ ) to achieve sufficient precision. For instance, we were not able to  
533 accurately measure JCt-1 and our speleothem samples with the femtosecond laser due to  
534 insufficient Sr concentration. In contrast, the standard bracketing approach with JCt-1 and JCp-  
535 1 with the nanosecond laser was successful and the data from MACS-3 were similar to literature  
536 values. The results from the femtosecond LA-MC-ICP-MS measurements show that our  
537 approach can be transferred to other laser ablation systems. The raw measurements of JCp-1  
538 and MACS-3 are in good agreement with literature values and the performance of our standard  
539 bracketing approach does not affect the resulting  $^{87}\text{Sr}/^{86}\text{Sr}$  significantly. Overall, the  $^{87}\text{Sr}/^{86}\text{Sr}$   
540 RM data obtained with both laser ablation systems agree within error and are therefore probably  
541 not affected by differences in matrix effects between the different setups.

542

### 543 **6.3. Tuning parameters and suitable reference materials**

544 An aspect of major importance identified during the development of the LA-MC-ICP-MS  
545 technique is to adjust the tuning after changing the cones to obtain correct  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of a  
546 reference solution. Tuning for maximum signal intensity does not always result in the  $^{87}\text{Sr}/^{86}\text{Sr}$   
547 ratio of the RM (Fig. 2). To achieve the correct  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio we adjusted the lens settings. In  
548 comparison to the tuning of the high voltage lenses, the source and transfer lenses had a larger  
549 effect on stability and reliability of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios with our NU Plasma MC-ICP-MS  
550 (Fig. 2). In addition, the laser ablation system itself alters the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the  
551 measurements. Since different RMs and samples have variable Sr contents, the laser energy and  
552 spot size may have to be adjusted to prevent signal intensities larger than  $\sim 10$  V on cup H4 ( $^{88}\text{Sr}$   
553 signal). It is important to use similar measurement parameters for RMs and speleothem samples  
554 when the standard bracketing technique is applied. Therefore, it is essential to use a RM with  
555 similar Sr concentration and a similar matrix as the speleothem sample. By not using matrix-  
556 matched samples and RMs, potential differences in the occurrence of interference may alter the

557 correction (Irrgeher et al., 2016). In case of different matrices and/or large differences in Sr  
558 concentration, the resulting  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the unknown sample needs to be handled with care  
559 and might be less precise. For instance, the use of RM Jct-1 for correcting GP5 measurements  
560 was critical, due to low intensities on the sample (1 – 2 V,  $^{88}\text{Sr}$ ) and high intensities on the RM  
561 (up to 8 – 9 V,  $^{88}\text{Sr}$ ) when using the same laser parameters. Fluence decreases with laser energy  
562 and it is not guaranteed that the same measurement parameters are available for all samples and  
563 RMs. For speleothem samples with much higher Sr concentration than in this study, JcP-1 and  
564 MACS-3 are suitable RMs.

565 Furthermore, the signal intensity of the Sr isotope measurements is important. Measurements  
566 suffering from very low intensities on  $^{88}\text{Sr}$  ( $\sim < 1$  V) show large errors. A scatter plot of the  
567 intensity of the  $^{88}\text{Sr}$ -signal against the  $2\sigma$  standard error for the linescan measurements of Jct-  
568 1, the bivalve shell of *Glycimeris* sp., GP5 and MAW-4 (Fig. 7) reveals in particular for GP5 a  
569 high dependency on a sufficiently high Sr signal for precise measurements. Intensities of  $^{88}\text{Sr}$   
570 below  $\sim 1.5$  V cause a dramatic shift towards large errors. Similar patterns are visible for Jct-1  
571 and the *Glycimeris* sp. shell. The Sr intensity difference found in MAW-4 is too low to show  
572 the effect of signal intensity on the uncertainty. All measurements with low Sr intensities suffer  
573 from low counting statistics and the background correction of Kr might be insufficient.

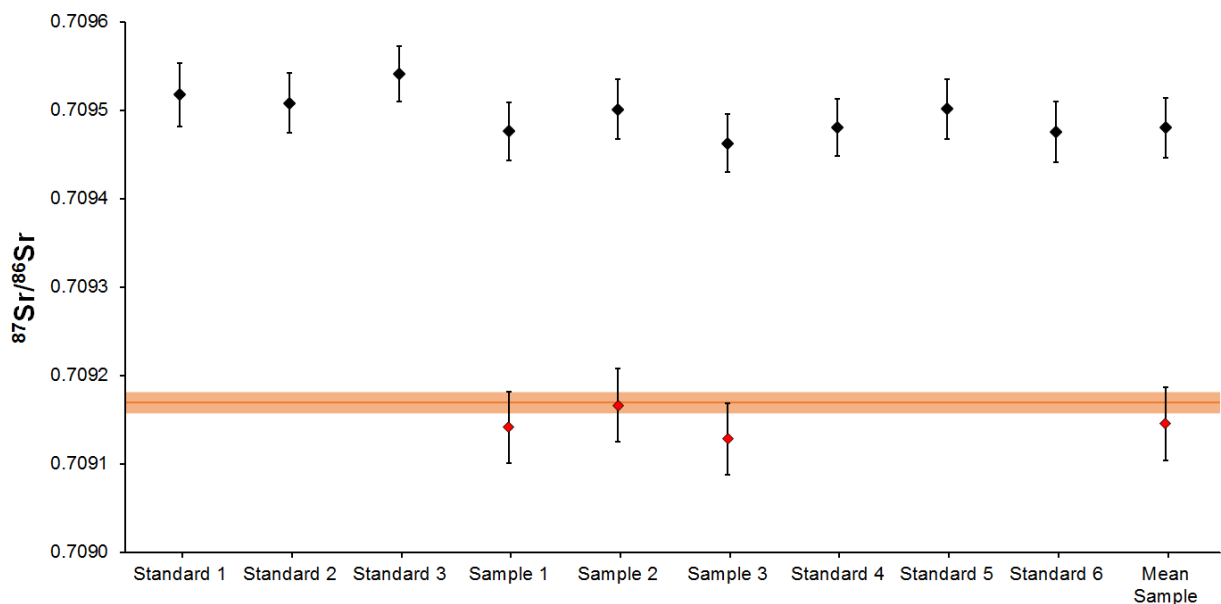
574 Another effect that can have major detrimental influence on the analysis is progressive clogging  
575 of the cones. When a decrease in Sr intensity is observed, it is important to evaluate if this  
576 change results from a change of the Sr content in the sample or from clogging of the cones by  
577 deposition of Ca. Additional information on the performance of the mass spectrometer is  
578 provided by monitoring the mass bias. In our study, the mass bias for the  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratio was  
579 usually between 0.45 – 2.09 % ( $R_{\text{corr}}/R_{\text{meas}} = 0.9791 - 0.9955$ , Eq. 3). Especially for the  
580 linescans of sample MAW-4, the mass bias remained very stable (1.24 – 1.27 %;  $R_{\text{corr}}/R_{\text{meas}} =$   
581 0.9873 – 0.9877, Eq. 3). When the mass bias shows increased variability over the day, careful

582 evaluation of the results is necessary. We observed that a decrease in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and an  
583 increase in the  $2\sigma$  standard error is often related to a high mass bias (e.g., for samples GP5-17-  
584 21, Table 2).

585

#### 586 6.4 Standard bracketing

587 Our results highlight the importance of the standard bracketing correction scheme for LA-MC-  
588 ICP-MS Sr isotope analysis. Prior to the first sample measurements, a test of the standard  
589 bracketing method was performed using Jct-1. For this purpose, Jct-1 was used as a RM and  
590 also treated as a sample. The raw and corrected results are shown in Fig. 8. The standard  
591 bracketing method seems to be generally applicable for  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio correction, since the  
592 corrected Sr isotope ratios of Jct-1 agree within uncertainties. A similar test performed on the  
593 RMs JcP-1 and MACS-3 with the femtosecond LA-MC-ICP-MS setup also showed reliable  
594 results (Fig. 5).



595

596 **Figure 8:** Black rhombs show the raw results of the  $^{87}\text{Sr}/^{86}\text{Sr}$  LA-MC-ICP-MS linescan  
597 measurements performed using Jct-1 as a reference material and a sample. Corrected  $^{87}\text{Sr}/^{86}\text{Sr}$



598 ratios of Jct-1 are shown as red rhombs. Note that the errors increased in comparison to the raw  
599 data due to correction via the reference material. The orange line represents the reference value  
600 of Jct-1 of  $0.70917 \pm 0.00001$  (Weber et al., In Revision).

601

## 602 **6.5 LA-MC-ICP-MS of Sr isotopes on speleothem samples**

603 Traditional Sr isotopes analysis by solution MC-ICP-MS or TIMS requires careful chemical  
604 treatment. A recent study by Wortham et al. (2017) presented a speleothem Sr isotope record  
605 obtained by LA-MC-ICP-MS. These authors performed linescan measurements parallel to the  
606 growth axis of a speleothem from Brazil and traced an increasing  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio over the last  
607 two millennia. Their approach is slightly different to ours. While their linescan is performed  
608 parallel to the growth axis, we measure three linescans for each growth layer perpendicular to  
609 the growth axis, which enables us to test whether results from individual growth layers are  
610 reproducible (similar to the Hendy test for stable carbon and oxygen isotopes, Hendy (1971)).  
611 In addition, the change of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the Brazilian speleothem was on the third  
612 decimal, which is relatively large. Detecting smaller changes (i.e., on the fourth to fifth  
613 decimal), is only possible by conducting a set of measurements perpendicular to the growth  
614 axis. Otherwise the obtained  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is largely influenced by a time-averaging effect.  
615 Wortham et al. (2017) used a different sampling approach and do not provide the Sr  
616 concentration of their speleothem and the used RM which complicates the comparison of both  
617 studies. Nevertheless, they showed that it is possible to track large changes in speleothem Sr  
618 isotope ratios using linescans parallel to the growth axis. Our results show that it is also possible  
619 to obtain higher precision Sr isotope data by LA-MC-ICP-MS using a set of linescans, as well  
620 as spot analyses orientated perpendicular to the growth axis. With the state-of-the-art MC-ICP-  
621 MS systems, it is unlikely that small scale changes in Sr isotope composition can be detected  
622 by performing a linescan parallel to the growth axis. This is further complicated by the typically

623 low Sr concentration of speleothems (few hundred  $\mu\text{g/g}$  or even less). However, aragonitic  
624 speleothems can have much higher Sr concentrations of several thousand  $\mu\text{g/g}$ . Thus, in  
625 aragonitic samples, a linescan parallel to the growth axis may reveal small-scale changes in Sr  
626 isotope composition.

627

## 628 **7. Conclusions**

629 We show that LA-MC-ICP-MS is a powerful tool for the analysis of Sr isotopes in speleothems.  
630 Best results are obtained from samples with Sr concentrations of  $>1000 \mu\text{g/g}$ . For our setup, the  
631 minimum  $^{88}\text{Sr}$  concentration required to obtain reliable  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios was ca.  $300 \mu\text{g/g}$ . In  
632 order to retrieve reliable results, appropriate tuning of both the mass spectrometer and the laser  
633 ablation system is of great importance. Tuning for maximum intensity does not always result  
634 in correct  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. We highly recommend to tune for the correct Sr-isotope ratio of a  
635 reference material prior to an analytical session. The Sr concentration of the RM should be in  
636 the same range as that in the samples. In order to account for potential drifts in the mass  
637 spectrometer during an analytical session, we recommend to apply standard bracketing using  
638 appropriate RMs.

639 Linescans provide higher precision than spot analyses. The latter might be advantageous  
640 however if only a limited surface is available for sampling, for instance in case of a irregular  
641 layering. While speleothem samples tested here contain only low amounts of REEs and Rb,  
642 appropriate correction procedures are required to minimise the influence of interferences from  
643 these elements. In addition, potential interferences resulting from Ca argides and dimers should  
644 be accounted for.

645 The use of a femtosecond laser ablation system provides a more stable signal intensity and  
646 therefore more precise measurements, but its application on samples with low Sr concentrations

647 (ca. >1400  $\mu\text{g/g}$ , since measurements with Jct-1 were not precise enough) is not recommended  
648 due to lower signal intensities compared to the nanosecond laser leading to less precise results.

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864



865 **Table 1:** NU Plasma collector block assignments used for *in-situ* LA-MC-ICP-MS Sr isotope analysis of speleothems. Collectors H1, H2, H4, Ax  
 866 and L1 – L5 are Faraday cups, IC-1 is an ion counter.

867

Collector	H4	H2	H1	Ax	L1	L2	L3	IC-1	L4	L5
Single Mass	88	87	86.5	86	85.5	85	<u>84</u>	83.5	83	82
Double Mass	176	174	173	172	171	170	168	167	166	164
Isotope of interest	<sup>88</sup> Sr <sub>82.58%</sub>	<sup>87</sup> Sr <sub>7.00%</sub>	-	<sup>86</sup> Sr <sub>9.86%</sub>	-	-	<sup>84</sup> Sr <sub>0.56%</sub>	-	-	-
Singly-charged interferences	-	<sup>87</sup> Rb <sub>27.83%</sub>	-	<sup>86</sup> Kr <sub>17.28%</sub>	-	<sup>85</sup> Rb <sub>72.17%</sub>	<sup>84</sup> Kr <sub>56.99%</sub>	-	<sup>83</sup> Kr <sub>11.50%</sub>	<sup>82</sup> Kr <sub>11.59%</sub>
Doubly-charged interferences	<sup>176</sup> Yb <sub>12.99%</sub>	<sup>174</sup> Yb <sub>32.03%</sub>	<sup>173</sup> Yb <sub>16.10%</sub>	<sup>172</sup> Yb <sub>21.68%</sub>	<sup>171</sup> Yb <sub>14.09%</sub>	<sup>170</sup> Yb <sub>2.98%</sub>	<sup>168</sup> Yb <sub>0.12%</sub>	-	-	-
Molecular interferences	-	-	-	-	-	<sup>170</sup> Er <sub>14.91%</sub>	<sup>168</sup> Er <sub>26.98%</sub>	<sup>167</sup> Er <sub>22.87%</sub>	<sup>166</sup> Er <sub>33.50%</sub>	<sup>164</sup> Er <sub>1.60%</sub>
Molecular interferences	<sup>40</sup> Ca <sup>48</sup> Ca	<sup>44</sup> Ca <sup>43</sup> Ca	-	<sup>40</sup> Ca <sup>46</sup> Ca	-	<sup>42</sup> Ca <sup>43</sup> Ca	<sup>40</sup> Ca <sup>44</sup> Ca	-	<sup>40</sup> Ca <sup>43</sup> Ca	<sup>40</sup> Ca <sup>42</sup> Ca
Molecular interferences	<sup>40</sup> Ar <sup>48</sup> Ca	-	-	<sup>40</sup> Ar <sup>46</sup> Ca	-	-	<sup>40</sup> Ar <sup>44</sup> Ca	-	<sup>40</sup> Ar <sup>43</sup> Ca	<sup>40</sup> Ar <sup>42</sup> Ca

868

869 Note that only collectors used during analysis are shown in this table. Potential interferences affecting the Sr masses are also illustrated along with  
 870 natural abundances for Sr, Rb, Kr, Yb and Er (Berglund and Wieser (2011)). Abundances for molecular interferences of Ca dimers and argides are not

871 shown for reasons of clarity. Some masses have a large number of potential interferences of Ca argides and dimers (e.g. mass 86 with  $^{43}\text{Ca}^{43}\text{Ca}$ ,  
872  $^{40}\text{Ca}^{46}\text{Ca}$ ,  $^{42}\text{Ca}^{44}\text{Ca}$ ,  $^{48}\text{Ca}^{38}\text{Ar}$ ,  $^{46}\text{Ca}^{40}\text{Ar}$ ). Here, only the two most common molecular interferences are shown. Prior to each analysis, the peak center  
873 was determined on mass 84 (L3) using the signal of  $^{84}\text{Kr}$  in the gas flow of Ar. Therefore, mass 84 is underlined.

874 **Table 2:** Results of the linescan analysis from speleothem samples GP5 and MAW-4. The  
875 alignment of the different cups is presented with the corresponding signal intensities. For most  
876 sample layers, three runs were performed. For these samples, the mean of all runs is shown.

877

878 ♦ Sr-concentrations for sample GP5 were taken from Wassenburg et al. (2013) and Sr-  
879 concentrations for sample MAW-4 were taken from Wassenburg et al. (2016b).

880 ♦♦ Not all of the three measurements from each spot were taken into account due to shifts in  
881 the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of measurements with low Sr-intensities (approximately below 0.7 V for  
882  $^{88}\text{Sr}$ ).

Sample	Distance from top [mm]	$\bar{x}$ $\diamond$ Sr conc [ $\mu\text{g/g}$ ]	$\bar{x}$ Total Sr [V]	$\bar{x}$ Total Rb [mV]	$\bar{x}$ Rb/Sr $\times 10^{-3}$	$\bar{x}$ Er/Sr $\times 10^{-6}$	$\bar{x}$ Yb/Sr $\times 10^{-6}$	$\bar{x}$ $^{87}\text{Sr}/^{86}\text{Sr}$	$\bar{x}$ 2 $\sigma$ Std Err	$\bar{x}$ Mass Bias $^{87}\text{Sr}/^{86}\text{Sr}$	Sample	Distance from top [mm]	$\bar{x}$ Total Sr [V]	$\bar{x}$ Total Rb [mV]	$\bar{x}$ Rb/Sr $\times 10^{-3}$	$\bar{x}$ Er/Sr $\times 10^{-6}$	$\bar{x}$ Yb/Sr $\times 10^{-6}$	$\bar{x}$ $^{87}\text{Sr}/^{86}\text{Sr}$	$\bar{x}$ 2 $\sigma$ Std Err	$\bar{x}$ Mass Bias $^{87}\text{Sr}/^{86}\text{Sr}$	
<i>Linescans</i>											<i>Spotscans</i>										
<i>GP5</i>																					
GP5-1	118.4	344	0.9	0.08	0.09	1.3	703	0.70872	0.00013	1.23%	GP5-Spot-2	118.2	1.4	0.12	0.08	3.4	529	0.70906	0.00013	1.18%	
GP5-2	118.2	349	1.4	0.08	0.06	1.3	257	0.70893	0.00009	1.22%											
GP5-3	118.0	354	1.2	0.12	0.10	1.0	419	0.70886	0.00011	1.22%											
GP5-4	117.7	310	1.1	0.08	0.07	1.0	~ 0	0.70879	0.00011	1.21%											
GP5-5	117.5	292	1.2	0.10	0.09	1.0	1136	0.70875	0.00013	1.20%											
GP5-6	117.2	354	1.1	0.10	0.09	1.1	664	0.70891	0.00013	1.20%											
GP5-7	117.3	328	1.3	0.06	0.04	1.3	~ 0	0.70883	0.00006	1.18%											
GP5-8	118.1	357	2.1	0.12	0.05	1.2	363	0.70895	0.00007	1.02%											
GP5-9	117.8	335	2.0	0.13	0.06	1.2	497	0.70906	0.00007	1.05%											
GP5-10	117.1	343	1.5	0.19	0.13	1.0	121	0.70898	0.00009	1.14%	GP5-Spot-10	117.1	1.0	0.10	0.09	3.5	865	0.70901	0.00015	1.12%	
GP5-11	116.9	321	1.6	0.12	0.07	0.9	424	0.70900	0.00008	1.31%											
GP5-12	116.8	348	1.9	0.16	0.08	1.0	349	0.70893	0.00007	1.05%	GP5-Spot-12	116.8	1.4	0.11	0.08	2.7	919	0.70895	0.00014	1.95%	
GP5-13	116.6	338	1.9	0.15	0.08	1.1	289	0.70896	0.00007	1.07%											
GP5-14	116.5	340	1.8	0.11	0.06	1.0	268	0.70920	0.00007	1.38%	GP5-Spot-14	116.5	1.7	0.13	0.08	2.7	327	0.70904	0.00011	1.92%	
GP5-15	116.3	336	1.8	0.13	0.07	1.0	803	0.70902	0.00008	1.61%											
GP5-16	115.3	385	1.2	0.20	0.17	1.0	405	0.70890	0.00011	1.75%	GP5-Spot-16	115.3	1.6	0.08	0.05	2.7	487	0.70907	0.00011	1.93%	
GP5-17	114.3	416	1.1	0.10	0.10	1.0	501	0.70895	0.00011	2.03%	GP5-Spot-17♦♦	114.3	1.1	0.08	0.08	2.6	1116	0.70897	0.00011	1.87%	
GP5-18	113.3	353	0.9	0.14	0.16	1.1	441	0.70878	0.00014	2.09%											
GP5-19	112.3	363	0.8	0.17	0.22	1.1	179	0.70896	0.00014	1.82%											
GP5-20	111.3	381	0.7	0.16	0.22	0.9	136	0.70868	0.00015	1.87%											
GP5-21	110.3	427	0.7	0.13	0.19	1.1	285	0.70856	0.00017	2.23%	GP5-Spot-21	110.3	1.1	0.08	0.07	3.5	867	0.70895	0.00014	1.94%	
GP5-22	113.1	351	1.4	0.26	0.18	1.4	435	0.70898	0.00009	1.19%	GP5-Spot-22	113.1	1.2	0.07	0.06	2.9	757	0.70903	0.00013	1.91%	
GP5-23	112.1	425	1.5	0.19	0.13	1.6	~ 0	0.70913	0.00008	1.18%											
GP5-24	111.1	384	1.4	0.16	0.12	1.6	91	0.70909	0.00009	1.16%	GP5-Spot-24♦♦	111.1	0.9	0.11	0.12	3.0	763	0.70901	0.00014	1.93%	
GP5-25	110.1	497	1.3	0.16	0.12	1.5	~ 0	0.70907	0.00009	1.16%	GP5-Spot-25	110.1	1.3	0.08	0.06	2.9	244	0.70892	0.00013	1.96%	
GP5-26	109.3	412	1.3	0.20	0.16	1.7	~ 0	0.70905	0.00010	1.16%	GP5-Spot-26♦♦	109.3	1.1	0.12	0.12	3.3	564	0.70894	0.00014	1.98%	
GP5-27	108.3	373	1.4	0.23	0.17	1.6	233	0.70893	0.00009	1.16%	GP5-Spot-27♦♦	108.3	0.5	0.06	0.12	2.8	708	0.70872	0.00024	2.00%	
<i>Linescans</i>											<i>Spotscans</i>										
<i>MAW4</i>																					
MAW4-1	8.4	1729	4.8	0.06	0.01	0.4	1181	0.70862	0.00004	1.24%	MAW4-Spot-1	8.4	4.1	0.15	0.04	1.3	432	0.70867	0.00007	0.92%	
MAW4-2	8.9	1629	5.7	0.03	0.01	0.4	2295	0.70861	0.00004	1.25%	MAW4-Spot-2	8.9	3.6	0.08	0.02	1.2	694	0.70866	0.00007	0.97%	
MAW4-3	9.4	1526	4.8	0.04	0.01	0.5	623	0.70867	0.00004	1.25%	MAW4-Spot-3	9.4	4.2	0.09	0.02	1.3	1155	0.70870	0.00008	0.95%	
MAW4-4	9.9	1585	5.0	0.04	0.01	0.4	925	0.70870	0.00004	1.25%	MAW4-Spot-4	9.9	3.9	0.07	0.02	1.4	1011	0.70873	0.00008	0.88%	
MAW4-5	10.4	1600	4.9	0.06	0.01	0.4	1421	0.70870	0.00004	1.26%	MAW4-Spot-5	10.4	4.3	0.08	0.02	1.3	654	0.70874	0.00007	0.45%	
MAW4-6	10.9	1560	4.5	0.06	0.01	0.4	149	0.70871	0.00004	1.26%	MAW4-Spot-6	10.9	4.2	0.05	0.01	1.3	1116	0.70874	0.00007	0.49%	
MAW4-7	11.4	1595	4.7	0.12	0.02	0.4	552	0.70870	0.00004	1.27%											
MAW4-8	11.9	1458	4.2	0.07	0.02	0.5	624	0.70869	0.00004	1.27%	MAW4-Spot-8	11.9	5.6	0.10	0.02	0.8	609	0.70867	0.00006	1.99%	

884 **Table 3:** Operating parameters of the NU Plasma MC-ICP-MS and the two laser ablation  
 885 systems.

886

**NU Plasma MC-ICP-MS**

RF Power	1300 W
Argon cooling gas flow rate	13 L/min
Auxiliary gas flow rate	0.93 L/min
Interface cones	Ni
Lens settings	Optimized for maximum signal intensity and <sup>87</sup> Sr/ <sup>86</sup> Sr ratio
Mass resolution	Low
Mass analyzer pressure	3-5 x 10 <sup>-9</sup> mbar
Detection system	Nine Faraday collectors and one Ion Counter
Sampling mode	Time Resolved Analysis

**New Wave UP213 nm  
Laser ablation system**

**NWR Femto 200  
Laser ablation system**

	Linescan	Spot	Linescan
Sampling approach	Linescan	Spot	Linescan
Wavelength	213 nm	213 nm	200 nm
Line length	750 μm		750 μm
Ar flow rate	0.65-0.79 L/min	0.68-0.78 L/min	0.77 L/min
He flow rate	0.65-0.81 L/min	0.68-0.78 L/min	0.77 L/min
<i>Pre-Ablation</i>			
Frequency	10 Hz	10 Hz	5 Hz
Translation rate	80 μm/s		60 μm/s
Beam width	100-110 μm	110 μm	65 μm
<i>Ablation</i>			
Frequency	10 Hz	5-10 Hz	25 Hz
Translation rate	5 μm/s		5 μm/s
Beam width	80-100 μm	100 μm	55 μm
Dwell time		120 s	
Fluence	20-30 J/cm <sup>2</sup>	20-30 J/cm <sup>2</sup>	0.7-0.8 J/cm <sup>2</sup>
<i>Data Collection</i>			
Gas background	45 s	45 s	45 s
Sample	145 s	85-115 s	145 s
Integration	0.2 s	0.2 s	0.2 s

887