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1 **Laser Ablation – Accelerator Mass Spectrometry: a** 2 **novel approach for rapid radiocarbon analyses of** 3 **carbonate archives at high spatial resolution**

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16

17

18 **Keywords:** Radiocarbon, Laser Ablation, Accelerator Mass Spectrometry, Carbonate record, bomb peak

19

20 **Abstract**

21 A new instrumental setup, combining laser ablation (LA) with accelerator mass spectrometry (AMS), has
22 been investigated for the online radiocarbon (¹⁴C) analysis of carbonate records. Samples were placed in
23 an in-house designed LA-cell and CO₂ gas was produced by ablation using a 193 nm ArF excimer laser. The
24 ¹⁴C/¹²C abundance ratio of the gas was then analyzed by gas ion source AMS. This configuration allows
25 flexible and time resolved acquisition of ¹⁴C profiles in contrast to conventional measurements, where only
26 the bulk composition of discrete samples can be obtained. Three different measurement modes, i.e.
27 discrete layer analysis, survey scans and precision scans, were investigated and compared using a

28 stalagmite sample and, subsequently, applied to terrestrial and marine carbonates. Depending on the
29 measurement mode, a precision of typically 1-5 % combined with a spatial resolution of 100 μm can be
30 obtained. Prominent ^{14}C features, such as the atomic bomb ^{14}C peak, can be resolved by scanning several
31 cm of a sample within one hour. Stalagmite, deep-sea coral and mollusk shell samples yielded comparable
32 signal intensities, which again were comparable to those of conventional gas measurements. The novel
33 LA-AMS setup allowed rapid scans on a variety of sample materials with high spatial resolution.

34 1. Introduction

35 Carbonate radiocarbon (^{14}C) records are of great interest in a variety of research fields, such as
36 paleoclimatology^{1,2}, establishing or improving chronologies³⁻⁵ understanding the carbon cycle^{6,7}, and age
37 validation of marine organisms⁸. Because carbonates usually can be radiometrically dated (e.g., Uranium-
38 Thorium (U/Th) disequilibrium methods^{9,10}), ^{14}C in stalagmites and corals provides a powerful geochemical
39 tracer to study, for example for soil carbon dynamics¹¹⁻¹³ and/or past ocean circulation^{14,15}. In very young
40 carbonates (<200 years) where U/Th dating becomes less precise, the detection of the atomic bomb ^{14}C
41 peak caused by nuclear weapon tests during the 1950s and 1960s may provide indirect, stratigraphic age
42 information^{16,17}. Either of the above applications requires access to the ^{14}C signature along the archive's
43 growth axis at high spatial resolution, which involves the analysis of a great quantity of small subsamples.
44 Micro-sampling for conventional ^{14}C analysis is commonly done by micromilling techniques, reaching
45 spatial resolutions of a few dozen to hundreds of μm , but requiring an enormous work load^{11,13,18}. In
46 addition to the tedious sampling process, the following multi-step chemical procedure (including
47 graphitization) necessary for the ^{14}C analysis by accelerator mass spectrometry (AMS) involves the risk of
48 sample contamination.

49 The coupling of laser ablation (LA) with inductively coupled plasma mass spectrometry (LA-ICPMS) is a
50 widely used analytical technique that allows rapid analyses of solid materials at high spatial resolution,
51 while little to no sample preparation is required¹⁹⁻²¹. To date, LA has mainly been applied to elemental and
52 isotopic analyses of solid materials, and there are few studies that deal with ^{14}C measurements where LA
53 is used as a sampling technique. Rosenheim, et al.²² showed that when focusing a UV laser (quintupled
54 Nd:YAG, 213 nm) onto a carbonate sample, approximately 30 % of the ablated material was converted
55 into CO_2 . In this pilot study, the CO_2 was converted into graphite for a conventional accelerator mass
56 spectrometry (AMS) measurement and therefore it did not benefit from the online injection of CO_2 when
57 using gas ion source AMS^{23,24}. Fractionation effects that may occur during the ablation event and might
58 lead to fractionation of the C isotopes are not of concern in AMS analyses, as the internal normalization

59 using the $^{13}\text{C}/^{12}\text{C}$ ratio should also correct for mass dependent fractionation effects that occur during
60 ablation. Wacker, et al. ²⁵ performed the first direct coupling of LA with AMS using a commercial LA unit
61 (LSX 213, CETAC Technologies, Omaha, USA) and a simple LA-cell design. In the proof of principle
62 experiment they performed, the known $^{14}\text{C}/^{12}\text{C}$ ratio of a natural sample was reproduced within
63 uncertainty. Subsequently, an LA-setup with optimized cell geometry was designed^{26,27}. This novel LA-AMS
64 setup offers high flexibility regarding analysis time, spatial resolution and measurement precision.
65 Standards were reproduced within uncertainties and the blank level allows ^{14}C -measurements to ages as
66 old as 35 000 years.

67 The aim of this study was to demonstrate the applicability of the novel LA-AMS setup in the analysis of
68 natural carbonate samples. First, different laser scanning modes implemented into the new setup were
69 compared with regard to analysis time, material consumption, spatial resolution and measurement
70 precision. Second, the applicability of the system to different materials such as stalagmites, corals and
71 shells was investigated and $^{14}\text{C}/^{12}\text{C}$ data from conventional graphite AMS analysis could be reproduced
72 within the uncertainties using LA-AMS.

73

74 2. Methods

75 2.1. Instrumental Setup

76 An ArF excimer laser (Ex5, Argon Fluoride 193 nm, GAM LASER, Orlando, USA) operating at a wavelength
 77 of 193 nm is used to generate pulses at a repetition rate ranging from 150 - 250 Hz and a fluence between
 78 1 and 2.5 J/cm² on the sample surface, delivered as a rectangular spot of 110 x 680 μm². The ablation
 79 process can be observed via a monochrome CCD camera (AVT MANTA G-125B, Allied Vision Technologies,
 80 Stadtroda, Germany) combined with a zoom lens (OPTO TUBUS Z-1,0/146, Opto, Gräfelfing, Germany).
 81 The ablation rate of the LA-AMS system is approximately 100 μg/min of CaCO₃ when ablating at a laser
 82 repetition rate of 200 Hz. Samples with maximum dimensions of 150 x 25 x 15 mm³ can be placed in the
 83 sample holder of an in-house designed LA-cell (Figure 1, adapted from ²⁷), which is equipped with a xy-
 84 positioning system (SLC, SmarAct GmbH, Germany) that allows precise positioning of the sample relative
 85 to the laser beam. Helium is used as a carrier gas to transport the laser-produced CO₂ from the ablation
 86 spot to the ion source via a fused silica capillary ("5" in Figure 1). The background helium pressure in the
 87 LA-cell was adjusted to provide a gas flow rate on the order of 1.5 mL/min through the capillary. A detailed
 88 description of the LA-cell and the gas handling system can be found in ²⁷.

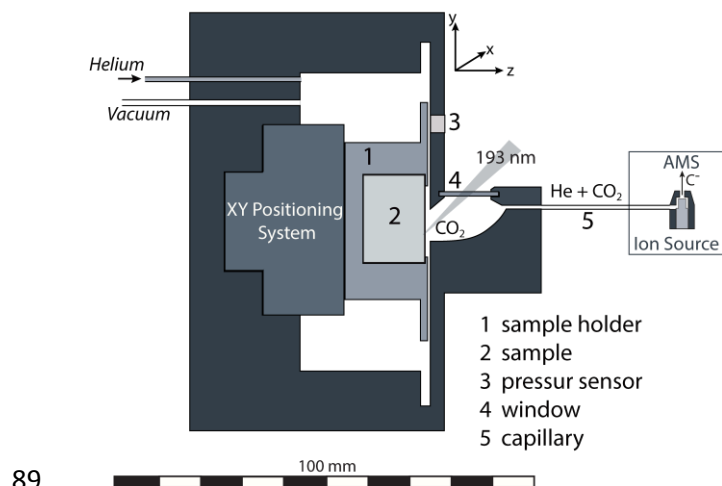


Figure 1 Schematic of the LA-AMS setup: CO₂ is produced in the ablation cell by focusing an ArF laser operating at 193 nm on the carbonate sample. The CO₂ is transported with helium as carrier gas into the gas ion source of the AMS, where negative C ions are formed and the ¹⁴C content is measured.

90
 91
 92 The ¹⁴C-measurements were performed with the ETH Zurich MIniCarbonDAtingSystem AMS system^{28,29}
 93 (MICADAS, Ionplus AG, Dietikon, Switzerland) that is routinely used for gas measurements^{23,24}. Prior to LA-
 94 AMS measurements the AMS was optimized for highest sensitivity by direct injection of a 5 % CO₂ in helium
 95 gas mixture. Subsequently, two to three conventional gas standards (NIST Ox-I or NIST Ox-II) and two to

96 three conventional ^{14}C blanks (5 % CO_2 in helium, Messer Schweiz AG, Lenzburg, Switzerland) were
97 measured to ensure optimum working conditions of the MICADAS. A blank and fractionation correction
98 was applied to the measured $^{14}\text{C}/^{12}\text{C}$ -ratios and, subsequently, normalization to the calibration standard
99 was performed using the data evaluation software BATS³⁰. The final data are reported as $F^{14}\text{C}$ (fraction
100 modern), which corresponds to the activity ratio of the sample relative to a modern reference material^{10,31}.
101 Initially, conventional OxI and OxII gas standards were used for calibration of the samples because no
102 suitable solid standard material was available. Subsequently, a homogenized and compacted carbonate
103 powder from a coral (CSTD)³² with a nominal $F^{14}\text{C}$ of 0.9445 ± 0.0018 was measured before and after each
104 sample analysis and used for normalization. Details on the standards used for normalization can be found
105 in Table 1.

106

107 2.2. Modes of measurement

108 Requiring only minimal sample preparation (compare ²⁷), the LA-AMS setup provides discrete data with a
109 minimum integration time of 10 sec. The XY-positioning system in the LA-cell was controlled by an in-house
110 implemented LabVIEW program (National Instruments, Austin, Texas, USA) and allowed precise
111 movement of the sample relative to the laser beam. Three contrasting sampling strategies (Modes 1-3)
112 were developed in order to provide flexibility in adapting to the analysis purpose and the required
113 precision (Figure 2).

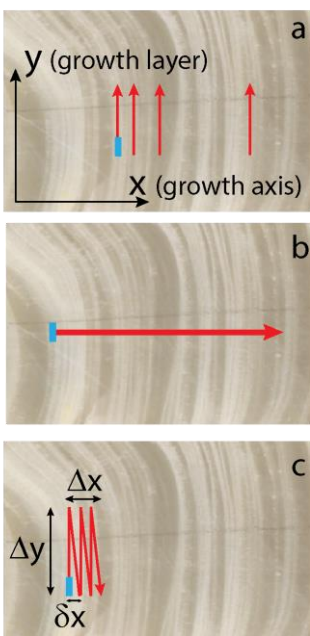
114

115 1) **Discrete layer analyses (Mode 1, Figure 2a)** are equivalent to conventional drilling of samples
116 by ablating material parallel to individual growth layers only (i.e. within carbonate deposits
117 that formed at the same time). The spatial resolution along the growth axis depends on the
118 laser beam width (i.e., 110 μm).

119 2) A **survey scan (Mode 2, Figure 2b)** allows scanning along a sample parallel to the growth
120 direction. The spatial resolution depends on laser beam size, laser repetition rate and scan
121 speed.

122 3) **Precision scan (Mode 3, Figure 2c)** aims for continuous sampling along the growth axis, while
123 the sampling time within the growth layer is increased by scanning in a zig-zag pattern. Part of
124 the scan (Δy) is performed within single growth layers, followed by a return scan with a
125 displacement δx along the x-axis. The entire scan length along the growth axis will be denoted
126 as Δx . In the following the parameters are reported as (Δx , Δy , δx).

127



128

Figure 2 Comparison of the three scanning modes available for LA-AMS measurements. (a) Mode 1: Discrete layer analysis within discrete growth layers, (b) Mode 2: Survey scans parallel to the growth direction, (c) Mode 3: Precision scans. The red arrows represent the scanning direction and the blue rectangle indicates the orientation of the laser spot.

129

130 In the case of conventional ^{14}C AMS measurements, data evaluation had the following scheme: individual
 131 samples were measured and the normalized $^{14}\text{C}/^{12}\text{C}$ -ratios were integrated yielding one averaged $^{14}\text{C}/^{12}\text{C}$
 132 ratio per sample. Hence, the data integration period was equal to the data acquisition period, which was
 133 also the case for Mode 1 in LA-AMS analysis. Modes 2 and 3 required a different data evaluation
 134 procedure: the $^{14}\text{C}/^{12}\text{C}$ -ratio continuously changes as the laser scans across different growth layers of the
 135 carbonate record and depending on the measurement time one or more sputter targets of the gas ion
 136 source were used. This offered the greatest flexibility concerning data evaluation, such as the data
 137 integration periods; hence, spatial resolution and measurement precision could be selected according to
 138 the needs of the application after the analysis. Thus, by integrating fewer or more data points along the
 139 scan pathway, the measurement precision can be adjusted.

140

141 2.3.Samples

142 Fast to slow growing stalagmites and biogenic carbonates (corals, shells) were used in this study (Table 1).
 143 Samples were selected according to their (i) ^{14}C signal sequence, i.e. whether they exhibit a distinct signal

144 such as the bomb peak, (ii) the magnitude of the signal rise, and (iii) the spatial expansion of the signal in
145 the sample (detailed information can be found in the SI).

146 **Table 1** Overview of the different samples and sample materials as well as their expected and LA-AMS derived $F^{14}C$ (fraction
147 modern).

Sample label	Type of sample	mineral	Growth rate ($\mu\text{m}/\text{a}$)	Known $F^{14}C$	Measured $F^{14}C$ (LA-AMS, this study)
ER-77	stalagmite	calcite	120	0.88 – 1.19 ¹³	0.81 – 1.30 ^a
BU-4	stalagmite	calcite	30-50	0.88 – 1.00 ³³	0.82 - 1.04 ^a
SOP-20	stalagmite	calcite	3-15		0.03 – 0.77 ^a
BS_1299m	coral	calcite	35-75	0.92 – 0.98 ³⁴	0.90 – 1.00 ^a
Oyster PH3-A	mollusk	aragonite		1.11 – 1.15*	1.09 – 1.22 ^b
Arctica islandica	mollusk	aragonite		0.925±0.002*	0.88 – 0.92 ^b

148 *this work; ^anormalized to OxII, ^bnormalized to CSTD

149

150 3. Results and Discussion

151 3.1. Applying the three scanning modes

152 Stalagmite ER-77 was considered “ideal” for comparing the scanning modes due to its distinct ^{14}C profile
153 and high growth rate (120 $\mu\text{m}/\text{a}$). It exhibits a pronounced ^{14}C bomb-peak with an $F^{14}C$ increase of 0.3
154 within several mm. Conventional sampling had been performed at the center of the stalagmite’s growth
155 axis with a spatial resolution of 0.6 mm per subsample¹³. The bomb peak expands across the six topmost
156 samples covering a width of ca. 4 mm (Figure 3). The three LA-AMS scanning modes were performed with
157 different offsets to the growth axis: the precision scan (Mode 3) was placed closest to the growth axis
158 covering an effective distance of 3 mm. Discrete layer analysis (Mode 1) covering 4 mm and the survey
159 scan (Mode 2) covering 2.5 mm were performed with increasing distance from the growth axis (detailed
160 information can be found in the SI).

161 3.1.1. Discrete layer analyses (Mode 1)

162 Nine discrete scans were made, each covering a length of 2–2.6 mm. The scan velocity was set between
163 2.5 and 5 $\mu\text{m}/\text{s}$ and the spacing between the individual scans covered 300 μm for the seven topmost

164 samples and 1 mm for the two lower ones. The $^{14}\text{C}/^{12}\text{C}$ raw data (blue dots) of the nine sub-scans are
165 depicted in Figure 3 a, with the onset of the bomb peak found within 60 minutes of analysis. Horizontal
166 red bars indicate the lifetime of a sputter target and represent the period of continuous data acquisition.
167 The vertical dashed and horizontal black lines represent the “data integration period”, which is equal to
168 the “data acquisition period” in the case of “Mode 1.” Integrated, background corrected and normalized
169 data are depicted in Figure 3 b, where red circles represent the LA-data and black squares the conventional
170 measurements. For LA-AMS a measurement precision on the order of 2% is achieved corresponding to the
171 uncertainty from counting statistics and the spatial resolution, defined by the crater width, is 110 μm . The
172 material consumption lies between 1 – 1.5 mg per subsample and the measurement time per aliquot
173 ranges from 8 – 15 min, resulting in ca. 2 hours total analysis time. The LA-derived data match the
174 conventionally derived $F^{14}\text{C}$ values very well and within the statistical uncertainties, as confirmed by a χ^2 -
175 test (95% confidence limit). Since the spacing between individual scans was not minimal, there is capacity
176 for placing two to three additional subsamples between the topmost seven samples and up to nine
177 between the two lower ones.

178

179 3.1.2. Survey scan (Mode 2)

180 A survey scan across the top 2.5 mm of the stalagmite was performed with a scan velocity of 2.5 $\mu\text{m}/\text{s}$
181 resulting in an overall measurement time of 17 minutes. The $^{14}\text{C}/^{12}\text{C}$ ratios are shown as blue dots in Figure
182 3 c. The scan was performed on one sputter target and data integrated for 60 sec, or a span (Δx) of 150
183 μm respectively. The resulting $F^{14}\text{C}$ is represented by the red circles in Figure 3 d. The survey scan was
184 performed within less than 20 minutes, yielding a precision on the order of 4% for each aliquot and a
185 spatial resolution of ca. 260 μm . 1.6 mg of CaCO_3 were consumed for the entire scan corresponding to
186 0.1 mg per integration period. A χ^2 -test was performed to test the agreement between LA and
187 conventional data within a 95% confidence limit. When the LA-data is shifted by a $F^{14}\text{C}$ 0.03 to higher
188 values, the χ^2 -test yields good agreement between the two data sets. This offset of the data is discussed
189 in Section 3.3. The LA-scan was performed with an offset of approximately ca. 1 cm relative to the
190 stalagmite growth axis. The growth layer structure at this region is different to that at the center of the
191 stalagmite as growth layers thin out and start to slope with increasing distance from the center. Thus, the
192 bomb peak is found in the upper 2.5 mm instead of the upper 4 mm, as found with conventional analysis,
193 where samples were taken at the stalagmite’s growth axis.

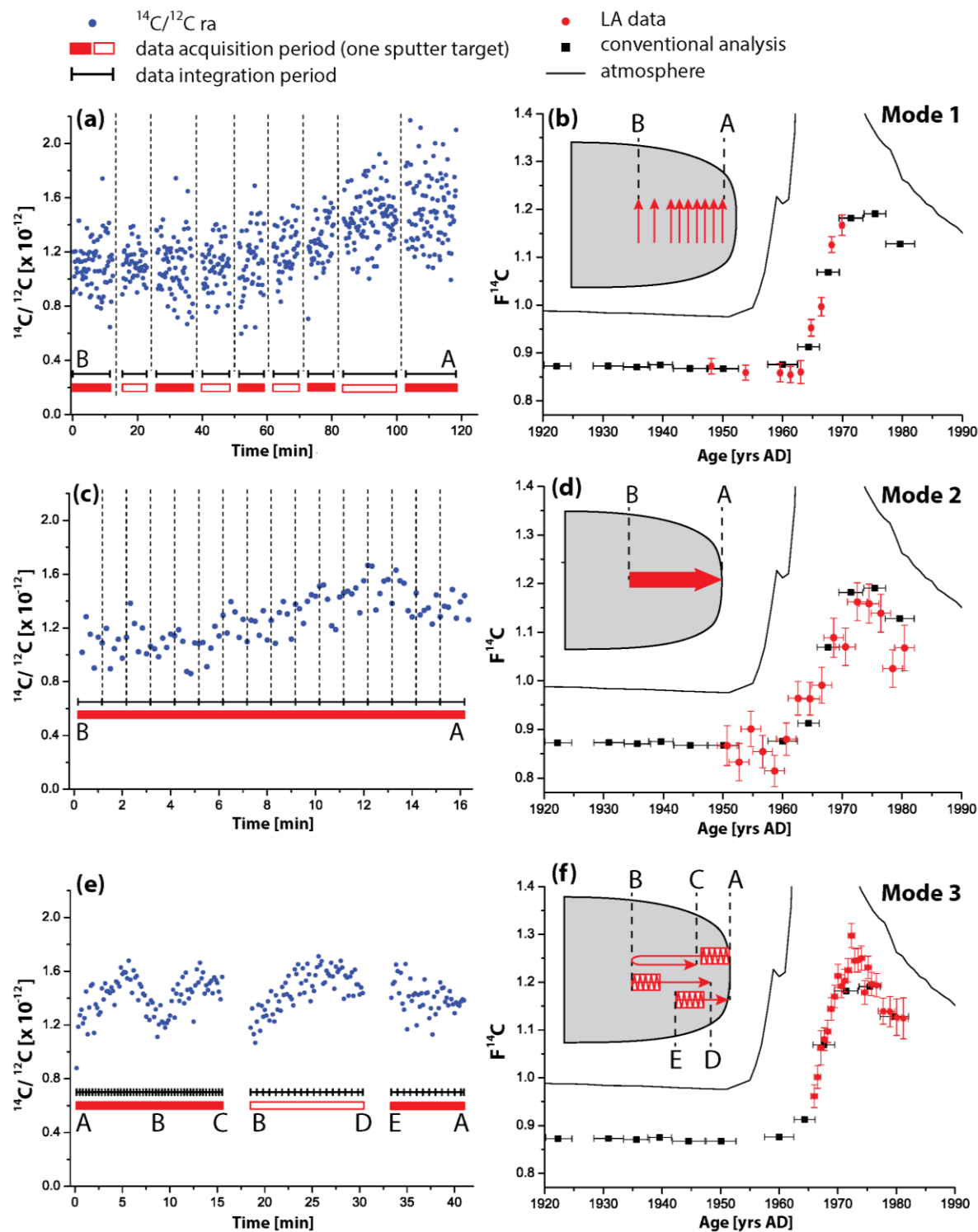


Figure 3 Comparison of the three measurement modes using stalagmite ER-77: (a) and (b) discrete layer analyses, (c) and (d) survey scan, (e) and (f) precision scan. In the left part of the figure corrected $^{14}\text{C}/^{12}\text{C}$ -ratios are plotted against the acquisition time. Red bars (open and solid) correspond to one sputter target and black bars/vertical dashed lines to the integration time. In the right part of the figure, the integrated $F^{14}\text{C}$ values are shown and the inserts indicate the path of the scan (not to scale).

195 3.1.3. Precision scan (Mode 3)

196 Three precision scans were performed within the top 3 mm of stalagmite ER-77. The velocity was set to
197 200 $\mu\text{m/s}$ for the first scan, allowing scanning back and forth while using a single sputter target. The scan
198 parameters were $\Delta x = 3 \text{ mm}$, $\Delta y = 2 \text{ mm}$, $\delta x = 100 \mu\text{m}$. A second and third scan stacked on the track of the
199 first one, this time facing towards the top, were performed with a scan velocity of 100 $\mu\text{m/s}$, while all other
200 parameters were kept constant. The scanning paths are shown in the inset of Figure 3 (f) and are reflected
201 in the $^{14}\text{C}/^{12}\text{C}$ raw data (blue circles in Figure 3 e). The two peaks on the first sputter target correspond to
202 the back and forth movement across the bomb peak in the sample. The second and third scan were
203 performed with two sputter targets. They overlap at the transition and the bomb peak was crossed only
204 once. The integration time is 60 s, which equals the duration of one zig-zag step (compare black horizontal
205 bars in Figure 3 e) and corresponds to a material consumption of 130 $\mu\text{g CaCO}_3$. The average $F^{14}\text{C}$ of the
206 three scans was calculated (red squares in Figure 3 f) and, since the signal intensity at the top of the sample
207 was much lower than for the other samples, the mean of two zig-zag steps was taken for the topmost four
208 data points. The spatial resolution is 300 μm compared to 200 μm achieved for the other subsamples. A
209 measurement precision on the order of 2% is obtained, except for the four data points at the top, for which
210 4% was achieved. The overall measurement time was 40 minutes.

211

212 3.1.4. Comparison of the three LA-AMS scanning modes

213 Each of the presented scanning modes has certain strengths with regard to measurement time, achievable
214 precision, spatial resolution and sample consumption. Spatial resolution and measurement precision
215 depend on the scan velocity, laser parameters and the efficiency of the setup. The major advantage of the
216 three measurement modes, when compared to conventional methods, is the shorter analysis time, and
217 thus sample throughput. This is especially true for the survey scan (Mode 2), which allows analyzing a
218 comparably large section of the sample (i.e., several centimeters within one hour). A quick overview of the
219 ^{14}C -content across a carbonate record can be established using Mode 2 and subsequently a precision scan
220 (Mode 3) at selected regions can be performed to achieve higher measurement precisions. Ablating across
221 different growth layers is only desired in the case of survey scans. For discrete layer analysis (Mode 1) and
222 precision scans (Mode 3) material is collected within individual growth layers. Since the laser beam is a
223 rectangular shape, the maximum scanning distance within each growth layer is limited by the region of
224 parallel growth in the sample and with respect to the laser spot geometry. This could be improved by using
225 a smaller, quadratic or circular laser spot at the expense of CO_2 production. To achieve higher precision at

226 a smaller spot size, signal intensities obtained with the LA-AMS setup need to be improved and is the
227 subject of future studies.

228 With the three measurement modes, the ^{14}C signal in stalagmite ER-77 was reproduced within the
229 statistical uncertainties. The precision scan revealed that bomb ^{14}C reaches $F^{14}\text{C}$ levels of up to 1.30,
230 whereas conventional data suggested that the peak was at approximately 1.20. This highlights the
231 enormous potential of this novel method because of the increased resolution. The key findings for all three
232 LA-AMS scanning modes and the conventional AMS measurements are summarized in Table 2.

233

234

235 *Table 2 Comparison of the three LA-measurement modes with conventional graphite-AMS measurements of ER-77.*

Measurement mode	time/data point (min)	spatial resolution (μm)	material consumption (mg CaCO_3)	measurement precision (%)
micromill and conventional graphite	60	≥ 400	8	0.4
LA – discrete layer	10	100 – 200	1 – 1.5	1 – 2
LA - survey scan	0.5 – 2	300 – 1700	0.1 – 0.2	4 – 6
LA – precision scan	0.5 – 4	200 – 1000	0.1 – 0.4	2 – 4

236

237 3.2.Potential of LA-AMS for stalagmites, corals and other marine carbonates

238 LA-AMS analysis bears enormous potential for the analysis of carbonate archives. Reconnaissance
239 scanning allows rapid identification of the potential of a given sample, thus reducing analysis time and
240 effective costs. In many cases, the ^{14}C -variability is not as pronounced as observed in stalagmite ER-77. In
241 the following section, the potential of the LA-AMS setup for samples with smaller variations in their ^{14}C
242 content, as well as for other carbonate materials is addressed. First, a slow growing stalagmite will be
243 investigated that exhibits an attenuated bomb peak. Second, a stalagmite record is analyzed that exhibits
244 a growth interruption of more than 350 ka. Finally, the LA-AMS setup will be used to investigate a deep-
245 sea coral sample exhibiting a bomb ^{14}C peak, and its potential for use on aragonite shell samples.

246

247

248

3.2.1. Attenuated bomb ^{14}C peak in a stalagmite (BU-4)

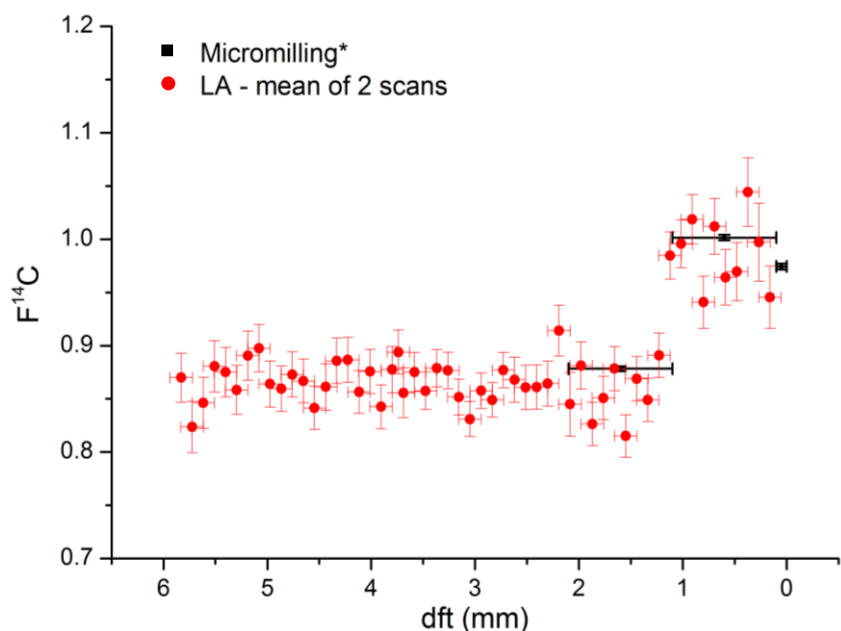


Figure 4 LA-AMS data (red circles) compared to conventionally derived solid AMS measurements (black squares). The high resolution achieved with LA-AMS allows identification of the abrupt onset of the bomb peak in the upper-most mm of the stalagmite sample.

249

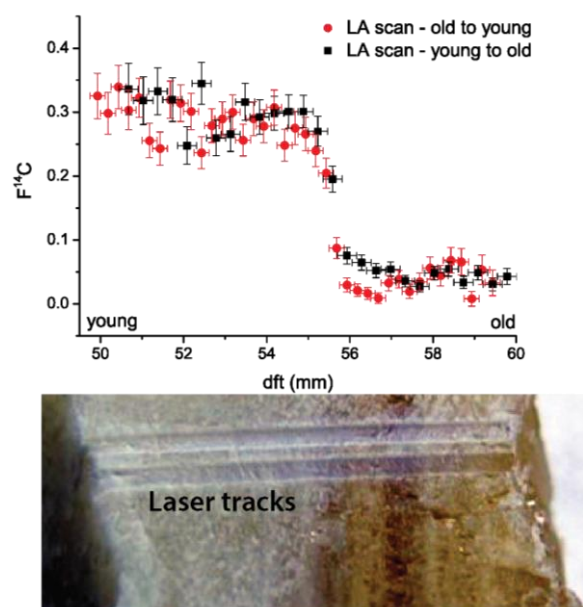
250 Two precision scans were performed in opposite directions within the top 6 mm of the slow growing
 251 stalagmite BU-4. Conventionally obtained and LA-AMS derived data match well within the statistical
 252 uncertainties (Figure 4). The abrupt onset of the bomb peak was revealed, even though it covered a $F^{14}\text{C}$
 253 rise of only 0.12 and is located within the uppermost millimeter of the stalagmite (detailed information
 254 can be found in the SI). A χ^2 test was performed confirming that the LA and conventional data are not
 255 significantly different (95% confidence limit).

256

257 3.2.2. Growth interruption in a stalagmite (SOP-20)

258 Scans in Mode 2 and 3 were performed on all three sections of the Siberian sample. The results for the
 259 upper sections can be found in the SI. Two survey scans facing in opposite direction were performed on
 260 SOP-20-bottom. Both scans exhibit a clear step in $F^{14}\text{C}$ caused by a growth interruption at approximately
 261 55 to 56 mm (Figure 5). Assuming an ideal step between the ^{14}C -dead (> 55.5 mm, see Section 1c in SI for
 262 details) and ^{14}C -containing (<55.5 mm) sections, carry-over effects and washout of the laser system can be
 263 studied. Based on the comparison of both scans, a washout time of approximately 10 sec was estimated.

264



265

266 Figure 5 Two survey scans were performed on the bottom part of stalagmite SOP-20 confirming the growth interruption identified
 267 by U-Th ages of 8.711 ± 0.012 ka BP and 377 ± 7 ka BP. (DFT: distance from top).

268

269 3.2.3. Other samples

270 To further exemplify the potential of the new LA-AMS method, a calcitic bamboo coral (*Keratoisis* sp.
 271 sample BS_1299m³⁴) was analyzed using the precision scan (Mode 3). At the outer edge of the sample the
 272 bomb peak with an $F^{14}C$ increase of 0.06 was found, which is in agreement with the conventional data
 273 (compare Section 2 c and Figure 4 in SI).

274 Two stacked precision scans were performed in opposite directions on a sectioned shell from a black-lip
 275 pearl oyster (*Pinctada margaritifera*) from the Hawaiian Islands. Comparison of LA-AMS and conventional
 276 ^{14}C data from a series of micromill extractions (both within the shell and from a regional hermatypic coral
 277 record) showed good agreement within the statistical uncertainties (compare Section 2 d and Figure 5 in
 278 SI).

279 One survey scan was performed on another shell sample from a long-lived species, *Arctica islandica*, found
 280 on the beach of Fur, Denmark. Within the topmost 30 mm a $F^{14}C$ of 0.92 ± 0.01 was measured, while the
 281 average value of the older part was lower with an $F^{14}C$ value of 0.88 ± 0.02 . The LA-data was confirmed by
 282 one conventional graphite sample that was in agreement. The sample was taken at the youngest part of
 283 the shell and yielded a $F^{14}C$ of 0.925 ± 0.002 . In contrast to the initial assumption that this shell contained

284 the bomb peak, the LA-AMS analyses revealed within less than one hour, that the shell was much older
285 (compare Section 2 e and Figure 6 in SI).

286

287 3.3. Potential and limits of LA-AMS

288 The applicability of the novel LA-AMS technique for ^{14}C analyses of various carbonate archives and its
289 potential with regard to spatial resolution and measurement precision has been exemplified with the
290 above described samples. Signal intensities obtained for aragonite and calcite samples were on the same
291 order of magnitude and comparable to ion currents reached for conventional gas measurements. The
292 major advantages of the novel technique are short measurement times and its high spatial resolution. LA-
293 AMS is especially useful for the rapid identification of pronounced ^{14}C signatures, such as the ^{14}C bomb
294 peak or a growth interruption. A major drawback is the measurement precision, which is worsened by a
295 factor of two or even higher compared with conventional graphite analyses. χ^2 tests were performed to
296 confirm the agreement between LA-derived $F^{14}\text{C}$ data of samples with conventional data. For samples
297 where external standard gas was used for calibration (compare Table 1), the χ^2 test verified the compliance
298 either directly, or after applying an $F^{14}\text{C}$ offset correction between 0.02 – 0.03. The offset is most likely
299 caused by the calibration method, because in this case a standard gas was used, which is introduced into
300 the AMS directly from the gas cylinder. It is still a matter of investigation to identify the origin of the offset.
301 One sample was normalized using the LA-AMS standard CSTD. Even though, the LA-derived data reflects
302 the trend of the conventional data, in this case, the χ^2 test did not confirm that LA-derived and
303 conventional data matched within the 95% confidence interval, not even after performing offset
304 corrections. During the analyses of this sample, exceptionally high background on ^{14}C caused by broken up
305 molecules was observed (see Section 2 c in SI), which is most likely the reason for the discrepancy between
306 LA.

307 For each analyzed sample, the ^{14}C range obtained by LA-AMS was larger than in the case of the
308 conventional analyses (Table 1). Due to the higher spatial resolution achieved with LA-AMS, more detailed
309 insight in the ^{14}C -content within the carbonate record can be gained.

310

311 4. Conclusion

312 The LA-AMS technique was successfully applied to ^{14}C analyses of carbonate archives including stalagmites,
313 deep-sea coral and mollusk shells. Different sampling strategies were compared with regard to

314 measurement precision, spatial resolution, analysis time and material consumption. LA-AMS samples
315 required between 0.05 to 1.5 mg of CaCO_3 with measurement times ranging from 1 to 10 minutes,
316 whereby a precision of 1 to 6 % and a spatial resolution between 100 and 1700 μm were reached. The
317 different scanning modes complement each other and can be combined in order to yield optimal results
318 which may depend on the focus of the study. Continuous scanning provides great flexibility with regard to
319 measurement precision and spatial resolution. Studies with a limited amount of sample can profit from
320 this new technique because comparably only a small amount of material is consumed. A major advantage
321 of LA-AMS is the exceptional sample throughput that allows a rapid assessment of ^{14}C content on a large
322 number of subsamples. Nevertheless, it is desirable to further increase the measurement precision in
323 order to resolve less pronounced ^{14}C signals. Improving the overall efficiency with a modified LA-cell design
324 and an optimized optical setup would allow for a reduction of the scanning velocity, which would increase
325 the analysis time and consequently improve the counting statistics to close the gap in measurement
326 precision between analysis using LA-AMS compared to conventional gas and graphite analysis. A
327 modification of the cell design and the beam transportation system would also provide an opportunity to
328 operate at higher laser fluences. These improvements of the LA-AMS technique will allow establishing ^{14}C
329 profiles of carbonate archives with high precision and unprecedented spatial resolution at an exceptionally
330 high sample throughput.

331

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- 339 (1) Mangini, A.; Lomitschka, M.; Eichstadter, R.; Frank, N.; Vogler, S.; Bonani, G.; Hajdas, I.; Patzold, J.
340 *Nature* **1998**, *392*, 347-348.
- 341 (2) Fleitmann, D.; Burns, S. J.; Mudelsee, M.; Neff, U.; Kramers, J.; Mangini, A.; Matter, A. *Science* **2003**,
342 *300*, 1737-1739.
- 343 (3) Reimer, P. J.; Baillie, M. G. L.; Bard, E.; Bayliss, A.; Beck, W.; Bertrand, C. J. H.; Blackwell, P. G.; Buck, C.
344 E.; Burr, G. S.; Cutler, K. B.; Damon, P. E.; Edwards, R. L.; Fairbanks, R. G.; Friedrich, M.; Guilderson, T. P.;
345 Hogg, A. G.; Hughen, K. A.; Kromer, B.; McCormac, G.; Manning, S.; Ramsey, C. B.; Reimer, R. W.; Remmele,
346 S.; Southon, J. R.; Stuiver, M.; Talamo, S.; Taylor, F. W.; van der Plicht, J.; Weyhenmeyer, C. E. *Radiocarbon*
347 **2004**, *46*, 1029-1058.
- 348 (4) Hoffmann, D. L.; Beck, J. W.; Richards, D. A.; Smart, P. L.; Singarayer, J. S.; Ketchmark, T.; Hawkesworth,
349 C. J. *Earth and Planetary Science Letters* **2010**, *289*, 1-10.
- 350 (5) Ridley, H. E.; Asmerom, Y.; Baldini, J. U. L.; Breitenbach, S. F. M.; Aquino, V. V.; Prufer, K. M.; Culleton,
351 B. J.; Polyak, V.; Lechleitner, F. A.; Kennett, D. J.; Zhang, M. H.; Marwan, N.; Macpherson, C. G.; Baldini, L.
352 M.; Xiao, T. Y.; Peterkin, J. L.; Awe, J.; Haug, G. H. *Nat. Geosci.* **2015**, *8*, 195-200.
- 353 (6) Druffel, E. R.; Griffin, M. S.; Beaupre, S. R.; Dunbar, R. B. *Geophys. Res. Lett.* **2007**, *34*, L09601.
- 354 (7) Robinson, L. F.; Adkins, J. F.; Keigwin, L. D.; Southon, J.; Fernandez, D. P.; Wang, S. L.; Scheirer, D. S.
355 *Science* **2005**, *310*(5753), 1469-1473.
- 356 (8) Andrews, A. H.; Barnett, B. K.; Allman, R. J.; Moyer, R. P.; Trowbridge, H. D. *Can. J. Fish. Aquat. Sci.* **2013**,
357 *70*, 1131-1140.
- 358 (9) Scholz, D.; Hoffmann, D. *Quater. Sci. J.* **2008**, *57*, 52-77.
- 359 (10) Edwards, R. L.; Gallup, C. D.; Cheng, H. *Uranium-Series Geochemistry* **2003**, *52*, 363-405.
- 360 (11) Rudzka-Phillips, D.; McDermott, F.; Jackson, A.; Fleitmann, D. *Geochimica et Cosmochimica Acta* **2013**,
361 *112*, 32-51.
- 362 (12) Genty, D.; Vokal, B.; Obelich, B.; Massault, M. *Earth Planet. Sci. Lett.* **1998**, *160*, 795-809.
- 363 (13) Fohlmeister, J.; Kromer, B.; Mangini, A. *Radiocarbon* **2011**, *53*, 99-115.
- 364 (14) Adkins, J. F.; Cheng, H.; Boyle, E. A.; Druffel, E. R. M.; Edwards, R. L. *Science* **1998**, *280*, 725-728.
- 365 (15) Frank, N.; Paterne, M.; Ayliffe, L.; van Weering, T.; Henriot, J. P.; Blamart, D. *Earth Planet. Sci. Lett.*
366 **2004**, *219*, 297-309.
- 367 (16) Hodge, E.; McDonald, J.; Fischer, M.; Redwood, D.; Hua, Q.; Levchenko, V.; Drysdale, R.; Waring, C.;
368 Fink, D. *Radiocarbon* **2011**, *53*, 345-357.
- 369 (17) Hua, Q.; McDonald, J.; Redwood, D.; Drysdale, R.; Lee, S.; Fallon, S.; Hellstrom, J. *Quat. Geochronol.*
370 **2012**, *14*, 67-80.
- 371 (18) Noronha, A. L.; Johnson, K. R.; Southon, J. R.; Hu, C. Y.; Ruan, J. Y.; McCabe-Glynn, S. *Quaternary*
372 *Science Reviews* **2015**, *127*, 37-47.
- 373 (19) Gray, A. L. *Analyst* **1985**, *110*, 551-556.
- 374 (20) Pisonero, J.; Fernandez, B.; Guenther, D. *Journal of Analytical Atomic Spectrometry* **2009**, *24*, 1145-
375 1160.
- 376 (21) Koch, J.; Guenther, D. *Applied Spectroscopy* **2011**, *65*, 155A-162A.
- 377 (22) Rosenheim, B. E.; Thorrold, S. R.; Roberts, M. L. *Rapid Communications in Mass Spectrometry* **2008**,
378 *22*, 3443-3449.
- 379 (23) Ruff, M.; Wacker, L.; Gaeggeler, H. W.; Suter, M.; Synal, H. A.; Szidat, S. *Radiocarbon* **2007**, *49*, 307-
380 314.
- 381 (24) Fahrni, S. M.; Wacker, L.; Synal, H. A.; Szidat, S. *Nuclear Instruments & Methods in Physics Research*
382 *Section B-Beam Interactions with Materials and Atoms* **2013**, *294*, 320-327.
- 383 (25) Wacker, L.; Muensterer, C.; Hattendorf, B.; Christl, M.; Guenther, D.; Synal, H. A. *Nuclear Instruments*
384 *& Methods in Physics Research Section B-Beam Interactions with Materials and Atoms* **2013**, *294*, 287-290.

- 385 (26) Münsterer, C.; Wacker, L.; Hattendorf, B.; Christl, M.; Koch, J.; Dietiker, R.; Synal, H. A.; Guntherk, D.
386 *Chimia* **2014**, *68*, 215-216.
- 387 (27) Welte, C.; Wacker, L.; Hattendorf, B.; Christl, M.; Koch, J.; Synal, H. A.; Günther, D. *Radiocarbon* **2016**
388 **(in press)**.
- 389 (28) Synal, H. A.; Stocker, M.; Suter, M. *Nuclear Instruments & Methods in Physics Research Section B-Beam*
390 *Interactions with Materials and Atoms* **2007**, *259*, 7-13.
- 391 (29) Wacker, L.; Bonani, G.; Friedrich, M.; Hajdas, I.; Kromer, B.; Nemeč, M.; Ruff, M.; Suter, M.; Synal, H.
392 A.; Vockenhuber, C. *Radiocarbon* **2010**, *52*, 252-262.
- 393 (30) Wacker, L.; Christl, M.; Synal, H. A. *Nuclear Instruments & Methods in Physics Research Section B-*
394 *Beam Interactions with Materials and Atoms* **2010**, *268*, 976-979.
- 395 (31) Reimer, P. J.; Brown, T. A.; Reimer, R. W. *Radiocarbon* **2004**, *46*, 1299-1304.
- 396 (32) Gao, P.; Xu, X.; Zhou, L.; Pack, M. A.; Griffin, S.; Santos, G. M.; Southon, J. R.; Liu, K. *Limnol. Oceanogr.*
397 *Meth.* **2014**, *12*, 174-190.
- 398 (33) Fohlmeister, J.; Schroeder-Ritzrau, A.; Scholz, D.; Spoetl, C.; Riechelmann, D. F. C.; Mudelsee, M.;
399 Wackerbarth, A.; Gerdes, A.; Riechelmann, S.; Immenhauser, A.; Richter, D. K.; Mangini, A. *Climate of the*
400 *Past* **2012**, *8*, 1751-1764.
- 401 (34) Farmer, J. R.; Robinson, L. F.; Honisch, B. *Deep-Sea Research Part I-Oceanographic Research Papers*
402 **2015**, *105*, 26-40.
- 403
- 404