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1 **Carbon and oxygen isotope fractionation in the water-calcite-aragonite system**

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17 **Abstract**

18 The precise determination of the stable C and O isotope fractionation between water and
19 calcite (CC) and water and aragonite (AR) is of special interest for climate reconstructions, e.g.
20 paleotemperatures. Previous studies reported results from both laboratory and field
21 experiments, but their results are only partly consistent. Here we present C and O isotope data
22 of a stalagmite from the Swiss Alps, which shows CC-AR transitions along individual growth

23 layers. Using detailed analyses both laterally and perpendicular to such layers we examined the
24 difference in the C and O isotope fractionation factor of the HCO_3^- - CC and the HCO_3^- - AR
25 system. For O this difference is similar to the water-CC and water-AR offset provided in
26 experimental studies. The O isotope fractionation difference in the water-CC and water-AR
27 system is comparable to those determined in laboratory studies but shows a statistically
28 significant correlation with the CaCO_3 precipitation rate. For C we found a fractionation
29 difference, which is independent of CaCO_3 precipitation rate and with slightly smaller values for
30 the fractionation offset between HCO_3^- - CC and HCO_3^- - AR compared to literature values.
31 However, we also found an unexpected decrease in $\delta^{13}\text{C}$ along growth layers, which contradicts
32 the widely used concept of Rayleigh fractionation during CO_2 degassing and CaCO_3
33 precipitation. The results of this study can be used e.g., to correct stable isotope time series of
34 stalagmites showing CC-AR transitions along their growth axes.

35

36 **1. Introduction**

37 Laboratory experiments of C and O stable isotope fractionation between dissolved inorganic
38 carbon and calcite (CC) revealed the strength of isotope change during this reaction. These
39 experiments, however, often show differing values for isotope fractionation even under similar
40 conditions (e.g., Rubinson and Clayton, 1969; Emrich et al., 1970; Romanek et al., 1992; Kim and
41 O'Neil 1997; Dietzel et al., 2009, Watkins et al., 2013). Additionally, fractionation factors seem
42 to vary with temperature and most likely depend also on the carbonate precipitation rate
43 (Dietzel et al., 2009; Feng et al., 2012; Gabitov et al., 2012; Stoll et al., 2015). Studies of calcite
44 precipitates have also been carried out in caves (e.g., Coplen, 2007; Tremaine et al., 2011; Feng
45 et al., 2012; 2014; Johnston et al., 2013), but these observations only partially agree with those
46 of laboratory experiments (e.g., Kim & O'Neil, 1997). Watkins et al. (2013) show that the
47 observed discrepancies might be related to the calcite precipitation rate.

48 A few experimental laboratory studies investigated the fractionation between water (or the
49 aqueous carbonate species) and aragonite (AR; Romanek et al., 1992; Zhou and Zheng, 2003;

50 Kim et al., 2007; Gabitov 2013). For C and O, isotope fractionation was found to be larger for AR
51 than for CC. In addition, the fractionation difference depends on temperature as the individual
52 water-carbonate fractionation processes of C and O for AR and CC appear to be temperature-
53 dependent. Ideally, the fractionation systematics of CC and AR should be studied in-situ in the
54 field, e.g. in caves in the case of speleothems. Such studies, however, do not exist, nor has it
55 been feasible to form speleothems of both polymorphs in the laboratory. In this respect the
56 study of differences in isotope fractionation between the water-CC and the water-AR system in
57 speleothems of the same setting or, ideally, within the same speleothem, are of high relevance.

58 Therefore, we studied the stable isotope composition of a Holocene stalagmite showing
59 transitions from CC to AR along growth layers. These lateral transitions provide the unique
60 opportunity to investigate in detail the offset in the C and O isotope fractionation within the
61 same specimen, thereby shedding new light on the CC-AR isotope fractionation differences.

62

63 **2. Material and methods**

64 **2.1 Stalagmite description**

65 Stalagmite M39-764-1 was obtained from Betten Cave (N 46° 47.3' E 8° 16.8') in central
66 Switzerland at an altitude of 1,364 m a.s.l. Present-day cave temperature close to the
67 stalagmite location is about 5°C year-around. A more comprehensive monitoring at the drip site
68 of this stalagmite was not possible due to logistic reasons. Vegetation in the catchment above
69 the cave consists of sparse grass and shrub land with sporadic occurrence of dwarf pines. The
70 stalagmite consists of dark calcite and white aragonite with transitions both vertically along the
71 growth axis and laterally along individual growth layers (Fig. 1). The stalagmite is about 60 cm
72 high with a diameter of 7-10 cm. Based on U-Th data its growth period covers the entire
73 Holocene without growth stops (Arps, 2017). The large number of U-Th dates in combination
74 with their high precision provides a detailed record of the growth history of this stalagmite (see
75 Sec. 4.1). As this speleothem grew during the climatically rather stable Holocene, we expect
76 that the temperature in the cave did not change by more than ± 2 °C at most, rendering

77 temperature effects on isotope fractionation differences between the water-CC and the water-
78 AR systems insignificant, as the temperature dependence is similar for both polymorphs (e.g.,
79 compare Kim and O'Neil, 1997; Kim et al., 2007).

80

81

82 <FIG. 1>

83

84 **Fig. 1:** Slabbed section of stalagmite M39-764-1 and close-up of its upper part where most
85 analyses were made. Note the succession of dark (CC) and white (AR) layers along the growth
86 axis as well as laterally along several growth layers. Analyses include stable isotopes (lines), XRD
87 (black dots) and a petrographic thin section (red rectangle). Rectangular holes near the growth
88 axis represent samples for U-Th dating. The letters refer to Hendy test-like stable isotope tracks
89 (black lines). The red numbers represent bundles of short stable isotope sub-tracks across
90 individual growth layers from the center towards the flank (sub-track colors correspond to those
91 in Figs. 5 and S3).

92

93 **2.2 Methods**

94 X-ray diffraction (XRD) data were recorded in reflection mode with an Empyrean diffractometer
95 (PANalytical, Almelo, NL) using Ni-filtered Cu-K α radiation at 40 kV voltage and 40 mA. The
96 diffractometer was equipped with a programmable XYZ-stage, a focusing X-ray mirror and a
97 PIXcel1D detector. Data were collected in a two theta range of 24-54° with a step size of 0.013
98 degree and a total measuring time of 216 minutes. A monocapillary (135x0.3mm, divergence
99 0.3°) with the option of photographic recording of the interested area was used to obtain a
100 small spot diameter. The analysis was directly made on the stalagmite slab.

101 We followed two different approaches for sampling for stable C and O isotope analyses. First,
102 we applied a strategy following the Hendy test at six different depths (black lines/letters in Fig.
103 1). These transects cross the CC-AR transition within individual laminae. The samples were
104 taken by a handheld drill. The distance between individual points on these tracks varied
105 between 3 and 5 mm. Following the same lamina proved to be difficult. Therefore, several
106 isotope sub-tracks (typically about four per layer, see Fig. 1, colored lines) were drilled at nine
107 different depths along the growth direction crossing the same laminae. These sub-tracks were
108 drilled perpendicularly to the growth layers. This resulted in short tracks subparallel to the main
109 growth axis (colored lines in Fig. 1). These samples were obtained using a Sherline 5410 milling
110 machine at increments of 200 μm .

111 Stable C and O isotopes of samples taken along near-parallel sub-tracks perpendicular to the
112 growth lamina were measured using an automated carbonate-extraction system (KIEL IV)
113 interfaced with a MAT253 IRMS (ThermoFisher Scientific) at the Helmholtz Centre Potsdam
114 GFZ. Samples of around 60-90 μg were dissolved in 103 % H_3PO_4 at 72°C and the isotopic
115 composition was measured on the released and cryogenic purified CO_2 . All isotopic ratios were
116 expressed in the delta notation relative to VPDB. Replicate analysis of reference material
117 (NBS19) reported relative to VPDB yielded 1 sigma errors of 0.06‰ for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

118 Stable C and O isotopes of those samples taken along laminae (Hendy-test like approach) were
119 measured using the triple collector gas source IRMS of the University of Innsbruck. The mass
120 spectrometer is linked to an on-line, automated Gasbench II carbonate preparation system. The
121 H_3PO_4 acidification temperature is 72°C (for more details, see Spötl and Matthey, 2006). Isotope
122 ratios are also reported relative to the VPDB scale, and the 1 sigma precision is 0.06 and 0.08‰
123 for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively.

124 As no international AR-standards are available it was necessary to correct the $\delta^{18}\text{O}$ results of
125 AR samples due to phosphoric acid fractionation effects, which are different for CC and AR (Kim
126 et al., 2007b). At the acidification temperature of 72°C AR samples were corrected by +0.38‰.

127

128 **3 Results**

129 **3.1 Petrography**

130 XRD proved that the dark sections of M39-764-1 are CC while the white sections are AR.
131 Microscopic analysis of thin sections reveal that the CC has less air inclusions than the AR. While
132 for AR the holes are numerous but small in size, the size of the few air inclusions in the CC
133 section are considerably larger. The AR consists of thin, needle-like crystals (Fig. 2). From the AR
134 seeds the needle-like crystals spread out fan-like in the general growth direction of the
135 stalagmite and unite with other AR needles - also arranged in fans - from neighboring AR seeds
136 about 200µm in growth direction. When the AR layer is closed no CC is observed and the fan-
137 like structure diminished and the needle-like AR crystals are now parallel aligned. Then the
138 main direction of the AR crystals is parallel to the growth direction. The CC consists of up to
139 400µm-long columnar crystals with a width of not more than about 50µm (Fig. 2). Crystal
140 terminations are usually flat. This fabric can be classified as type C following Frisia (2015). Again
141 the growth of the crystals is parallel to the stalagmite growth direction. Aragonitic remnants
142 within the CC, which would indicate diagenesis, are not present.

143

144

145 <FIG. 2>

146

147 **Fig. 2:** Thin-section micrographs of CC and AR fabrics of a stratigraphic CC-AR transition, where
148 the AR material is younger than the CC. All images (a to c) show the same CC to AR transition
149 under different magnification: a) transmitted light, b) and c) cross-polarized light.

150

151 **3.2 Growth rate**

152 Stalagmite M39-764-1 was previously dated using Th/U (Arps, 2017). In total 57 samples were
153 analysed along the stalagmite (Fig. 3). Typically, dating uncertainties are smaller than 1 % to
154 about 3 %. We used StalAge (Scholz and Hoffmann, 2011) for age-depth modeling, but only
155 focus on the growth rate here (Fig. 3). Growth rate is defined as the time needed for a certain
156 growth increment along the vertical growth axis of the stalagmite. The errors of growth rate
157 were calculated using Gaussian error propagation the of the StalAge-provided age uncertainty.

158 The stalagmite started growing slowly and increased its growth rate subsequently. For most of
159 its growth the rate varied between about 37 ± 2 and 113 ± 12 $\mu\text{m}/\text{a}$. The sampling depths for
160 the isotope measurements were chosen based on the growth rate and the presence of lateral
161 CC-AR transitions. The growth rate at these 15 depth intervals where stable isotopes along the
162 laminae were measured ranges between 39 ± 2 and 99 ± 3.5 $\mu\text{m}/\text{a}$.

163

164

165 <FIG. 3>

166

167 **Fig. 3:** Growth rate vs depth along stalagmite M39-764-1. The large number of Th/U dates
168 (squares; Arps, 2017) allows to calculate growth-rate variations (line). The circles mark the
169 position of the Hendy test-like stable isotope tracks and the open triangles represent the depths
170 at the growth axis where sub-tracks were measured. The equivalent of growth rate is given in
171 CaCO_3 precipitation rate of CC on the left y-axis. The gray shaded area represents the standard
172 deviation of the growth rate.

173

174 For convenience and for comparison with laboratory experiments we calculated the CaCO_3
175 precipitation rate from the stalagmite growth rate by

176 $r = GR * \sigma * 10^4 / (365.25*24)$

177 where r is the average CaCO₃ deposition rate (μmol/m²/h) and GR is the speleothem growth
178 rate (μm/a). The density (σ in g/cm³) of CC is used (2.71 g/cm³) since age and growth rate
179 determination were performed on the central calcitic material. The stalagmite growth rate
180 corresponds to CaCO₃ precipitation rates between 120 ± 11 and 305 ± 3 μmol/m²/h. We
181 assumed zero porosity in the CC. A porosity of 10% would lead to a reduction in the deposition
182 rate by 12 to 29 μmol/m²/h.

183

184 **3.3 Stable isotopes**

185 All stable isotope measurements are provided in the supplement to this study. Two typical data
186 sets for the Hendy test-like transects (tracks B and C in Fig. 1) reveal jumps in the C and O
187 isotopic composition between the last sample in the CC and the first one in the AR (Fig. 4).

188

189

190 <FIG. 4 a and b>

191

192 **Fig. 4:** Stable C (solid squares) and O (open circles) isotope values for Hendy test-like isotope
193 transects B (a) and C (b; see Fig. 1). The grey shaded area represents AR. The offset in C and O
194 between the last sample in the CC and the first in the AR is indicated (solid double arrow - δ¹³C;
195 dashed double arrow - δ¹⁸O). The position of the individual sub-tracks of transects 7 (Fig. 5) and
196 8 (suppl. Fig. S2) are indicated by the solid triangles in the lower part of the figures.

197

198 The offset in $\delta^{13}\text{C}$ between the last CC and the first AR sample is -1.87‰ for track B and -1.30‰
199 for track C. For $\delta^{18}\text{O}$ the difference is -0.72 and -0.67‰ for tracks B and C, respectively. Table 1
200 provides an overview of all offsets in these transects revealing a large variability (between -0.6
201 to -1.7‰ for $\delta^{13}\text{C}$ and -0.66 and -0.99‰ for $\delta^{18}\text{O}$). Notable is the decrease in $\delta^{13}\text{C}$ in the AR
202 sections of transect B and C and in the CC section of transect B. This might (1) reflect imprecise
203 sampling due to missing of the target growth layer (where neighboring layers have significantly
204 lower $\delta^{13}\text{C}$ values but no change in $\delta^{18}\text{O}$), or (2) an intrinsic feature for several sections of the
205 stalagmite.

206

207 **Tab. 1:** Stable C and O isotope offset (CC minus AR) in individual transects and growth rate at
208 the central axis.

209

210 <TAB. 1>

211

212

213 In contrast to the lateral Hendy test-like transects the parallel sub-tracks of transects 1-9 aimed
214 at crossing individual growth layers vertically. Using this strategy enables to reliably identify the
215 isotopic composition of individual growth layers (solving point (1)). Transect 7 (Fig. 5) shows
216 large offsets in C and O isotopic composition between the last sub-track in the CC and the first
217 one in the AR confirming the results of the Hendy test-like transect B (Fig. 4). The other eight
218 transects with their various sub-tracks are shown in the supplementary material. The isotopic
219 variations of all those sub-tracks were aligned to the C isotopic variability observed in the last
220 CC sub-track before the transition to the AR (Fig. 5; all light blue colored sub-tracks).

221

222

223 <FIG. 5 a and b>

224

225 **Fig. 5:** Stable C (a) and stable O (b) isotope composition of the individual sub-tracks in transect
226 7. The color coding is according to Fig. 1. The innermost sampling track in CC is in dark blue. The
227 values for the sampled CC sub-track shortly before the transition to AR are shown in light blue,
228 while the first track after the transition to AR is shown in light orange and the outermost sub-
229 track in the AR in dark orange. The shaded area represents samples situated on the AR 'tongue'
230 or the corresponding samples of the CC section. The black triangle represents the location of the
231 Hendy test-like transect B. Note that for the sub-track in CC near the CC-AR transitions (light
232 blue) the top and bottom three samples were drilled in AR (compare Fig. 1).

233

234 To calculate the offset between the CC and AR, only the outermost sub-track in the CC and the
235 innermost sub-track in the AR was used. The reason for this choice is broadly discussed in Sec.
236 4.2 and 4.3. The average $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for both growth sections were calculated and
237 their difference defined as the fractionation offset between the water-CC and water-AR system.
238 For transect 7 this offset is -0.77‰ with respect to $\delta^{13}\text{C}$ and -0.71‰ for $\delta^{18}\text{O}$. The fractionation
239 offset for all transects (Tab. 1) range from -0.4 to -1.9‰ for $\delta^{13}\text{C}$ and between -0.54 and -1.02‰
240 for $\delta^{18}\text{O}$.

241 At 1.7mm depth of the near parallel sub-tracks of transect 7, which is equal to the position of
242 the Hendy test-like transect B (black triangle in Fig. 5), the C isotope values decrease laterally in
243 both polymorphs. This agrees with the C isotope data of the Hendy test-like transect B and
244 proves that this decrease is not a mismatch in drilling along the growth layer. The decrease in
245 $\delta^{13}\text{C}$ along the growth layer is opposite to what is expected from modelling studies, which
246 investigated the evolution of the isotopic composition of drip water and precipitated CaCO_3
247 (e.g., Hendy 1971; Dreybrodt 2008; Scholz et al., 2009). Interestingly, the relationship is

248 reversed between 2.4 to 3.2 mm for the CC sub-tracks (dark and light blue in Fig. 5a). There, the
249 C isotopic value becomes higher with increasing distance from the growth axis, as predicted by
250 modelling studies (e.g., Hendy 1971; Dreybrodt 2008; Scholz et al., 2009).

251 A depletion in ^{13}C along growth layers is also observed in the sub-tracks of isotope transects 1,
252 3, 4, 8. The more expected behavior of a constant or increasing $\delta^{13}\text{C}$ value is observed in the
253 other transects (transects 2, 5, 6, 9; compare suppl. Fig. S2). For $\delta^{18}\text{O}$ no such anomalies have
254 been observed. For all transects $\delta^{18}\text{O}$ is constant or increases along the growth layer.

255

256 **4 Discussion**

257 **4.1 Primary origin of CC and AR**

258 The petrography of stalagmite M39-764-1 is of major importance for evaluating the stable
259 isotope offsets between CC and AR. Diagenetically unaltered material is essential for the
260 determination of fractionation offsets between the water-CC and water-AR system. Thin-
261 section microscopy (Fig. 2) reveals no AR within the CC sections, suggesting that the CC is of
262 primary origin and not a replacement of precursor AR. Furthermore, the presence of a
263 columnar fabric and the lack of mosaic types both argue against a secondary origin of the
264 calcite. The shape of the AR sections also supports a primary origin of CC, because these
265 “tongues” follow individual growth lines and do not cross them. Diagenetic fronts as observed
266 in stalagmites elsewhere (e.g., Zhang et al., 2014; Frisia 2015; Domínguez-Villar et al., 2017)
267 usually do not follow individual growth layers as in our specimen (see Fig. 1) and also
268 macroscopically show a cloudy appearance. Thus, we conclude that both CC and AR are of
269 primary origin.

270 Additional support for the primary origin of both polymorphs is provided by the U
271 concentration which varies by more than one order of magnitude between CC and AR (200 vs.
272 2600 ng/g - Arps, 2017). Previous studies reported that during diagenetic alteration of primary
273 AR to secondary CC the U concentration would not show a large change (e.g., Scholz et al.,

274 2014; Domínguez-Villar et al., 2017). Furthermore, a diagenetic loss of U of this magnitude
275 would likely also have disturbed the Th/U isotope systematics, and provide inconsistent age
276 control. However, all ages are in perfect stratigraphic order (Arps 2017). Thus, diagenesis is
277 incompatible with the difference of one order of magnitude in U concentration between the
278 two polymorphs. These observations provide strong additional evidence for the primary origin
279 of both CC and AR in this stalagmite.

280

281 **4.2 Mechanism of lateral CC-AR transitions**

282 Changes in the CaCO₃ polymorphs were previously attributed to changes in drip water
283 chemistry (e.g., Frisia et al., 2002; Wassenburg et al., 2012; Riechelmann et al., 2014).
284 Especially, the pH of drip water, the calcite saturation index and in particular its Mg/Ca ratio
285 seem to be important. In detail, a drip water pH > 8.2, a drip water Mg/Ca molar ratio > 0.5, and
286 a calcite saturation index < 0.8 (saturation state $\Omega < 6.3$) favor AR precipitation (Riechelmann et
287 al., 2014). Thus, CC-AR transitions along the growth direction can be explained by changes in at
288 least one of those factors. This implies changes in the initial drip water composition with time,
289 which do not have to be large in order to cross the threshold from one to the other polymorph.
290 However, large variations drip water chemistry cannot be excluded with those type of CC-AR
291 transitions. A similar argumentation is also valid for the stable isotope composition of CC-AR
292 transitions along the growth direction of the speleothem. Even when the period of the CC-AR
293 transition is short, isotope shifts in drip water cannot be excluded and contribute to the isotope
294 offset measured for those CC-AR transitions. Especially, for $\delta^{13}\text{C}$ the isotope shifts along the
295 growth axis can be large as the innermost CC sub-tracks of transects 1 to 9 illustrate (Fig. 5a and
296 suppl. Fig. S2). Neighboring points - only 0.2 mm apart - can show differences of more than 0.5
297 ‰.

298 In contrast to CC-AR transitions along the growth axis, CC-AR transitions along growth layers
299 require that the drip water chemistry and isotopic composition is very similar for carbonate
300 precipitating first as CC and later as AR. The drip water composition must have been close to

301 the threshold, which dictates if CC or AR precipitates from a supersaturated solution. Thus, for
302 large sections of stalagmite M39-764-1, close to its central axis, the drip water composition
303 favors CC precipitation. When the water runs along the stalagmite surface towards the flanks
304 CO₂ degasses and CaCO₃ precipitates. This leads to increasing pH and Mg/Ca ratios in the drip
305 water as well as to a decreasing CC saturation index. At a certain distance from the central axis
306 the AR precipitation threshold is crossed and AR precipitates from the drip water with a nearly
307 identical chemical composition as before. The same argument is valid for the isotopic
308 composition of the drip water. Following the results of laboratory and modelling studies (e.g.,
309 Mickler et al., 2006; Polag et al., 2010; Day and Henderson 2011; Dreybrodt, 2008; Romanov et
310 al., 2008; Mühlinghaus et al., 2009; Deininger et al. 2012) $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CaCO₃ along the
311 growth layer are generally slowly increasing but can be assumed to be quasi-constant over
312 short distances. Thus, stalagmites with lateral CC-AR transitions have nearly the same drip
313 water isotopic composition before and after the transition. Therefore, any change in $\delta^{13}\text{C}$ and
314 $\delta^{18}\text{O}$ of CaCO₃ over short distances before and after the transition can solely be attributed to
315 the offset in the stable isotope fractionation between the water-CC and the water-AR system.

316

317 **4.3 Isotope fractionation along growth layers**

318 Since the results of the Hendy test-like transects might be influenced by missing the target
319 growth layer during sampling, we focus in this section on the results obtained from the sub-
320 tracks of transects 1 to 9. The isotopic composition of O either increases along individual
321 growth layers or remains constant. This result is expected, since this behavior is predicted by
322 modelling studies and documented by cave analogue laboratory experiments. In contrast, $\delta^{13}\text{C}$
323 values often decrease with increasing distance from the stalagmite's growth axis. To our
324 knowledge, this feature has never been reported in speleothems elsewhere. In laboratory and
325 cave experiments, where the isotopic composition of CaCO₃ has been investigated along glass
326 plates or channels (Mickler et al., 2006; Wiedner et al., 2008; Polag et al., 2010; Day and
327 Henderson 2011) the $\delta^{13}\text{C}$ values remained constant or increased.

328 One option to explain the observed decrease in $\delta^{13}\text{C}$ along growth layers is provided by the
329 results of a modelling study investigating the stable isotopic composition of HCO_3^- during CO_2
330 degassing and precipitation of CaCO_3 along the stalagmite surface (Dreybrodt, 2008). A system
331 of differential equations was presented from which the evolution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for HCO_3^-
332 and precipitated CaCO_3 was derived. The results showed that the $\delta^{13}\text{C}$ values can indeed
333 decrease after an initial increase. This is in contrast to other models, which are based on
334 Rayleigh fractionation (e.g., Romanov et al., 2008; Mühlinghaus et al., 2009; Scholz et al., 2009),
335 which do not predict a decrease in $\delta^{13}\text{C}$ during the CaCO_3 precipitation.

336 According to the model of Dreybrodt (2008) the buffering effect of H_2O on the $\delta^{18}\text{O}$ of HCO_3^-
337 and CaCO_3 becomes important on the same time interval as the predicted decrease in $\delta^{13}\text{C}$. Our
338 measurements show, however, that $\delta^{18}\text{O}$ values still increase or are constant while $\delta^{13}\text{C}$
339 decreases. Hence the fractionation model of Dreybrodt (2008) does not completely explain our
340 observations.

341 Another possibility for the lateral decrease in $\delta^{13}\text{C}$ is the exchange of HCO_3^- in the solution with
342 the cave air CO_2 . This mechanism is only mentioned in a few dedicated cave studies in order to
343 explain temporal variations in the C isotopic of stalagmites (Frisia et al., 2011; Smith et al.,
344 2009). In modelling studies, however, this process is more widely discussed (e.g., Hendy, 1971;
345 Scholz et al., 2009; Dreybrodt and Scholz, 2011; Deininger et al., 2012). A recent study
346 combined laboratory experiments with a new, complete reaction diffusion model describing
347 carbon isotope exchange between gaseous CO_2 and the DIC in thin solution films and explored
348 the temperature-dependent C-exchange times between HCO_3^- and gaseous CO_2 (Hansen et al.,
349 2017). For 10°C they reported a C-exchange time of ~ 400 to $\sim 15,800$ s, depending on the state
350 of supersaturation of the solution with respect to cave air CO_2 . Our cave is 5°C cooler, which
351 suggests an even larger C exchange time. The following conditions have to be fulfilled in order
352 for this process to cause a decrease in $\delta^{13}\text{C}$ along growth layers: (1) the C exchange time has to
353 be short in comparison to the time between two drops impinging on the stalagmite; (2) the
354 degree of supersaturation of the solution with respect to CO_2 must have been small (otherwise
355 the C exchange time becomes too long; Hansen et al., 2017), which requires slow rates of

356 CaCO₃ precipitation and thus a slow growth of the stalagmite; (3) the cave air $\delta^{13}\text{C}$ value is
357 sufficiently depleted compared to the enriched $\delta^{13}\text{C}$ values of the drip water (due to the
358 measured high $\delta^{13}\text{C}$ values of the CaCO₃). Unfortunately, no data on the chemical composition
359 of the drip water feeding this stalagmite nor on the $\delta^{13}\text{C}$ value of cave air at the location of the
360 stalagmite are available. Therefore, we are not able to judge, with respect to points (1) and (3),
361 if this process is responsible for the observed decrease in $\delta^{13}\text{C}$ along the growth layers.
362 However, we can examine the role of the CaCO₃ precipitation rate by comparing the offset of
363 the average $\delta^{13}\text{C}$ values of two consecutive sub-tracks in the AR and putting them in
364 relationship to growth rate (Fig. 6). If C exchange processes with cave air CO₂ are modifying the
365 C isotopic compositions of DIC, a decrease in $\delta^{13}\text{C}$ at higher growth rates are expected, while for
366 smaller growth rates $\delta^{13}\text{C}$ should show a decrease.

367

368

369 <FIG. 6>

370

371 **Fig. 6:** *The offset between the average $\delta^{13}\text{C}$ of two consecutive sub-tracks within the AR tongues*
372 *of transects 1 to 9 shows no statistically significant change with growth rate. Positive values*
373 *represent a decrease in $\delta^{13}\text{C}$ with increasing distance from the central axis. Since the distance*
374 *between consecutive sub-tracks differs for the nine individual transects, the $\delta^{13}\text{C}$ offset between*
375 *the consecutive sub-tracks is normalized to a distance of 1 mm. The corresponding y-axis errors*
376 *are also normalized to this distance using Gaussian error propagation. It is important to note*
377 *that the growth rate, given on the X-axis, is obtained from the central axis, while the offset in*
378 *$\delta^{13}\text{C}$ between two AR sub-tracks is determined at a certain distance from this axis (compare Fig.*
379 *1). This might have some influence of the precipitation rate at those locations.*

380

381 Although there appears to be a weak trend between $\delta^{13}\text{C}$ variations along growth layers and
382 growth rates, the correlation is statistically insignificant ($r \sim 0.3$; $p = 0.43$). Therefore, the null
383 hypothesis of a growth rate-dependent $\delta^{13}\text{C}$ change along the growth layer must be rejected.
384 Thus, with the available data it is not possible to verify or falsify the existence of the C-exchange
385 process between cave air CO_2 and the C in the drip water for this speleothem. To conclude, it is
386 not yet obvious which of the two mentioned explanations is responsible for the C isotope
387 decrease along growth layers.

388 Our data show that it is essential to compare only the C isotope values in CC and AR closest to
389 the CC-AR transition, when determining the offset in isotope fractionation between the water-
390 CC and the water-AR system. We applied this strategy to the Hendy test-like transects A to G
391 and to the sub-tracks of transects 1 to 9. For transects 1 to 9 we calculated the average values
392 of the sub-tracks in the AR and CC closest to the CC-AR transition. The average isotopic
393 composition for both sub-tracks was calculated over the range of samples given by the shaded
394 area in Fig. 5 and supplementary Fig. S2, representing the width of the AR ‘tongues’.

395

396 **4.4 Carbon isotope fractionation**

397 **4.4.1 Calcite – aragonite differences**

398 The isotopic offset between CC and AR across lateral transitions is equivalent to the difference
399 in fractionation between the $\text{HCO}_3^- - \text{CaCO}_{3,\text{CC}}$ and $\text{HCO}_3^- - \text{CaCO}_{3,\text{AR}}$ systems presented in
400 laboratory experiments with synthetic CC and AR (e.g., Romanek et al., 1992). Since the pH of
401 cave drip water is usually around 8 to 8.5, it is only necessary to account for HCO_3^- in our study
402 as this is the most abundant species in this pH range (>95%; Dreybrodt 2008; Romanov et al.,
403 2008; Mühlinghaus et al., 2009, Scholz et al., 2009). The offset range observed in stalagmite
404 M39-764-1 is between -1.94 to -0.39 ‰ (Fig. 7). The Hendy-test like transects have a mean
405 offset value of -1.31 ± 0.49 ‰ and the analysis of the parallel sub-tracks across the individual
406 growth sections indicate a mean offset value of -1.07 ± 0.41 ‰. Thus both types of analysis

407 show no systematic offset and both approaches can be combined. The average value for all 15
408 transects is -1.16 ‰ with a standard deviation of 0.46 ‰.

409

410

411 <FIG. 7>

412

413 **Fig. 7:** The fractionation difference for $\delta^{13}\text{C}$ in the water-CC and water-AR system shows no
414 relationship on growth rate (bottom) /precipitation rate (top). The results for the Hendy-test-like
415 transects (grey squares) and the near-parallel sub-track approach (black circles) obtained no
416 statistically significant difference in the mean $\delta^{13}\text{C}$ offset. The vertical bars and according central
417 lines at the right of the plot indicate the standard deviation and average value for the offset in
418 $\delta^{13}\text{C}$ by the two approaches (color coded as the data) and their overall average (bar with striped
419 pattern). For comparison the mean and standard deviation derived by Romanek et al. (1992) for
420 10°C are shown (white bar). Note that the cave temperature is about 5°C.

421

422 The variation of the C isotope fractionation is relatively large, but in the range of analysis of
423 synthetic carbonates from laboratory experiments (Romanek et al., 1992). Two effects are
424 often mentioned, when variations in fractionation are discussed: temperature and carbonate
425 precipitation rate. Since temperature variations are small throughout the Holocene (about ± 2
426 °C at maximum for the northern rim of the Alps; e.g., Davis et al., 2003; Mangini et al., 2005)
427 and the fractionation effect on temperature changes have also been shown to be small
428 (Rubinson & Clayton, 1969; Emrich et al., 1970; Romanek et al., 1992) temperature effects are
429 most likely of minor importance.

430 The effect of CaCO_3 precipitation rate on fractionation differences can be checked with the
431 growth rate. Unfortunately, CaCO_3 precipitation rate covers only a range of half an order of
432 magnitude. On this small range, no dependence of CaCO_3 precipitation with respect to the

433 fractionation offset is observed. The correlation coefficient for all transects is -0.14, for the
434 Hendy-test-like transects -0.03 and for the transects composed of the (near)-parallel sub-tracks
435 the correlation coefficient is about -0.25. None of those numbers is statistically significant.

436 Two types of systematical uncertainty have to be accounted for in our analysis. The numbers
437 for the $\delta^{13}\text{C}$ difference in fractionation during the precipitation of CaCO_3 in form of CC and AR
438 might be somewhat influenced by the lateral distance of neighbored isotope
439 measurement/sub-tracks with respect to the location of the CC-AR transition. Although our
440 sampling strategy was to drill the samples as close as possible with respect to the CC-AR
441 transition, this was not possible for each transect (e.g., transect 9, compare Fig. 1). This might
442 have a small influence on the $\delta^{13}\text{C}$ isotope offset as sometimes $\delta^{13}\text{C}$ is decreasing along the
443 individual growth layers (see Sec. 4.3). The second effect is related to the growth rate. The
444 growth rate is very precisely determined by means of Th/U (Arps, 2017) and in a very high
445 resolution. However, the growth rate is calculated for the central axis, while most of the CC-AR
446 transitions occur with some distance to the central growth axis. Usually the growth rate is
447 smaller for non-central sections of stalagmites. However, we expect this type of error also as
448 relatively small since most of the AR tongues (e.g., transects 1, 3, 4, 5) do not experience a
449 strong thinning towards the outermost sections of the stalagmite (Fig. 1). This suggests that
450 growth rate along individual growth layers might be approximately constant.

451

452 **4.4.2 Comparison with laboratory experiments**

453 In laboratory experiments the fractionation of C between HCO_3^- - $\text{CaCO}_{3,\text{CC}}$ is about $1 \pm 0.2 \text{ ‰}$
454 (Rubinson & Clayton, 1969; Emrich et al., 1970; Romanek et al., 1992; Mook, 2000) and appears
455 to be nearly temperature independent (Romanek et al., 1992; Mook, 2000); the fractionation
456 effect between HCO_3^- and CaCO_3 in its AR polymorph was also evaluated to be nearly
457 temperature independent and has an absolute value of about $2.7 \pm 0.6 \text{ ‰}$ (Romanek et al.,
458 1992). We can compare our results with the difference from both types of laboratory
459 experiments with synthetic carbonates. The laboratory experiment suggests that the

460 fractionation offset (CC minus AR) is -1.7 ± 0.6 ‰ (Romanek et al., 1992). Although our
461 stalagmite based value is about 0.54 ‰ smaller than deduced by the laboratory experiments,
462 their error estimates overlap largely with each other (Fig. 7).

463 For a range between 120 – 310 $\mu\text{mol}/\text{m}^2/\text{h}$ in precipitation rate, there is no statistically
464 significant relationship observed in our results (Fig. 7). This is in agreement with the results of
465 Romanek et al. (1992), which also found no dependence between C isotope fractionation and
466 precipitation rate for both polymorphs (at precipitation rates between 400-58000 $\mu\text{mol}/\text{m}^2/\text{h}$).
467 Thus, especially for any application in natural environments changes in the fractionation offset
468 between water-CC and water-AR appear insignificant with respect to the relatively moderate
469 variations in growth rate observed in natural abiogenic carbonates (e.g., growth rates changes
470 in stalagmites).

471

472 **4.5 Oxygen isotope fractionation**

473 **4.5.1 Calcite – aragonite differences**

474 The differences in $\delta^{18}\text{O}$ of CC and AR close to lateral CC-AR transitions can be regarded to
475 reflect the differences in fractionation between HCO_3^- and CaCO_3 precipitated as CC and AR. We
476 calculated the average value of $\delta^{18}\text{O}$ in CC and AR of the sub-tracks closest to the CC-AR
477 transition. For AR we used all measurements within the AR ‘tongue’ for the calculation of the
478 average and for CC we computed the average by using only those measurements, which
479 correspond to the samples used for the calculation of the averaged AR $\delta^{18}\text{O}$ value. The range in
480 the $\delta^{18}\text{O}$ offset between CC and AR is between -0.54 and -1.02 ‰. As for $\delta^{13}\text{C}$ we rule out
481 temperature variations as the cause. The average value of the CC-AR stable O isotope offset is
482 nearly identical for the two different sampling approaches (0.81 ± 0.13 ‰). Thus the overall
483 offset is also 0.81 ± 0.13 ‰ (Fig. 8).

484

485

486 <FIG. 8>

487

488 **Fig. 8:** Stable O isotope fractionation differences between CC and AR in comparison to growth
489 rate (CaCO_3 precipitation rate). The average offset (CC minus AR) including the standard
490 deviation of those values is indicated on the right-hand side by the short horizontal line and the
491 bar. The results for the Hendy test-like transects (grey squares) and the sub-track approach
492 (black circles) show a linear relationship with growth rate (solid line). Fit parameters and
493 correlation coefficient are indicated on the top right and refer to the CaCO_3 precipitation rate.

494

495 Analyzing the $\delta^{18}\text{O}$ offset data with respect to the CaCO_3 precipitation rate (Fig. 8) reveals a
496 statistically significant relationship between them. Smaller offsets are observed when the
497 CaCO_3 precipitation rate decreases and the linear fit is best described by

498
$$\Delta\delta^{18}\text{O} [\text{‰}] = -0.00134 (\pm 0.00045) * \text{precipitation rate } [\mu\text{mol}/\text{m}^2/\text{h}] - 0.546 (\pm 0.092)$$

499 Its equivalent for growth rate is

500
$$\Delta\delta^{18}\text{O} [\text{‰}] = -0.00418 (\pm 0.00141) * \text{growth rate } [\mu\text{m}/\text{a}] - 0.546 (\pm 0.093)$$

501 Isotope equilibrium fractionation is often referred to occur at extremely slow CaCO_3
502 precipitation rates. Interestingly, the difference in O isotope fractionation between HCO_3^- -
503 CaCO_3 precipitated as CC or as AR is supposed to be very small when growth rate approaches
504 zero. According to our analysis and their linear regression line, under slowest CaCO_3
505 precipitation conditions (e.g., near chemical and isotope equilibrium) the fractionation
506 difference is only $0.546 \pm 0.093 \text{ ‰}$.

507

508

4.5.2 Comparison with laboratory experiments

509 Most studies of O isotope fractionation with synthetic and natural carbonates examined the
510 H₂O – CaCO₃ transition. Here, we emphasize that we do not determine the isotope
511 fractionation offset between H₂O and CaCO₃, because a non-negligible amount of CaCO₃
512 already precipitated prior the CC-AR transition (see. Sec. 4.2). This means that the HCO₃⁻ is out
513 of isotopic equilibrium with respect to H₂O, while the isotopic composition of H₂O remains
514 sufficiently constant during this process (e.g., Deininger et al., 2012).

515 However, the measured difference in δ¹⁸O for CC and AR across lateral CC-AR transitions
516 resembles the difference in fractionation between H₂O and CaCO₃ precipitated as CC and AR as
517 determined in field and laboratory studies (e.g., O’Neil, 1969; Kim and O’Neil, 1997; Dietzel et
518 al., 2009; Feng et al., 2012; 2014; Watkins et al., 2013; 2014 for CC and Zhou and Zheng, 2003;
519 Kim et al., 2007 for AR). The reason is that there is no difference in fractionation between H₂O
520 and HCO₃⁻ from which CaCO₃ precipitates as CC or AR. Therefore, the only possibility to
521 introduce a δ¹⁸O offset between CC and AR precipitating from the same water is isotope
522 fractionation between HCO₃⁻ and solid CaCO₃. Thus, the offset between δ¹⁸O of CC and AR on
523 stalagmite M39-764-1 can be compared to the O isotope fractionation offset between the
524 water-CC and the water-AR system determined in laboratory studies.

525 Our analyses suggest that a precipitation rate-dependent fractionation exists for either the
526 HCO₃⁻ - CC system or the HCO₃⁻ - AR system or - more likely - for both (Fig. 8). As shown in
527 laboratory experiments using synthetic CC, the CaCO₃ precipitation rate is a governing factor for
528 the O isotope fractionation (e.g., Dietzel et al., 2009). Faster CC precipitation was found to be
529 accompanied with a smaller fractionation effect. This was also shown to be valid for CC in cave
530 environments (e.g., Feng et al., 2012), although the average growth rate-dependence for the
531 cave study yielded a smaller slope in the isotope fractionation – CaCO₃ precipitation rate
532 relationship than in the laboratory experiments. The slope found by Dietzel et al. (2009) was
533 $\Delta 1000\ln(\alpha_{CC-H_2O})/\Delta\log(R) = -1.1$ (no uncertainty was given in this study) for a temperature of 5
534 °C and typical pH values of cave drip water (pH = 8.3). Feng et al. (2012) found a lower slope,
535 but argued for lower pH values in the drip water that potentially could explain the difference.

536 The negative slope in the $\delta^{18}\text{O}$ offset between CC and AR with respect to CaCO_3 precipitation
537 rate (Fig. 8) obtained from our measurements requires that for AR the slope of the O
538 fractionation process with respect to CaCO_3 precipitation rate is smaller than observed for CC.
539 The slope of our CC-AR offset data is $\Delta 1000\ln(\alpha_{\text{CC-AR}})/\Delta\log(R) = -0.6 \pm 0.2$. From both slopes, CC
540 vs precipitation rate (Dietzel et al., 2009) and CC-AR offset vs precipitation rate determined in
541 our study, it is possible to calculate the slope of the water-AR system. It is found to be
542 $\Delta 1000\ln(\alpha_{\text{AR-H}_2\text{O}})/\Delta\log(R) \sim 0.5 \pm 0.2$. This slope, however, is in contrast to the argumentation of
543 Kim et al. (2007) with respect to the results of their laboratory experiments with synthetic AR,
544 where no growth rate-specific trend in the stable O isotope fractionation was reported.
545 However, reevaluation of some data of the Kim et al. (2007) study revealed that the $\delta^{18}\text{O}$ of the
546 synthetic AR was – in contrast to statements in the original work – indeed influenced by the
547 rate of CaCO_3 precipitation (Dietzel et al., 2009). Later, the precipitation rate-dependence of
548 water-AR $\delta^{18}\text{O}$ fractionation has been proven experimentally (Gabitov, 2013).

549 Comparing our offset in fractionation between water-CC and water-AR with literature data is
550 difficult, because there are many studies available dealing with either inorganic O isotope
551 fractionation between water and CC or water and AR. Therefore, we focus only on a few
552 laboratory and cave experiments. For comparison purposes, we chose for CC the study of Kim
553 and O'Neil (1997) (because this is one of the most cited), the laboratory study by Dietzel et al.,
554 (2009) (because they investigate also pH and CaCO_3 precipitation rate) and that of Tremaine et
555 al. (2011) as this was the first substantial study of water-CC fractionation performed in caves.
556 For AR, the work of Kim et al. (2007) appears to be the best suited study, because it seems to
557 be the most comprehensive evaluation of isotope and chemical data. No in-cave stalagmite
558 water-AR values were published so far.

559 When provided in the earlier studies, we differentiated the published O isotope fractionation
560 factors with respect to precipitation rate. If not available, we compared our average in the O
561 isotope offset between CC and AR with those of earlier studies (Tab. 2).

562

563 **Tab. 2:** *Stable O isotope offsets between the water-CC and water-AR system for a temperature*
564 *of 5 °C. KO – Kim and O’Neil (1997); K – Kim et al. (2007); T – Tremaine et al. (2011); D – Dietzel*
565 *et al. (2009). D-K (10% porosity) is the $\delta^{18}\text{O}$ difference between CC and AR when assuming that*
566 *CaCO₃ in their experiments had a porosity of 10% (a common value for stalagmites, e.g., Baker*
567 *et al. 1998)*

568

569 <TAB. 2>

570

571

572 The $\delta^{18}\text{O}$ CC-AR offsets determined by the isotope measurements of stalagmite M39-764-1 are
573 close to the results of the offset determined from the Kim and O’Neil (1997) minus the Kim et
574 al. (2007) data and can be regarded as identical with respect to the uncertainty range. In
575 contrast, there is an approximately 1 ‰ difference with respect to the fractionation offset as
576 determined by the results calculated from Tremaine et al. (2011) minus Kim et al. (2007). This
577 suggests that our speleothem-based offset is much closer to the CC-AR difference obtained
578 when using the laboratory data of Kim and O’Neil (1997) for CC than the speleothem-based
579 equation of Tremaine et al. (2011). The Tremaine et al. (2011) derived water-CC fractionation is
580 even larger than that of the water-AR fractionation determined by Kim et al. (2007), leading to
581 a positive value when calculating the CC minus AR offset. However, as shown by our analysis of
582 M39-764-1, the CC-AR offset is not positive. Thus, either the water-AR fractionation factor
583 determined by Kim et al. (2007) is not completely correct and must be larger or the in-cave
584 determined CC fractionation offset (Tremaine et al., 2011; Johnston et al., 2013) is too large.

585 Finally, when comparing the CaCO₃ precipitation rate-dependent fractionation factors for CC
586 (Dietzel et al., 2009) with the water-AR fractionation factor (Kim et al., 2007) the offset is also
587 very close to our results for small growth rates (Tab. 2). For large growth rates our results
588 suggest significantly smaller fractionation offsets than derived from the two laboratory studies.

589 However, when accounting for a 10% porosity of the CC of stalagmite M39-764-1, a common
590 value for stalagmites (e.g., Baker et al., 1998), the O isotope offsets for larger growth rates are
591 more consistent between our study and those of Dietzel et al. (2009) and Kim et al. (2007) but
592 then disagree for smaller growth rates.

593

594 **5 Conclusions**

595 The $\delta^{18}\text{O}$ offset between CC and AR is more similar to that observed in laboratory experiments
596 than observed by in-cave studies. This implies that either the water-AR fractionation factor
597 obtained by laboratory experiments is considerably underestimated, or the interpretation of
598 the cave data for isotope fractionation between HCO_3^- and $\text{CaCO}_{3,\text{CC}}$ is incorrect. E.g., (cave-
599 related) processes might be important for the observed large isotope enrichment between H_2O
600 and $\text{CaCO}_{3,\text{CC}}$. Please note, that cave-related processes such as prior CC precipitation, are not
601 relevant for our study, because we investigated only differences in fractionation between CC
602 and AR which precipitated from the same fluid, i.e. with a nearly identical chemical and isotopic
603 composition.

604 Furthermore, our results suggest that the fractionation differences for $\delta^{13}\text{C}$ between HCO_3^- - CC
605 and HCO_3^- - AR are slightly smaller than shown by laboratory experiments, but well in the range
606 of the according uncertainties. No growth rate-dependent $\delta^{13}\text{C}$ variations were observed, again
607 in line with laboratory experiments. We also reported for the first time evidence of a $\delta^{13}\text{C}$
608 decrease along individual growth layers. This is in contrast to the Rayleigh approach often used
609 to describe stable isotope fractionation along individual growth layers. The reason for this
610 behavior still unclear and requires further investigations.

611 The isotope offset between the water-CC and water-AR system obtained in this study could be
612 used for correcting $\delta^{18}\text{O}$ time series of stalagmites showing CC-AR transitions along their growth
613 axis. It is also possible to account for growth rate-dependent fractionation differences for $\delta^{18}\text{O}$
614 when correcting stable O isotope measurements of AR with respect to CC.

615 In addition, we established an alternative method to perform Hendy test-like analysis. This
616 method is labor-intensive, but offers a more trustworthy evaluation of the stable isotope
617 composition along individual growth layers. For future studies, which might investigate kinetic
618 isotope effects on stalagmites, we suggest to follow the parallel drilling approach presented in
619 this study. Performing one or two additional transects parallel to the isotope track in the center
620 of the stalagmite should be sufficient to evaluate if kinetic effects were important for CaCO₃
621 precipitation. Those additional transects can be short (e.g., 1-2 cm) but should be performed at
622 a similar resolution as the sampling at the central axis to allow wiggle matching the isotope
623 patterns.

624

625

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630

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