

1 **Determination of aragonite trace element distribution coefficients from speleothem**
2 **calcite-aragonite transitions**

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31 **Abstract:**

32 The processes that govern the incorporation of (trace) elements into speleothems can often be
33 linked to environmental changes. Although element incorporation into speleothem *calcite* is
34 now reasonably well understood, current knowledge regarding trace element variability in
35 speleothem *aragonite* is very limited. Of particular interest is whether trace element
36 distribution coefficients are above or below one in order to assess the extent to which prior
37 aragonite precipitation has affected speleothem aragonite trace element records.

38 This study uses nine calcite-to-aragonite transitions in seven speleothems from diverse
39 environmental settings to derive the first quantitative estimates of the distribution coefficients
40 for several elements in speleothem *aragonite*: $D_{\text{Mg(Ar)}} = 9.7\text{E-}5 \pm 9.01\text{E-}5$,
41 $D_{\text{Ba(Ar)}} = 0.91 \pm 0.88$, $D_{\text{Sr(Ar)}} = 1.38 \pm 0.53$, and $D_{\text{U(Ar)}} = 6.26 \pm 4.54$ (1σ SD). For one
42 speleothem from western Germany, the distribution coefficients are generally higher, which is
43 potentially related to the very low growth rates ($<11 \mu\text{m/year}$) of this sample. In particular,
44 $D_{\text{Sr(Ar)}}$ appears to show a negative correlation with growth rate when growth rate is below
45 $20 \mu\text{m/year}$.

46 In summary, our results demonstrate that speleothem aragonite $D_{\text{Mg(Ar)}}$ is below one, $D_{\text{U(Ar)}}$ is
47 considerably above one, and $D_{\text{Sr(Ar)}}$ is above one or close to unity. For $D_{\text{Ba(Ar)}}$, reaching a
48 similar conclusion is difficult due to the relatively high uncertainty. Enhanced prior aragonite
49 precipitation will thus result in lower U and higher Mg concentrations in speleothem
50 aragonite, although in many cases Mg in speleothem aragonite is most likely dominated by
51 other processes. This result suggests that U concentrations in aragonitic stalagmites could
52 serve as very effective proxies for palaeo-rainfall.

53

54 **1. Introduction**

55 Speleothems are secondary cave deposits mainly consisting of calcite or aragonite
56 with calcite being the more common polymorph of CaCO_3 (Hill and Forti, 1997).
57 Speleothems, and in particular stalagmites and flowstones are considered as some of the most
58 promising continental climate archives. They can serve as benchmarks, which can be reliably
59 contrasted and compared with proxy records from complementary archives, because they can
60 be precisely dated up to about 500 ka by the $^{230}\text{Th}/\text{U}$ -dating technique (e.g., Scholz and
61 Hoffmann, 2008). In addition, speleothem archives can be sampled and analysed with up to
62 sub-annual resolution for carbon and oxygen isotopes (Mattey et al., 2008; McDermott, 2004;
63 Myers et al., 2015) and trace and major elemental abundances (Fairchild and Treble, 2009).
64 Numerous studies on speleothem calcite trace element compositions have been published
65 recently (Borsato et al., 2007; Day and Henderson, 2013; Fairchild and Treble, 2009; Griffiths
66 et al., 2010; Treble et al., 2005; and references therein). Few studies, however, focus on trace
67 element compositions in aragonite speleothems (Finch et al., 2003; Finch et al., 2001;
68 McMillan et al., 2005; Tan et al., 2014; Wassenburg et al., 2012; Wassenburg et al., 2013).
69 The knowledge on element partitioning into speleothem aragonite is thus very limited.

70 Since aragonite speleothems contain much more U compared to their calcitic
71 counterparts, they can provide excellent age models (Cosford et al., 2008; Myers et al., 2015;
72 Ridley et al., 2015). However, aragonite is metastable and may recrystallize to calcite under
73 certain conditions, which results in post-depositional open system behaviour of the U-series
74 system and apparently incorrect $^{230}\text{Th}/\text{U}$ -ages (Lachniet et al., 2012; Ortega et al., 2005).
75 Where robust evidence that an aragonite speleothem is well preserved is available (Myers et
76 al., 2015; Wassenburg et al., 2013), the potential to obtain exceptionally precise chronologies
77 is high. Consequently, it is important to further investigate (i) how trace elements partition
78 into speleothem aragonite and (ii) which controls and processes are reflected by their temporal
79 and spatial variability.

80 The major crystallographic difference between calcite and aragonite lies in their
81 different crystal structures. Aragonite is characterized by an orthorhombic crystallography,
82 where the Ca-ion is coordinated by nine O-ions, whereas calcite has a trigonal
83 crystallography, where the Ca-ion is coordinated by six O-ions (Swart, 2015). Due to these
84 crystallographic differences, larger cations, such as Sr, Ba and U, are preferentially
85 incorporated into aragonite, whereas calcite also tends to incorporate small cations, such as
86 Mg. The corresponding trace element distribution coefficients, D_X , are defined as:

87

88
$$D_X = \frac{X/Ca_{Solid}}{X/Ca_{Solution}}, \quad (1)$$

89

90 where X represents a certain trace element. Due to the crystallographic differences, the
91 distribution coefficients may be very different for calcite and aragonite.

92 Recently, Stoll et al. (2012) introduced a model that facilitates quantitative
93 interpretations of speleothem calcite Mg, Ba, and Sr signals in terms of prior calcite
94 precipitation (PCP) (Fairchild et al., 2000). This process refers to the precipitation of calcite
95 before the dripwater reaches the stalagmite (Fairchild and Treble, 2009), which occurs when
96 the dripwater encounters empty voids within the karst with a lower partial CO₂ pressure
97 compared to the water. This forces degassing of CO₂, temporarily increasing supersaturation
98 with respect to calcite and calcite precipitation. PCP usually refers to calcite precipitation in
99 the aquifer above the cave, although it may also occur inside the cave (e.g., at the cave ceiling
100 or on the surface of a stalactite). Certain environmental conditions may favour prior aragonite
101 precipitation (PAP) instead of PCP. Fairchild and Treble (2009) first mentioned PAP, which
102 was subsequently documented and detailed by Wassenburg et al. (2013). Both PCP and PAP
103 are enhanced during periods of reduced aquifer recharge when more time is available for
104 degassing and more air-filled voids exist in the aquifer. If trace element distribution
105 coefficients are below (above) one, elevated concentrations in speleothems are typically
106 interpreted as reflecting reduced (enhanced) infiltration and drier (wetter) climatic conditions
107 (Johnson et al., 2006). However, cave ventilation may also control PCP (Sherwin and Baldini,
108 2011; Wong et al., 2011).

109 Quantitative and qualitative interpretations of speleothem trace element records
110 strongly depend on well constrained D_X values. Laboratory precipitation experiments indicate
111 that for calcite, temperature might affect D_{Mg(Cc)} (Day and Henderson, 2013; Oomori et al.,
112 1987). Other experiments suggest that precipitation rates (Gabitov et al., 2014; Lorens, 1981;
113 Tesoriero and Pankow, 1996) and/or solution composition (Mucci and Morse, 1983; Pingitore
114 and Eastman, 1986) may control D_{Mg(Cc)}, D_{Sr(Cc)}, and D_{Ba(Cc)}. For aragonite, temperature may
115 affect trace element distribution coefficients for Mg, Ba, and Sr (Dietzel et al., 2004; Gaetani
116 and Cohen, 2006), whereas precipitation rates may influence aragonite distribution
117 coefficients for U and Mg (Gabitov et al., 2008).

118 However, most of these experiments were designed to reflect marine environments.
119 Within cave environments, the conditions driving CaCO₃ precipitation are very different.
120 Spelean CaCO₃ precipitation is driven by rapid degassing of CO₂ from thin water films

121 (Hansen et al., 2013) with low ionic strength and the presence of (organic) colloidal phases
122 (Fairchild and Treble, 2009; Hartland et al., 2014), whereas marine deposition occurs in high
123 ionic strength waters and is often biologically mediated. The same arguments prompted a
124 series of studies that aimed to determine speleothem calcite D_X . These were based on both
125 field precipitation experiments, during which the trace element composition of calcite formed
126 within a cave over a known time period is compared with the trace element composition of
127 the associated dripwater (Fairchild et al., 2010; Gascoyne, 1983; Huang et al., 2001; Karmann
128 et al., 2007; Riechelmann et al., 2014; Tremaine and Froelich, 2013), and cave analogue
129 laboratory experiments (Day and Henderson, 2013; Huang and Fairchild, 2001). These
130 experiments demonstrate that D_X values determined under karst analogue conditions are
131 different from those in marine environments. Consequently, D_X values determined under
132 marine conditions are not necessarily transferable to karst settings, and doing so may lead to
133 incorrect climate interpretations.

134 Karst analogue experiments aiming to determine D_X values for aragonitic stalagmites
135 have not been performed yet. Thus, these values remain almost entirely unknown. For
136 speleothem aragonite, only one $D_{Sr(Ar)}$ estimate is available, which is based on modern
137 dripwater Sr/Ca ratios corresponding to an actively growing stalagmite, the Sr concentration
138 at the top of the calcitic stalagmite and the ratio of the Sr content of a calcite and an aragonite
139 phase that precipitated approximately 900 years ago (McMillan et al., 2005). In order to
140 advance the present understanding, we analyse published (McMillan et al., 2005; Wassenburg
141 et al., 2012) and new trace element data from calcite-aragonite transitions in speleothems to
142 derive speleothem aragonite $D_{X(Ar)}$ values for Mg, Sr, Ba and U. To our knowledge, this study
143 provides the first aragonite $D_{X(Ar)}$ values determined entirely under cave environmental
144 conditions.

145

146 **2. Cave settings**

147 The data presented here are derived from speleothems from different geographic and
148 environmental settings (Fig. 1): Grotte Prison de Chien and Grotte de Piste (Morocco)
149 (Wassenburg et al., 2012), Mawmluh Cave (Breitenbach et al., 2015) and Krem Umsynrang
150 Cave (NE India), an unnamed cave located 8 km south of Trevélez (S Spain) (Richter et al.,
151 2002), Grotte de Clamouse (S France) (Frisia et al., 2002; McMillan et al., 2005), and
152 Hüttenbläuserschachthöhle (Central Germany) (Jochum et al., 2012; Yang et al., 2015). We
153 emphasize that the settings of these caves cover a wide range of climates varying from
154 summer dry temperate, all year wet temperate, to summer wet temperate conditions (Peel et

155 al., 2007). For most of the caves, dolostone is a primary host rock component (Table 1). This
156 results in high dripwater Mg/Ca ratios, one of the boundary conditions to precipitate aragonite
157 (Riechelmann et al., 2014). For further details, the reader is referred to Table 1.

158

159 **3. Materials and methods**

160

161 3.1. Samples

162 For this study, both lateral and stratigraphic calcite-aragonite (Cc-Ar) transitions from
163 seven speleothems were investigated (Table 1; Fig. 1 and 2). Datasets from Grotte de
164 Clamouse (Frisia et al., 2002; McMillan et al., 2005) as well as Grotte Prison de Chien and
165 Grotte de Piste (Wassenburg et al., 2012) were previously published, and the reader is referred
166 to these publications for a detailed documentation of these samples. In addition, one Cc-Ar
167 transition in each of the stalagmites KRUM11 (Krem Umsynrang Cave), MAW4 (Mawmluh
168 Cave; Breitenbach et al., 2015), and MO (unnamed cave) were analysed. Furthermore, four
169 transitions in stalagmite HBSH1 (Hüttenbläuserschachthöhle; Jochum et al., 2012; Yang et al.,
170 2015) were studied in detail.

171 Sample KRUM11 is approximately 280 mm long and consists of two parallel
172 stalagmites, which lay on the cave floor when collected. On top of those, a younger, 52 mm
173 long speleothem grew upwards, perpendicularly to the broken precursor sample. The sample
174 exhibits a stratigraphic Cc-Ar transition in the older part of the speleothem and a lateral Cc-Ar
175 transition in the youngest part (Fig. 2). Stalagmite MAW4 is 30 mm long and actively grew at
176 the time of collection in March 2006. MAW4 contains one stratigraphic Cc-Ar transition
177 (Fig. 2). Flowstone MO has a maximum thickness of 74 mm and exhibits multiple
178 stratigraphic and lateral Cc-Ar transitions (Fig. 2). Stalagmite HBSH1 is described in Yang et
179 al. (2015). For all samples, the boundaries between calcite and aragonite mineralogies are
180 macroscopically visible and distinct (Fig. 2).

181

182 3.2. Petrography

183 Aragonite is a polymorph of CaCO_3 and metastable under Earth surface conditions.
184 Thus, it has a tendency to recrystallize to calcite within months to up to hundred's of
185 thousands of years when exposed to diagenetic fluids (Frisia et al., 2002; Lachniet et al.,
186 2012; Martin-Garcia et al., 2009; Perrin et al., 2014; Zhang et al., 2014). In this study, thin-
187 sections were examined under a polarization microscope in order to assess whether the
188 samples show petrographic evidence for diagenetic alteration. Diagenetic alteration of calcite

189 and aragonite can be identified by the appearance of dissolution features (Figs. 9c and 10 in
190 Perrin et al., 2014), micritization and aragonite relics (Figs. 3 and 8 in Martin-Garcia et al.,
191 2009) and calcite mosaics (Fig. 14 in Frisia and Borsato, 2010, and Fig. 3 in Scholz et al.,
192 2014). In addition, the mineralogy of the samples was determined by X-ray diffraction at the
193 ETH Zurich, Switzerland, using approximately 30 mg of sample powder, as well as by Raman
194 spectroscopy performed at the University of Mainz, Germany. The Raman spectrometer used
195 was a HR 800 from the company Horiba Jobin Yvon, with an attached Olympus BX41
196 Microscope equipped with an automatic xyz-stage to undertake the 2-dimensional mappings.
197 A frequency doubled Nd-YAG laser (532.12nm), a grating of 1800 grooves/mm, an entrance
198 slit of 100 μm and a confocal hole of 400 μm were used for the measurements. Every point
199 was measured twice to eliminate spikes; each measurement was performed with an
200 accumulation time of 1 s. To evaluate the calcite content, the intensity of the band at 282 cm^{-1}
201 was used. For aragonite, the band at ca. 207 cm^{-1} was used.

202

203 3.3. Dating

204 Dating of all samples was performed by the $^{230}\text{Th}/\text{U}$ -method to assess whether the
205 speleothems grew continuously across the Cc-Ar transitions and to quantify growth rates.
206 Four samples from stalagmite MAW4 were dated at the Minnesota Isotope Laboratory at the
207 University of Minnesota, USA, with a multi-collector inductively coupled plasma mass
208 spectrometer (MC-ICPMS, Thermo Finnigan Neptune-Plus) following the procedures
209 described by Cheng et al. (2000), Cheng et al. (2013), and Edwards et al. (1987). Two
210 samples from stalagmite KRUM11 and four samples from flowstone MO were dated using a
211 Nu Plasma MC-ICPMS at the Max Planck Institute for Chemistry, Mainz, Germany,
212 following the procedures of Obert et al. (2016). The top sample of flowstone MO was dated at
213 the Helmholtz Centre for Ocean Research Kiel (GEOMAR) following the procedure of
214 Fietzke et al. (2005). Eight samples from stalagmite HBSH1 were dated at Bristol University,
215 UK, following the procedures described by Hoffmann et al. (2007). All ages are reported as
216 thousands of years before present (ka BP) with reference to the year 1950 AD.

217

218 3.4. Trace element analysis

219 Trace element compositions of sub-samples from speleothems KRUM-11, MAW-4,
220 and MO were analysed at the Max Planck Institute for Chemistry, Mainz, Germany. Mg/Ca,
221 Al/Ca, Si/Ca, P/Ca, Mn/Ca, Sr/Ca, Y/Ca, Ba/Ca, Pb/Ca, Th/Ca, and U/Ca ratios were
222 determined with a Thermo Finnigan Element 2 Inductively Coupled Plasma Mass

223 Spectrometer (ICPMS) coupled to a New Wave UP213 laser ablation system. The isotopes
224 ^{25}Mg , ^{27}Al , ^{29}Si , ^{31}P , ^{43}Ca , ^{55}Mn , ^{88}Sr , ^{89}Y , ^{137}Ba , ^{208}Pb , ^{232}Th , and ^{238}U were used. Pre-
225 ablation was performed using an 80 μm spot size at a scan speed of 80 $\mu\text{m}/\text{s}$ to clean the
226 sample surface. The line scan technique was employed using a scan speed of 5 $\mu\text{m}/\text{s}$ and a
227 55 μm spot size. Samples were ablated with a pulse rate of 10 Hz and an energy density of
228 9.5 J/cm^2 . Laser warm-up time (i.e., blank measurement time) was set at 11 s. In order to
229 assess potential sample inhomogeneity, ten individual spot analyses were performed parallel
230 to the line scans at a distance of approximately 100 μm using a 100 μm spot size, an energy
231 density of 10.4 J/cm^2 and a total dwell time of 70 s, including an 11 s blank measurement.
232 Both the line scans and the single spot transects covered the Cc-Ar transitions of interest.
233 Measurements were corrected for background, and ^{43}Ca was used as an internal standard to
234 convert count rates into trace element/Ca mass ratios, which were then converted into molar
235 ratios in order to calculate distribution coefficients. Relative sensitivity factors were
236 determined using the NIST612 glass and MACS3 CaCO_3 reference materials using the values
237 published in Jochum et al. (2012). In order to avoid matrix effects, Pb was corrected using the
238 relative sensitivity factor derived from MACS3 (Jochum et al., 2012). Three NIST612 and
239 MACS3 analyses, respectively, were performed ca. every hour of sample analysis in order to
240 assess and correct for a potential drift of the mass spectrometer. The line scan data were
241 smoothed with a 5-point-running median. For further information on the methodology and
242 data evaluation, the reader is referred to Jochum et al. (2009; 2012).

243 The Cc-Ar transitions from stalagmite HBSH1 were analysed at Bristol University,
244 UK. Mg/Ca, P/Ca, Sr/Ca, Y/Ca, Ba/Ca, Pb/Ca, Th/Ca and U/Ca were determined with a
245 NewWave UP193HE Excimer laser coupled to a Thermo Finnigan Element2 ICPMS. The
246 isotopes ^{26}Mg , ^{31}P , ^{43}Ca , ^{88}Sr , ^{89}Y , ^{137}Ba , ^{208}Pb , ^{232}Th , and ^{238}U were used for analysis. Spots
247 were ablated at 200 μm resolution with a 30 μm spot size. The laser warm-up time was set at
248 40 s (blank measurement time), followed by 104 s of ablation and 60 s wash-out. ^{43}Ca was
249 used as an internal standard to convert count rates into concentrations. Samples were ablated
250 with an energy density of 5 J/cm^2 and a pulse rate of 5 Hz. The glass reference materials
251 NIST610 and NIST612 were used for calibration. Data evaluation was performed with the
252 software package “Glitter”.

253 The uncertainty of the trace element results is represented by the relative standard
254 deviation associated with the mean trace element concentration of the reference materials
255 NIST610 and NIST612 for speleothem HBSH1. For speleothems KRUM11, MAW4 and MO,
256 uncertainties were determined by calculating a mean uncertainty from the individual MACS3

257 line scans. For speleothem HBSH1, only glass reference materials were measured. Since the
258 trace element concentrations of these reference materials differ, it is possible to use a different
259 uncertainty for high and low trace element concentrations. This is an advantage considering
260 the difference in trace element concentrations between calcite and aragonite. For an overview,
261 the reader is referred to Table 2. The uncertainties for trace element concentrations in
262 speleothems HK3 and GP2 are based on the MACS1 reference material and were published
263 by Wassenburg et al. (2012).

264

265 3.5. Derivation of speleothem aragonite distribution coefficients

266

267 3.5.1. Approach

268 Aragonite distribution coefficients were determined using the following procedure: Firstly, we
269 calculated the trace element/Ca ratio of the dripwater feeding the stalagmite using the trace
270 element/Ca ratio of the calcite section of the corresponding Cc-Ar transition and the calcite
271 distribution coefficients (Day and Henderson, 2013). Assuming that the dripwater trace
272 element/Ca ratio did not undergo major changes with time, the speleothem aragonite
273 distribution coefficient can be estimated by combining the trace element/Ca ratio of the
274 aragonite section of the transition and the calculated trace element/Ca ratio of the dripwater.

275 This approach can be mathematically summarized as follows: The distribution
276 coefficient is a function of the trace element to Ca ratio of the solid divided by the trace
277 element to Ca ratio of the solution (i.e. equation 1). Thus, the calcite distribution coefficient,
278 $D_{X(Cc)}$, is given by:

279

$$280 \quad D_{X(Cc)} = \frac{X/Ca_{Cc}}{X/Ca_{Solution}} \quad (2)$$

281

282 Accordingly, the distribution coefficient for aragonite $D_{X(Ar)}$ is given by:

283

$$284 \quad D_{X(Ar)} = \frac{X/Ca_{Ar}}{X/Ca_{Solution}} \quad (3)$$

285

286 $D_{X(Cc)}$ is available from previous studies (Day and Henderson, 2013), and $X/Ca_{(Cc)}$ and
287 $X/Ca_{(Ar)}$ are measured values. Using the assumption that the dripwater trace element/Ca ratio
288 was similar for precipitation of calcite and aragonite (see below for a critical discussion),

289 X/Ca_{Solution} can be calculated from equation (2). Inserting this value in Eq. (3), D_{X(Ar)} can be
290 calculated. In summary, D_{X(Ar)} is given by:

291

$$292 \quad D_{X(Ar)} = \frac{X/Ca_{Ar}}{X/Ca_{Cc} / D_{X(Cc)}} \quad (4)$$

293

294 The calcite distribution coefficients used for the calculations were taken from the
295 cave-analogue precipitation experiments performed by Day and Henderson (2013). These are:
296 $D_{Mg(Cc)} = 0.01 * e^{0.02 * T}$, $D_{Sr(Cc)} = 0.12$ and $D_{Ba(Cc)} = 0.11$. According to the experiments from
297 Day and Henderson (2013), the relation between $D_{Sr(Cc)}$ and temperature was statistically not
298 significant, for $D_{Ba(Cc)}$ no relation could be identified either. Day and Henderson (2013)
299 indicate that $D_{U(Cc)}$ does not show a clear relationship with temperature although the D_U
300 values for experiments conducted at 7°C and 15°C were slightly different (i.e., 0.11 and 0.12,
301 respectively). Therefore, we estimated cave temperatures during speleothem growth from the
302 literature and cave monitoring data and used the corresponding values for $D_{U(Cc)}$ and $D_{Mg(Cc)}$.

303 Our approach strongly depends on the validity of the assumption that the trace
304 element/Ca ratio of the dripwater did not undergo a major change during the time covered by
305 the Cc-Ar transition. However, in order to initiate aragonite precipitation, a change in
306 dripwater chemistry is absolutely necessary (Frisia et al., 2002; Riechelmann et al., 2014;
307 Wassenburg et al., 2012). At first glance this seems to be contradictory to our assumption, but
308 if the potential change in dripwater chemistry is accounted for by the uncertainty assigned to
309 the values used for the calculations, the error introduced by our assumption can be propagated
310 to the calculated aragonite distribution coefficients. This is critically discussed in the next
311 section.

312

313 3.5.2. Error propagation

314 Because assessing potential past changes in dripwater trace element composition is
315 challenging, speleothem trace element data variability must be considered carefully. In order
316 to solve this, we included the standard deviation of the trace element data in the error
317 propagation of the aragonite distribution coefficients. In addition, the uncertainty of the trace
318 element analysis and the uncertainty related to the published calcite trace element distribution
319 coefficients (Day and Henderson, 2013) are included. The error bars on the calculated

320 aragonite distribution coefficients are, thus, very conservative. We used the following
321 equation to calculate the absolute error of the speleothem aragonite D_X values:

322

$$323 \quad \Delta D_{X(Ar)} = D_{X(Ar)} * \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \sigma_4^2}, \quad (5)$$

324

325 where σ_1 is the relative standard deviation determined from the external reference materials
326 (Table 2), σ_2 is the relative uncertainty of the calcite distribution coefficient (Day and
327 Henderson, 2013), and σ_3 and σ_4 are the relative uncertainties of the mean calcite and
328 aragonite trace element to Ca ratios. We note that a potential change in drip water
329 composition during the time that the mineralogy changed from calcite to aragonite remains
330 challenging to assess, therefore we cannot incorporate a fixed uncertainty in the error
331 propagation. However, in the results and interpretation section we discuss the effect of an
332 additional 50% uncertainty of the mean trace element values.

333

334 3.5.3. Boundary conditions for aragonite precipitation

335 For precipitation of aragonite in cave environments, specific boundary conditions must be
336 fulfilled. In detail, dripwater pH > 8.2, dripwater Mg/Ca > 0.5, and the calcite saturation index
337 < 0.8 (Riechelmann et al., 2014). However, if dripwater pH < 8.2 or the calcite saturation
338 index > 0.8, calcite will continue to precipitate even though dripwater Mg/Ca > 0.5 (see, for
339 example, drip site BM8 in Bab Maфраque Cave (Riechelmann et al. 2014). Therefore, a
340 change from calcite to aragonite within a speleothem does not always reflect a change in the
341 trace element composition of the dripwater. In addition, calcite and aragonite can co-
342 precipitate from dripwaters with only slightly different chemical composition. This result is
343 corroborated by the existence of lateral Cc-Ar transitions in samples HK1 (Wassenburg et al.,
344 2012), KRUM11 and MO. Therefore, the balance between all three dripwater characteristics
345 (i.e., pH, calcite saturation index, and Mg/Ca) is delicate, and only a small, short-lived (i.e.,
346 seasonal - annual) change in one of these parameters can initiate precipitation of aragonite.
347 Furthermore, it is energetically advantageous to continue precipitating the same mineral
348 (termed “syntaxial overgrowth”, Fairchild and Baker, 2012). Thus, the return to the same
349 precipitation conditions does not necessarily initiate calcite precipitation. In short, very minor
350 water chemistry changes could surpass a threshold, triggering a sudden shift from calcite to
351 aragonite. Large shifts in water chemistry are neither required nor necessarily implied.

352

353 3.6. Sample and trace element data selection

354 The samples and trace element/Ca ratios selected for the calculations are subject to
355 strict criteria. Post-depositional diagenesis may alter the trace element composition of both
356 aragonite (Lachniet et al., 2012; Ortega et al., 2005) and calcite speleothems (Scholz et al.,
357 2014). Consequently, data derived from diagenetically altered sections were avoided. In
358 addition, only pure calcite and aragonite phases were used. This is important because even a
359 small amount of co-precipitated calcite (~2%) may have a large effect on the Mg/Ca ratio of
360 aragonite (Wassenburg et al., 2012). Likewise, a small amount of co-precipitated aragonite
361 may have a significant effect on the U/Ca ratio of calcite. Just before and after the change in
362 speleothem mineralogy, co-precipitation of both calcite and aragonite is the rule rather than
363 the exception. Usually, co-precipitation is spatially restricted and causes characteristic spikes
364 in the trace element data. Therefore, the selection of the first datapoint closest to the Cc-Ar
365 transition is based on the absence of spikes in the aragonite Mg/Ca data and the calcite U/Ca
366 data, which are both indicators of co-precipitation. This selection process implies that lateral
367 Cc-Ar transitions are not suitable for determination of distribution coefficients with this
368 strategy because at such sites co-precipitation is very likely to occur. However, due to the
369 slightly higher porosity associated with a larger surface area and higher number of sites for
370 nucleation, it is reasonable to expect that co-precipitation occurs preferentially within
371 aragonite zones. Therefore, the largest offsets are expected for $D_{Mg(Ar)}$, whereas the effect
372 should be negligible for $D_{Sr(Ar)}$, $D_{Ba(Ar)}$ and $D_{U(Ar)}$ because calcite Sr, Ba and U concentrations
373 are low compared to those in aragonite. Consequently, we use data from two lateral Cc-Ar
374 transitions from stalagmite HK1 (Wassenburg et al., 2012) to verify the values obtained from
375 stratigraphical Cc-Ar transitions in this study. Furthermore, a minimum of several years of
376 trace element data was averaged in order to avoid a bias towards extreme years; at least seven
377 data points are used to calculate the mean X/Ca values for the calcite and aragonite to increase
378 the statistical robustness. This minimum number of points is related to the maximum number
379 of laser spots available for the shortest speleothem section studied (stalagmite HBSH1).

380

381 **4. Results and interpretation**

382

383 4.1. Petrography and degree of preservation

384 Petrographic studies on the previously published samples indicate that the analysed
385 calcite and aragonite fabrics represent primary mineralogies with only very subtle, if any,
386 diagenetic features (McMillan et al., 2005; Wassenburg et al., 2012). The petrography and
387 degree of preservation of the newly analysed samples is described in the paragraphs below.

388

389 4.1.1. Stalagmite MAW4

390 The calcite portion of stalagmite MAW4 (Fig. 3a-c) shows discontinuous, inclusion-
391 rich layers composed of non-ordered, relatively small (10-100 μm wide) calcite crystals
392 (Fig. 3b). In between these layers, columnar, radiaxial calcite crystals occur (Neuser and
393 Richter, 2007; Richter et al., 2011) (Fig. 3b). Directly beneath an aragonite interval, calcite
394 fabrics consisting of fan-like structures with a sweeping extinction over several crystals exist
395 (Figs. 3a and 4d).

396 The aragonite fabrics consist of needle-like crystals, elongated along their c-axis,
397 organized in fans with a sweeping extinction across several crystals (Fig. 3a). This specific
398 type of fabric has been referred to as acicular by Frisia and Borsato (2010). A series of thin
399 brown layers alternating with translucent white layers that are possibly seasonal in origin has
400 been observed, similar to sample MAW-0201 from the same cave (Myers et al., 2015).

401 The small, non-ordered calcite crystals may represent competitive growth occurring
402 after a growth interruption and are regarded as primary, similar to the columnar, radiaxial
403 calcite. However, the fan-like calcite has a very similar structure as the acicular aragonite.
404 This may represent the product of a fabric-preserving aragonite-to-calcite transformation
405 (Martin-Garcia et al., 2009; Perrin et al., 2014). Therefore, this specific calcite fabric was
406 avoided for the calculations, and only well-preserved columnar calcite fabrics were used.
407 Aragonite fabrics lack signs of micritization, dissolution and aragonite-to-calcite
408 transformation and are thus considered primary.

409

410 4.1.2. Stalagmite KRUM11

411 The calcite fabric of stalagmite KRUM11 appears as mosaic-like in thin sections
412 (Figs. 3d-f) (Frisia and Borsato, 2010), whereas the aragonite directly above the calcite shows
413 an acicular fabric (Frisia and Borsato, 2010) (Fig. 3e). Under plane polarized light, darker,
414 non-translucent zones alternate with translucent crystals within the aragonite (Fig. 3f).

415 A calcite mosaic fabric is usually interpreted as a result of diagenesis (Frisia and
416 Borsato, 2010; Scholz et al., 2014). However, the calcite did not show any aragonite relicts or
417 dissolution features, and the cross section shown in Figs. 3d-f is not parallel to the c-axis of
418 the crystals, therefore, this calcite was considered to be of primary nature. The aragonite of
419 KRUM11 shows some opaque, non-translucent layers, which appear as micritized aragonite
420 (Fig. 3f). Therefore, this Cc-Ar transition has been excluded for the calculations of the
421 speleothem aragonite distribution coefficients.

422

423 4.1.3. Stalagmite HBSH1

424 The calcite layers within stalagmite HBSH1 are 5-10 mm thick and consist of
425 columnar calcite crystals. The aragonite has an acicular fabric characterised by a sweeping
426 extinction pattern across several crystals (Fig. 3g). The individual crystals are somewhat
427 longer and wider compared to those from stalagmite MAW4 (Fig. 2), and individual needle-
428 like aragonite crystals and spherulites are distributed between the relatively long and wide
429 aragonite crystals (Fig. 3g). No diagnostic features of diagenesis (e.g., micritization,
430 dissolution or calcite-to-aragonite transformation) are apparent, and the fabrics are therefore
431 considered primary.

432

433 4.1.4. Flowstone MO

434 Flowstone MO consists of an elongated columnar, radiaxial calcite fabric with an
435 undulose extinction (Richter et al., 2011). The aragonite consists of clear, translucent crystals
436 belonging to an acicular fabric (Fig. 3i-j) (Frisia and Borsato, 2010). Both calcite and
437 aragonite do not show any sign of diagenetic alteration, and thus represent primary material.

438

439 4.2. Conditions of formation

440

441 4.2.1. Timing of calcite-to-aragonite transitions and determination of speleothem growth rates

442 Five samples from flowstone MO were dated. Four samples were beyond the dating
443 limit of the $^{230}\text{Th}/\text{U}$ -method. The top sample was dated at 106.9 ± 1.1 ka (Fig 2; Table 3).

444 The calcite phase of stalagmite KRUM11 occurred between 16.89 ± 0.11 and
445 16.42 ± 0.12 ka (Fig. 2; Table 3). The mean growth rate for this section is ca. $35 \mu\text{m}/\text{a}$.

446 Sample MAW4 was actively growing at the time of collection (2006 AD). The
447 aragonite samples were dated at -0.0476 ± 0.0018 and -0.0202 ± 0.0013 ka (Fig. 2; Table 3),
448 revealing high growth rates with a mean of $\sim 293 \mu\text{m}/\text{a}$. The two calcite samples were dated at
449 0.202 ± 0.011 and 0.395 ± 0.055 ka (Fig. 2; Table 3), which corresponds to a much lower
450 mean growth rate of ca. $24 \mu\text{m}/\text{a}$.

451 Eight aragonite sub-samples bracketing four Cc-Ar transitions in stalagmite HBSH-1
452 were dated (Table 3). The corresponding ages are between 216.6 ± 2.8 and 78.66 ± 0.81 ka
453 (Table 3). The corresponding growth rates for the four Cc-Ar transitions are between 1 and
454 $11 \mu\text{m}/\text{a}$. All growth rates are based on linear interpolation between two subsequent samples.

455

456 4.2.2. Temperature at time of deposition

457 Day and Henderson (2013) documented that calcite D_{Mg} and D_U in precipitation
458 experiments depend on temperature. In particular, $D_{U(Cc)}$ is 0.11 at 7°C and 0.12 at 15°C,
459 whereas $D_{Mg(Cc)} = 0.01 * e^{0.02 * T}$. Although the temperature dependency of $D_{Mg(Cc)}$ is relatively
460 small in comparison to cave site temperature variations, an approximate assessment of cave
461 temperatures is considered important here.

462 Cave temperature at the time of the Cc-Ar transitions in the investigated samples are
463 estimated using modern cave temperature compiled in the context of cave monitoring
464 programs (Table 1) (Breitenbach et al., 2015; Frisia et al., 2002; Riechelmann et al., 2014;
465 Wassenburg et al., 2013), geographical location of the cave sites (Table 1), and the timing of
466 the growth phases of the Cc-Ar transitions (Table 3). MAW4, KRUM11, HK3, GP2 and
467 CL26 cave air temperatures must have been closer to 15 than to 7°C (Table 4). Thus, we use
468 the higher calcite D_U of 0.12 (Day and Henderson, 2013). For flowstone MO, the timing of
469 the Cc-Ar transition is unknown, and formation temperature is not quantifiable. However, we
470 use the modern cave air temperature of 13°C for the calculations and, consequently, a D_U
471 value of 0.12.

472 Three of the four Cc-Ar transitions from stalagmite HBSH1 grew within the time
473 interval from 131 and 79 ka BP. For each of these transitions, we use a temperature estimate
474 from a pollen and plant macrofossil record from central Germany (Kühl et al. (2007)). This
475 record suggests mean January temperatures of -12°C and mean July temperatures of 17.5°C,
476 which corresponds to a mean annual temperature of ~3°C. For the oldest Cc-Ar transition in
477 stalagmite HBSH1, which occurred around 216 ka BP (Marine Isotope Stage 7; Table 3), no
478 temperature estimate can be derived due to a lack of data. Therefore, we assume the same
479 temperature as for the other Cc-Ar transitions from stalagmite HBSH1 (Table 4).
480 Consequently, a D_U value of 0.11 was used for all four mineralogical transitions found within
481 stalagmite HBSH1.

482

483 4.3. Distribution coefficients

484

485 4.3.1. Trace element data

486 Trace element data across the Cc-Ar transitions from the different speleothems are
487 presented in Fig. 5. The line scan data reproduce the single spot analyses very well indicating
488 sample homogeneity at the sub-millimeter scale. The Cc-Ar transitions are clearly visible in
489 Mg/Ca, Sr/Ca, Ba/Ca and U/Ca ratios (Fig. 5). As expected, Sr/Ca, Ba/Ca and U/Ca ratios are

490 higher in aragonite, whereas Mg/Ca is higher in calcite. For sample MAW4, a stepwise
491 increase (decrease) in Sr/Ca and U/Ca (Mg/Ca) is apparent starting ca. 3 mm below the Cc-Ar
492 transition and is followed by the actual Cc-Ar transition. A more detailed discussion is
493 required to clarify which data are most useful for the calculations of the aragonite distribution
494 coefficients.

495 Stalagmite MAW4 shows a fan-like calcite fabric (Fig. 3a-c), which is interpreted as
496 the result of aragonite-to-calcite transformation. It is possible that the intermediate values of
497 Sr/Ca, U/Ca and Mg/Ca are associated with this fabric because it is common that secondary
498 calcite may preserve the trace element signature of the precursor aragonite (Niggemann and
499 Richter, 2006). However, the thin section was taken from another portion of stalagmite
500 MAW4, thus preventing establishing a direct link with the trace element data. Therefore, an
501 area close to the trace element transect was mapped with Raman spectroscopy, which
502 indicated that both phases with the intermediate (Cc1) and high (Cc2) Mg/Ca ratios are indeed
503 calcite with negligible aragonite (Fig. 4). Sr/Ca and U/Ca ratios are higher, and the Mg/Ca
504 ratios are lower in Cc1 than in Cc2, suggesting that aragonite-to-calcite diagenesis may have
505 affected Cc1. Consequently, only the trace element data derived from Cc2 are used to
506 calculate distribution coefficients.

507

508 4.3.2. Speleothem aragonite distribution coefficients

509 The trace element/Ca ratios used to calculate speleothem aragonite $D_{X(Ar)}$ are shown in
510 Fig. 5 and Table 4. The time represented by each calcite or aragonite trace element value used
511 for the calculation varies from sample to sample, ranging from 2 to 771 years (Table 4). We
512 acknowledge that 771 years seems unreasonably long for the discussion of transitions.
513 However, the corresponding sample (HBSH1-20) has a growth rate of only 1 $\mu\text{m/a}$, and it is
514 necessary to calculate a mean X/Ca value based on multiple data points to obtain a reliable
515 estimate of both the X/Ca value and its uncertainty for the calculations. For stalagmite
516 MAW4, only the calcite part with the highest Mg/Ca ratios (Cc2) was used in order to prevent
517 a bias due to diagenetically altered calcite (see above).

518 The calculated aragonite distribution coefficients with associated uncertainties are
519 presented in Table 5 and Fig. 6. The mean aragonite $D_{Mg(Ar)}$ is $9.7 \cdot 10^{-5} \pm 9.0 \cdot 10^{-5}$, $D_{Sr(Ar)}$ is
520 1.38 ± 0.53 , $D_{Ba(Ar)}$ is 0.91 ± 0.88 , and $D_{U(Ar)}$ is 6.26 ± 4.53 . $D_{X(Ar)}$ values calculated from
521 stalagmite HBSH1 are higher for all elements examined and increase standard deviations
522 significantly (Table 6). This is especially the case for $D_{Ba(Ar)}$, which changes from 0.91 ± 0.88
523 to 0.46 ± 0.18 if the values calculated from stalagmite HBSH1 are excluded (Table 6).

524 Despite the uncertainty, the results demonstrate for the first time that under karst
525 environmental conditions $D_{Mg(Ar)}$ is considerably smaller than one, $D_{Sr(Ar)}$ is above one or
526 close to unity, and $D_{U(Ar)}$ is larger than one. As noted earlier, we used the trace element
527 datasets covering two lateral Cc-Ar transitions from stalagmite HK1 (Wassenburg et al.,
528 2012) to verify the $D_{Sr(Ar)}$, $D_{Ba(Ar)}$ and $D_{U(Ar)}$ derived from stratigraphical Cc-Ar transitions.
529 The corresponding $D_{X(Ar)}$ values are indistinguishable from those derived using stratigraphic
530 Cc-Ar transitions adding confidence to the validity of our estimates (Fig. 6). The large
531 difference in growth rate between the aragonite (295 $\mu\text{m/a}$) and the calcite (24 $\mu\text{m/a}$) sections
532 of stalagmite MAW4 does not seem to affect the calculated aragonite $D_{X(Ar)}$ value because the
533 results are consistent with the other values.

534

535 **5. Discussion**

536 To our knowledge, this is the first attempt to quantify speleothem aragonite $D_{X(Ar)}$
537 values (other than the determination of $D_{U(Ar)}$ of Jamieson et al. (submitted). Although our
538 approach is relatively simple, the results are consistent for most transitions (in particular for
539 aragonite D_{Sr}) (Fig. 6). This indicates that the incorporation mechanisms are similar for calcite
540 and aragonite, which is a basic requirement for the application of the concept of a distribution
541 coefficient (Fairchild and Treble, 2009). However, the values calculated using stalagmite
542 HBSH1 are higher. Furthermore, the calculated $D_{Mg(Ar)}$, $D_{Ba(Ar)}$ and $D_{U(Ar)}$ values show large
543 variability (Fig. 6). Variable environmental conditions and dripwater chemistry characteristics
544 of the different samples may partially explain these differences. Environmental factors, such
545 as temperature, drip rate, precipitation rate, and solution composition, may contribute to the
546 large spread in both calcite and aragonite D_X values. However, we emphasize that the
547 chemical composition of the dripwaters must have been similar across all transitions because
548 aragonite only tends to precipitate in case of dripwater Mg/Ca ratios ≥ 0.6 and dripwater pH
549 ≥ 8.2 and a relatively low (≤ 0.8) saturation-index with respect to calcite (Riechelmann et al.,
550 2014).

551

552 **5.1. Sensitivity analysis**

553 Although only the best available speleothem samples with calcite-aragonite transitions
554 were used, the calculated aragonite $D_{X(Ar)}$ values of course depend on the data selected for the
555 calculations. To assess any selection bias, all calculations were repeated with trace element
556 data representing only 2-155 years of stalagmite growth instead of 2-771 years. This transect
557 consisting of 2-155 years of data comprises the part of the original trace element transect of 2-

558 771 years closest to the Cc-Ar transition. This sensitivity analysis was performed on each
559 sample (input parameters used for the corresponding calculations are given in supplemental
560 Table EA1). The median $D_{X(\text{Ar})}$ values of both datasets are comparable (Table 6), indicating
561 that the calculated $D_{X(\text{Ar})}$ values do not strongly depend on the selected trace element transect.
562 Nevertheless, the mean X/Ca ratio calculated using the longer dataset should be statistically
563 more robust, and is thus the preferred value.

564 In addition to varying the number of trace element data points, the results were tested
565 using an aragonite-to-calcite transition from stalagmite HK3 (Wassenburg et al., 2012). We
566 applied the same approach to the data from the Ar-Cc transition to calculate the calcite
567 distribution coefficient by using the aragonite distribution coefficient. Using the same error
568 propagation as for the calculated aragonite distribution coefficients, the calculated calcite
569 distribution coefficients are 0.019 ± 0.004 , 0.14 ± 0.02 , 0.13 ± 0.02 and 0.13 ± 0.05 for
570 $D_{\text{Mg}(\text{Cc})}$, $D_{\text{Sr}(\text{Cc})}$, $D_{\text{Ba}(\text{Cc})}$ and $D_{\text{U}(\text{Cc})}$, respectively. Although this transition was interpreted as a
571 hiatus (Wassenburg et al. 2012), $D_{X(\text{Cc})}$ values calculated across this transition are, with
572 exception of $D_{\text{Mg}(\text{Cc})}$, within error of the $D_{X(\text{Cc})}$ values reported by Day and Henderson (2013).
573 We refer to section 5.5 for a detailed discussion of D_{Mg} . These cross-validations provide
574 further support that our approach yields reliable results.

575

576 5.2. Rayleigh distillation effects

577 Varying amounts of Rayleigh distillation occurring on stalagmite surfaces affect all
578 trace element distribution coefficients in a similar way (Johnson et al., 2006). The amount of
579 Rayleigh distillation controls the apparent D_X value and depends on (i) drip rate, which
580 controls the mixing between the solution on top of the stalagmite and the impinging drop
581 (Mühlinghaus et al., 2009), and (ii) super-saturation of the dripwater with respect to CaCO_3 ,
582 which controls the precipitation rate. Different drip sites are therefore characterized by
583 varying degrees of Rayleigh distillation and a range of apparent D_X values. The Rayleigh
584 distillation effect depends on the amount of Ca^{2+} that precipitates during a single drip interval,
585 i.e. the excess of Ca. Consequently, drip sites with similar CaCO_3 deposition rates are
586 characterized by small excess Ca^{2+} if (i) drip intervals are short, because there is little time to
587 precipitate CaCO_3 until replenishment of the water at the top of the stalagmite, (ii) dripwater
588 Ca concentration is high, and (iii) the water film covering the stalagmite surface is thick
589 (because it takes longer for dripwater to reach a higher supersaturation). Here we calculate
590 mean CaCO_3 deposition rates using the $^{230}\text{Th}/\text{U}$ -based speleothem growth rates:

591

592
$$r = \frac{v \cdot \sigma \cdot 9.48151 \cdot 10^{-4}}{31536000}, \quad (6)$$

593

594 where r is the average CaCO_3 deposition rate ($\text{mmol}/\text{cm}^2/\text{s}$), v is the speleothem growth rate
 595 ($\mu\text{m}/\text{year}$), and σ is the density of aragonite (g/cm^3). With assumptions for drip rate, initial
 596 dripwater Ca^{2+} concentration and film thickness, the amount of Ca removed from the
 597 dripwater per drip can be calculated for every Cc-Ar transition using the equation from Stoll
 598 et al. (2012):

599

600
$$Ca - excess = \frac{r \cdot \Delta t / \delta}{Ca_i}, \quad (7)$$

601

602 where δ is the thickness of the water film (cm), Δt is drip interval (s), and Ca_i is initial Ca
 603 concentration (mmol/cm^3). The boundary conditions were chosen relatively conservative,
 604 such that the calculated excess Ca^{2+} represents an overestimation rather than an
 605 underestimation. In particular, we assumed a very long drip-interval of 600 s (10 min), a low
 606 initial dripwater Ca concentration of 20 mg/l and a realistic film thickness of 0.01 cm (Baker
 607 et al., 2014; Hansen et al., 2013). The estimated amount of excess Ca^{2+} precipitation ranges
 608 from 0.08 to 3.9% (Table 5), except for stalagmite MAW4 aragonite, for which a value of
 609 19% is estimated. With only 0.08 to 3.9% of excess Ca^{2+} precipitation during one drip
 610 interval, Rayleigh distillation effects are minimal and within the range of our analytical
 611 uncertainties. For MAW4, an influence of Rayleigh distillation on the calculated aragonite
 612 $D_{\text{X(Ar)}}$ values cannot be excluded. However, we emphasize that an initial dripwater Ca
 613 concentration of 20 mg/l for the dripwater is very low, and typical values range from 30 to
 614 90 mg/l (Frisia et al., 2002; Karmann et al., 2007; Riechelmann et al., 2011; Tremaine and
 615 Froelich, 2013). Drip sites with lower dripwater Ca^{2+} concentrations are usually associated
 616 with low CaCO_3 saturation indices and low precipitation rates.

617

618 5.3. Speleothem aragonite $D_{\text{Sr(Ar)}}$

619 The aragonite $D_{\text{Sr(Ar)}}$ values calculated from the different calcite-to-aragonite
 620 transitions are in mutual agreement (Fig. 4), with the exceptions of values calculated from
 621 HBSH-1 (which are higher than the other values) and stalagmite CL26 (lower than the other
 622 values) (Table 4). A comparison with published aragonite $D_{\text{Sr(Ar)}}$ values shows that the mean
 623 value derived from all transitions is in a similar range as the values based on marine analogue
 624 laboratory experiments (Table 6).

625 The calculated aragonite $D_{Sr(Ar)}$ values depend on the value used for $D_{Sr(Cc)}$ of calcite.
626 Calcite $D_{Sr(Cc)}$ is known to be dependent on solution composition (Mucci and Morse, 1983;
627 Pingitore and Eastman, 1986), precipitation rate (Gabitov and Watson, 2006; Treble et al.,
628 2005), and possibly competition effects (Borsato et al., 2007). The latter may be related to the
629 availability of impurities in the crystal lattice, which in turn may be controlled by the
630 incorporation of Mg. The application of a universal $D_{Sr(Cc)}$ for all Cc-Ar transitions may
631 therefore not be appropriate.

632 Precipitation experiments from Mucci and Morse (1983) showed that the incorporation
633 of small sized Mg-ions is accompanied by increasing incorporation of larger Sr-ions. This
634 relationship appeared to be linear and is expressed by $D_{Sr(Cc)} = 0.146 + 0.01833 * \%MgCO_3$.
635 Although it is tempting to use this relationship to correct the calcite $D_{Sr(Cc)}$ values used for the
636 calculations, we do not consider this as a suitable approach since the precipitation
637 experiments from Mucci and Morse (1983) reflect marine conditions. In addition, a calcite
638 $D_{Sr(Cc)}$ value of 0.146 in absence of Mg seems high in comparison to the values reported from
639 cave precipitation experiments (Tremaine and Froelich, 2013). However, the laboratory
640 precipitation experiments of Day and Henderson (2013) were specifically designed to mimic
641 the solution composition of caves with a limestone host rock, and used dripwater Mg/Ca
642 ratios of 0.047. In our study, the calculated dripwater Mg/Ca ratios of all samples are between
643 0.6 and 2.8, reflecting the high Mg content of the corresponding host rock (Table 1).
644 Therefore, calcite $D_{Sr(Cc)}$ may have been generally underestimated resulting in an
645 underestimated value of aragonite $D_{Sr(Ar)}$. Since the calcite of HBSH1 is characterized by the
646 lowest Mg/Ca ratios, the aragonite $D_{Sr(Ar)}$ value calculated from HBSH1 may be least affected
647 by the underestimation of calcite $D_{Sr(Cc)}$.

648 Stalagmite CL26 provided aragonite D_{Sr} values <1 (0.70; Fig. 6, Table 5). Even
649 considering a calcite $D_{Sr(Cc)}$ value of 0.15 (McMillan et al., 2005) results in an aragonite
650 $D_{Sr(Ar)}$ value of 0.87. This value is still lower than the mean value calculated from the four Cc-
651 Ar transitions from stalagmite HBSH1 (1.83 ± 0.46). Considering the relatively similar
652 growth rates of $50 \mu\text{m/a}$ for stalagmite CL26 and $10 \mu\text{m/a}$ for HBSH1, a large growth rate
653 effect on calcite $D_{Sr(Cc)}$ is unlikely. Furthermore, Pingitore and Eastman (1986) showed that
654 calcite $D_{Sr(Cc)}$ increases with lower calcite Sr/Ca ratios. However, the calcite Sr/Ca ratios of
655 stalagmite HBSH1 are comparable to those of the other samples (Table 4). Thus, the different
656 values obtained from the different stalagmites may be realistic and explicable by differing
657 factors controlling aragonite $D_{Sr(Ar)}$.

658 Precipitation experiments suggest that aragonite $D_{\text{Sr}(\text{Ar})}$ is higher at lower temperatures,
659 and is defined by $D_{\text{Sr}(\text{Ar})} = 1.27 - 0.005212 \cdot T$ (Dietzel et al., 2004). Stalagmite HBSH1 grew
660 in central Europe during the Last Glacial with an estimated mean annual cave temperature of
661 3°C. All other samples grew under warmer conditions, i.e., between 12°C and 18°C (Table 4).
662 However, according to the temperature expression from Dietzel et al. (2004), a temperature
663 difference of 10°C would only result in a difference of 0.05 for $D_{\text{Sr}(\text{Ar})}$, insufficient to explain
664 the observed difference.

665 Gabitov et al. (2006) reported that Sr incorporation into aragonite shows little
666 dependency on growth rate. However, their experiments were conducted at precipitation rates
667 of 2-117 $\mu\text{m}/\text{day}$, which is not comparable to the slow growth rates of the speleothem samples
668 examined here. Figure 7 suggests a growth rate dependency of aragonite $D_{\text{Sr}(\text{Ar})}$, but only for
669 (very) slow growth rates in the range of 1-20 $\mu\text{m}/\text{a}$. For higher growth rates, $D_{\text{Sr}(\text{Ar})}$ seems to
670 converge to values around 1.01 (± 0.18), a value that overlaps with the results reported from
671 marine analogue precipitation experiments (Table 6). We emphasize that calcite $D_{\text{Sr}(\text{Cc})}$ has
672 not been corrected with respect to its Mg/Ca ratio and that the relationship is only based on a
673 small number of data points. In addition, uncertainties in the calculated speleothem growth
674 rate related to dating uncertainties indicate that this suggestion should be considered with
675 caution. Nonetheless, growth rate could be a potential factor, which may be important when
676 interpreting Sr signals of slowly growing aragonite speleothems. Lower growth rates may be
677 associated with higher aragonite $D_{\text{Sr}(\text{Ar})}$, contrasting the relationship between growth rate and
678 calcite $D_{\text{Sr}(\text{Cc})}$.

679

680 5.4. Speleothem aragonite $D_{\text{Ba}(\text{Ar})}$

681 Both Ba and Sr are characterized by large ionic radii and have similar chemical
682 properties. Therefore, their partitioning into aragonite and calcite is similar. Indeed,
683 precipitation experiments indicate that calcite $D_{\text{Ba}(\text{Cc})}$ and calcite $D_{\text{Sr}(\text{Cc})}$ are similar (Day and
684 Henderson, 2013) and increase with increasing growth rates (Tesoriero and Pankow, 1996).
685 Aragonite $D_{\text{Ba}(\text{Ar})}$ and $D_{\text{Sr}(\text{Ar})}$ respond in a similar manner to temperature changes, i.e., both Ba
686 and Sr incorporation decrease with increasing temperature (Dietzel et al., 2004; Gaetani and
687 Cohen, 2006). Similarly as for Sr, the relatively large ionic radius of Ba results in preferential
688 incorporation into the aragonite crystal lattice, and aragonite $D_{\text{Ba}(\text{Ar})}$ is (as $D_{\text{Sr}(\text{Ar})}$) expected to
689 be >1 , at least for temperatures below 40°C (Dietzel et al., 2004; Gaetani and Cohen, 2006)
690 (Table 6). However, only two of our aragonite $D_{\text{Ba}(\text{Ar})}$ values calculated from Cc-Ar

691 transitions in stalagmite HBSH1 meet this expectation, all other values have a mean of 0.46
692 ± 0.18 (Table 6; Fig. 6).

693 Values of aragonite $D_{Ba} < 1$ have been reported for temperatures of 40°C and higher
694 (Dietzel et al., 2004; Gaetani and Cohen, 2006). Such temperatures are not expected for cave
695 environments unless they are strongly affected by hydrothermal fluids. Furthermore, aragonite
696 $D_{Ba(Ar)}$ seems to be independent of growth rate. As for Sr, solution composition (i.e., high
697 Mg/Ca ratios) and an underestimation of calcite $D_{Ba(Cc)}$ may explain this potential
698 underestimation of aragonite $D_{Ba(Ar)}$. The ionic radii of Ca, Sr and Ba in sixfold coordination
699 are 1.08, 1.21 and 1.44 Å, respectively. Because Ba has the largest ionic radius, increased Mg
700 incorporation may affect calcite $D_{Ba(Cc)}$ more strongly than calcite $D_{Sr(Cc)}$, although this idea
701 has not been tested yet. Thus, it remains unclear whether this effect would be sufficient to
702 explain the observed difference with published aragonite $D_{Ba(Ar)}$ values derived from
703 precipitation experiments mimicking marine environments. It is possible that in cave
704 environments, Ba incorporation into aragonite is prohibited through competition effects with
705 other large cations. Alternatively, Ba may also be incorporated to a substantial extent through
706 adsorption to colloidal or particulate matter. In summary, our results show that aragonite
707 $D_{Ba(Ar)}$ values derived from precipitation experiments reflecting marine environments should
708 be considered with caution when applied to cave environments. Additional work is needed to
709 clarify the incorporation mechanisms in detail.

710

711 5.5. Speleothem aragonite $D_{Mg(Ar)}$

712 Our calculated aragonite $D_{Mg(Ar)}$ values agree with the values reported by Gabitov et
713 al. (2008) and Zhong and Mucci (1989) (Table 6), but Gaetani and Cohen (2006) found higher
714 values (Table 6). The discrepancy between Gaetani and Cohen (2006) and other estimates
715 may reflect different experimental setups and analytical techniques (Gabitov et al., 2008). The
716 variability of our calculated speleothem aragonite D_{Mg} values is relatively large (Fig. 6),
717 which is most likely related to the incorporation mechanism of Mg into aragonite because its
718 ionic radius in six-fold coordination is only 0.80 Å. Therefore, it is very unlikely to substitute
719 for Ca within the aragonite crystal lattice. Gabitov et al. (2008) found a strong precipitation
720 rate effect and explained it by the growth entrapment model (Watson, 1996, 2004). According
721 to this model, Mg is incorporated in equilibrium with the solution below a precipitation rate of
722 0.09 $\mu\text{m/day}$ (i.e., 33 $\mu\text{m/a}$) (Gabitov et al., 2008), leading to Mg concentrations close to zero
723 ppm. However, the aragonite sections of stalagmite HBSH1 are characterized by growth rates
724 lower than 17 $\mu\text{m/a}$ and contain 8 ppm Mg. Some studies showed that part of the Mg in

725 aragonite speleothems is associated with Al, Si, and Th, which was interpreted as detrital
726 material (Yang et al., 2015; Wassenburg et al., 2013).

727

728 5.6. Speleothem aragonite $D_{U(Ar)}$

729 Our calculated aragonite $D_{U(Ar)}$ values are in a similar range as the relatively high
730 values reported by Meece and Benninger (1993) (Table 6). Furthermore, Jamieson et al.
731 (submitted) also uses speleothem calcite-to-aragonite transitions to calculate $D_{U(Ar)}$ and report
732 a value of 3.74 ± 1.13 , confirming our values. In contrast, Gabitov et al. (2008) found
733 significantly lower aragonite $D_{U(Ar)}$ values, whereas Kitano and Oomori (1971) reported
734 intermediate values (Table 6). As discussed by Gabitov et al. (2008), U is mostly incorporated
735 into $CaCO_3$ as $UO_2(CO_3)_3$ (Reeder et al., 2000), which is most abundant at solution pH-values
736 between 7.5 and 8 (Djogic et al., 1986). For pH-values in this range, high aragonite $D_{U(Ar)}$
737 values can thus be expected. However, Meece and Benninger (1993) performed experiments
738 with pH-values between 8 and 8.8, which consequently should result in relatively low $D_{U(Ar)}$
739 values. As a consequence, U-incorporation into aragonite must be governed by multiple
740 factors.

741 The largest speleothem aragonite $D_{U(Ar)}$ values in our study were derived from
742 stalagmite HBSH1 (Table 6). HBSH1 is the sample with the lowest growth rate, indicating a
743 low supersaturation with respect to $CaCO_3$ and consequently a low dripwater pH. Compared
744 to the other samples, we thus argue that the pH values of the dripwater associated with
745 stalagmite HBSH1 must have been the lowest, although still high enough to precipitate
746 aragonite (i.e., 8.2, Riechelmann et al., 2014). The relatively high $D_{U(Ar)}$ values calculated
747 from stalagmite HBSH1 may thus, at least partly, be assigned to the relatively low pH values
748 of the dripwater.

749 Our calculated speleothem aragonite $D_{U(Ar)}$ values show a large variability (Fig. 6),
750 which, at least in part, must be assigned to variable calcite $D_{U(Cc)}$ values used for the
751 calculations. In calcite, UO_2 is likely incorporated in several different configurations and is
752 presumed to have a destabilizing effect (Reeder et al., 2000). Although Kelly et al. (2003)
753 indicated that UO_2 can substitute for Ca within calcite, calcite discriminates more strongly
754 against UO_2 -incorporation compared to aragonite (Reeder et al., 2000). Therefore, we suggest
755 that in calcite speleothems a larger percentage of the bulk U is adsorbed to colloidal phases, of
756 which the incorporation depends on multiple factors (Hartland et al., 2014), which might lead
757 to more variable calcite $D_{U(Cc)}$ values and thus relatively high variability in speleothem $D_{U(Ar)}$.

758

759 **6. Conclusions**

760 Aragonite speleothems may serve as excellent climate archives due to their
761 amenability to $^{230}\text{Th}/\text{U}$ dating, provided that potential environmental proxies (i.e., stable
762 isotopes, trace elements) contained within them can be well understood. This study represents
763 a significant improvement towards quantifying and understanding trace element partitioning
764 in speleothem aragonite, which is a prerequisite to assessing the extent to which prior
765 aragonite precipitation (PAP) has affected speleothem aragonite trace element variability. Of
766 special interest is whether $D_{\text{X}(\text{Ar})}$ is above or below one because this determines whether
767 enhanced PAP is associated with lower or higher speleothem trace element concentrations.

768 We derive mean speleothem aragonite values for $D_{\text{Mg}(\text{Ar})}$, $D_{\text{Sr}(\text{Ar})}$, $D_{\text{Ba}(\text{Ar})}$, and $D_{\text{U}(\text{Ar})}$ of
769 $9.7 \cdot 10^{-5} \pm 9.01 \cdot 10^{-5}$, 1.38 ± 0.53 , 0.91 ± 0.88 , and 6.26 ± 4.54 , respectively. All estimated
770 values indicate that $D_{\text{Mg}(\text{Ar})} \ll 1$ and $D_{\text{U}(\text{Ar})} > 1$ (with the exception of one value), and $D_{\text{Sr}(\text{Ar})} >$
771 1 or around unity. For $D_{\text{Ba}(\text{Ar})}$, the majority of our samples suggest values < 1 , although a few
772 values are > 1 . Our values show considerable variability, which may be due to variable
773 precipitation rates (particularly important for $D_{\text{Sr}(\text{Ar})}$ and $D_{\text{Mg}(\text{Ar})}$), pH (important for $D_{\text{U}(\text{Ar})}$),
774 temperature (important for $D_{\text{Sr}(\text{Ar})}$ and $D_{\text{Ba}(\text{Ar})}$) and uncertainties in the calcite $D_{\text{X}(\text{Cc})}$ used for
775 the calculations. Furthermore, our data suggest that speleothem aragonite $D_{\text{Sr}(\text{Ar})}$ may be
776 affected by precipitation rate if the speleothem growth rate is below $20 \mu\text{m}/\text{a}$. Lower
777 precipitation rates seem associated with higher $D_{\text{Sr}(\text{Ar})}$, although this should be confirmed by
778 additional work.

779 Even though the calculated $D_{\text{X}(\text{Ar})}$ are associated with considerable uncertainties, this
780 study provides the foundation for interpreting trace element concentrations in speleothem
781 aragonite in terms of climate change. In particular, dry climate conditions may lead to lower
782 karst recharge and enhanced prior aragonite precipitation, which results in lower speleothem
783 U but higher Mg concentrations if prior aragonite precipitation is indeed the dominating
784 process (for example, Jamieson et al., submitted). If $D_{\text{Sr}(\text{Ar})}$ is above one, then dry climate
785 conditions may also lead to lower speleothem Sr concentrations, although this remains to be
786 confirmed by additional research.

787

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803

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1027 **Figure captions**

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1029 Figure 1. Sampling locations of the speleothems used in this study. 1) Grotte Prison de Chien,
1030 north-west Middle Atlas, Morocco. 2) Grotte de Piste, north-west Middle Atlas, Morocco. 3)
1031 Unnamed cave 8 km south of Treveles, Alpujaras, southern Spain. 4) Grotte de Clamouse,
1032 southern France. 5) Hüttenbläuserschachthöhle, central Germany. 6) Krem Mawmluh Cave,
1033 Meghalaya plateau, north-east India. 7) Krem Umsynrang Cave, Meghalaya plateau, north-
1034 east India.

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1036 Figure 2. Slabs showing Cc-Ar transitions with the corresponding trace element transects and
1037 the positions of $^{230}\text{Th}/\text{U}$ -sampling. Blue dashed lines indicate boundaries between calcite and
1038 aragonite. Yellow and black arrows indicate speleothem growth direction. a-c) Stalagmite
1039 KRUM11. d-e) Stalagmite MAW4. f-g) Flowstone MO. h-i) Stalagmite HBSH1 part 4.

1040

1041 Figure 3. Thin section petrography of calcite and aragonite fabrics. a) Stalagmite MAW4,
1042 transition from undulose columnar calcite to calcite fans with sweeping extinction to acicular
1043 aragonite. The two calcite fabrics are separated by detrital material (cross-polarised light). b)
1044 Stalagmite MAW4, columnar undulose calcite (cross-polarised light). c) Stalagmite MAW4,
1045 undulose columnar calcite interbedded by two detrital layers. d) Stalagmite KRUM11, calcite
1046 (cross-polarised light). e) Stalagmite KRUM11, Cc-Ar transition with acicular aragonite.
1047 (cross-polarised light). f) Same as (e), but with plain polarized light. Arrows indicate primary
1048 aragonite (Ar-p) and potentially micritized aragonite (Ar-m). g) Stalagmite HBSH1, part 4,
1049 columnar calcite crystals and acicular aragonite (cross-polarised light). h) Same as (g), but
1050 with plain polarized light. i) Flowstone MO, undulose columnar calcite crystals and acicular
1051 aragonite (cross-polarised light). j) Same as (i), but with plain polarized light.

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1053 Figure 4. Results of Raman spectroscopy of stalagmite MAW4. Blue dashed lines indicate the
1054 main transition from calcite to aragonite. a) Scan from MAW4 with positions of linescan and
1055 spots indicated (red); Cc1 and Cc2 (separated by yellow dashed line) are also indicated. b) 5
1056 μm resolution Raman spectroscopy map covering the aragonite, Cc1 and Cc2. The image is
1057 stretched in horizontal direction. c) 2 μm resolution Raman spectroscopy map covering Cc1
1058 with very limited aragonite. Dark red represents aragonite, green represents calcite. d) Thin
1059 section of stalagmite MAW4 with Cc-Ar transition (cross-polarised light). e) 2 μm resolution

1060 Raman spectroscopy map covering fan-like calcite and aragonite. Blue represents aragonite,
1061 pink represents calcite.

1062
1063 Figure 5. Molar trace element Mg/Ca, U/Ca, Sr/Ca and Ba/Ca ratios across the investigated
1064 Cc-Ar transitions. a) Flowstone MO, b) Stalagmite MAW4. c) Stalagmite HBSH1 part 4.
1065 Linescan (grey) and single spot (black) analyses, respectively, are indicated. For stalagmite
1066 HBHS1, only spot analyses are available. Linescan data are shown as 5-point running
1067 medians. Data marked by the red shaded bar represent the data from the calcite section that
1068 have been used for the calculations. Data marked by the brown shaded bar represents the data
1069 from the aragonite section that have been used for the calculations.

1070
1071 Figure 6. Compilation of the speleothem aragonite distribution coefficients calculated from
1072 the Cc-Ar transitions studied. Diamonds (squares) indicate values derived from stratigraphic
1073 (lateral) Cc-Ar transitions. Shaded error bars include an additional uncertainty of 50% on the
1074 trace element to Ca ratio of the dripwater. Note that the y-axis has a logarithmic scale. For
1075 reference, the black horizontal line indicates a distribution coefficient value of 1 for the
1076 elements Sr, Ba, and U.

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1078 Figure 7. Relation between speleothem aragonite D_{Sr} and growth rate. Linear regression for
1079 the five data points corresponding to growth rates $< 20 \mu\text{m}/\text{year}$ and associated correlation
1080 coefficient and p-value is shown.

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