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

3

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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 distribution
36 coefficients are above or below one in order to assess the extent to which prior aragonite
37 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*: $D_{\text{Mg}(\text{Ar})} = 9.7\text{E-}5 \pm 9.01\text{E-}5$,
41 $D_{\text{Ba}(\text{Ar})} = 0.91 \pm 0.88$, $D_{\text{Sr}(\text{Ar})} = 1.38 \pm 0.53$, and $D_{\text{U}(\text{Ar})} = 6.26 \pm 4.54$ (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 ($<11 \mu\text{m}/\text{year}$) of this sample. In particular,
44 $D_{\text{Sr}(\text{Ar})}$ appears to show a negative correlation with growth rate when growth rate is below
45 $20 \mu\text{m}/\text{year}$.

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

53

54 **1. Introduction**

55 Speleothems are secondary cave deposits mainly consisting of calcite or aragonite with
56 calcite being the more common polymorph of CaCO_3 (Hill and Forti, 1997). Speleothems, and
57 in particular stalagmites and flowstones are considered as some of the most promising
58 continental climate archives. They can serve as benchmarks, which can be reliably contrasted
59 and compared with proxy records from complementary archives, because they can be precisely
60 dated up to about 500 ka by the $^{230}\text{Th}/\text{U}$ -dating technique (e.g., Scholz and Hoffmann, 2008).
61 In addition, speleothem archives can be sampled and analysed with up to sub-annual resolution
62 for carbon and oxygen isotopes (Mattey et al., 2008; McDermott, 2004; Myers et al., 2015) and
63 trace and major elemental abundances (Fairchild and Treble, 2009). Numerous studies on
64 speleothem calcite trace element compositions have been published recently (Borsato et al.,
65 2007; Day and Henderson, 2013; Fairchild and Treble, 2009; Griffiths et al., 2010; Treble et
66 al., 2005; and references therein). Few studies, however, focus on trace element compositions
67 in aragonite speleothems (Finch et al., 2003; Finch et al., 2001; McMillan et al., 2005; Tan et
68 al., 2014; Wassenburg et al., 2012; Wassenburg et al., 2013). The knowledge on element
69 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). Where
75 robust evidence that an aragonite speleothem is well preserved is available (Myers et al., 2015;
76 Wassenburg et al., 2013), the potential to obtain exceptionally precise chronologies is high.
77 Consequently, it is important to further investigate (i) how trace elements partition into
78 speleothem aragonite and (ii) which controls and processes are reflected by their temporal and
79 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 crystallography,
83 where the Ca-ion is coordinated by six O-ions (Swart, 2015). Due to these crystallographic
84 differences, larger cations, such as Sr, Ba and U, are preferentially incorporated into aragonite,
85 whereas calcite also tends to incorporate small cations, such as Mg. The corresponding trace
86 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 the
99 aquifer above the cave, although it may also occur inside the cave (e.g., at the cave ceiling or
100 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 coefficients
105 are below (above) one, elevated concentrations in speleothems are typically interpreted as
106 reflecting reduced (enhanced) infiltration and drier (wetter) climatic conditions (Johnson et al.,
107 2006). However, cave ventilation may also control PCP (Sherwin and Baldini, 2011; Wong et
108 al., 2011).

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

121 et al., 2013) with low ionic strength and the presence of (organic) colloidal phases (Fairchild
122 and Treble, 2009; Hartland et al., 2014), whereas marine deposition occurs in high ionic
123 strength waters and is often biologically mediated. The same arguments prompted a series of
124 studies that aimed to determine speleothem calcite D_x . These were based on both field
125 precipitation experiments, during which the trace element composition of calcite formed within
126 a cave over a known time period is compared with the trace element composition of the
127 associated dripwater (Fairchild et al., 2010; Gascoyne, 1983; Huang et al., 2001; Karmann et
128 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 at
138 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 summer
154 dry temperate, all year wet temperate, to summer wet temperate conditions (Peel et al., 2007).

155 For most of the caves, dolostone is a primary host rock component (Table 1). This results in
156 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 Clamouse
164 (Frisia et al., 2002; McMillan et al., 2005) as well as Grotte Prison de Chien and Grotte de Piste
165 (Wassenburg et al., 2012) were previously published, and the reader is referred to these
166 publications for a detailed documentation of these samples. In addition, one Cc-Ar transition in
167 each of the stalagmites KRUM11 (Krem Umsynrang Cave), MAW4 (Mawmluh Cave;
168 Breitenbach et al., 2015), and MO (unnamed cave) were analysed. Furthermore, four transitions
169 in stalagmite HBSH1 (Hüttenbläuserschachthöhle; Jochum et al., 2012; Yang et al., 2015) were
170 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 stratigraphic
178 and lateral Cc-Ar transitions (Fig. 2). Stalagmite HBSH1 is described in Yang et al. (2015). For
179 all samples, the boundaries between calcite and aragonite mineralogies are macroscopically
180 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 thousands
185 of years when exposed to diagenetic fluids (Frisia et al., 2002; Lachniet et al., 2012; Martin-
186 Garcia et al., 2009; Perrin et al., 2014; Zhang et al., 2014). In this study, thin-sections were
187 examined under a polarization microscope in order to assess whether the samples show
188 petrographic evidence for diagenetic alteration. Diagenetic alteration of calcite and aragonite

189 can be identified by the appearance of dissolution features (Figs. 9c and 10 in Perrin et al.,
190 2014), micritization and aragonite relics (Figs. 3 and 8 in Martin-Garcia et al., 2009) and calcite
191 mosaics (Fig. 14 in Frisia and Borsato, 2010, and Fig. 3 in Scholz et al., 2014). In addition, the
192 mineralogy of the samples was determined by X-ray diffraction at the ETH Zurich, Switzerland,
193 using approximately 30 mg of sample powder, as well as by Raman spectroscopy performed at
194 the University of Mainz, Germany. The Raman spectrometer used was a HR 800 from the
195 company Horiba Jobin Yvon, with an attached Olympus BX41 Microscope equipped with an
196 automatic xyz-stage to undertake the 2-dimensional mappings. A frequency doubled Nd-YAG
197 laser (532.12nm), a grating of 1800 grooves/mm, an entrance slit of 100 μm and a confocal hole
198 of 400 μm were used for the measurements. Every point was measured twice to eliminate
199 spikes; each measurement was performed with an accumulation time of 1 s. To evaluate the
200 calcite content, the intensity of the band at 282 cm^{-1} was used. For aragonite, the band at ca.
201 207 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. Four
206 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 samples
210 from stalagmite KRUM11 and four samples from flowstone MO were dated using a Nu Plasma
211 MC-ICPMS at the Max Planck Institute for Chemistry, Mainz, Germany, following the
212 procedures of Obert et al. (2016). The top sample of flowstone MO was dated at the Helmholtz
213 Centre for Ocean Research Kiel (GEOMAR) following the procedure of Fietzke et al. (2005).
214 Eight samples from stalagmite HBSH1 were dated at Bristol University, UK, following the
215 procedures described by Hoffmann et al. (2007). All ages are reported as thousands of years
216 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, and
220 MO were analysed at the Max Planck Institute for Chemistry, Mainz, Germany. Mg/Ca, Al/Ca,
221 Si/Ca, P/Ca, Mn/Ca, Sr/Ca, Y/Ca, Ba/Ca, Pb/Ca, Th/Ca, and U/Ca ratios were determined with
222 a Thermo Finnigan Element 2 Inductively Coupled Plasma Mass Spectrometer (ICPMS)

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

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

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

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

263

264 3.5. Derivation of speleothem aragonite distribution coefficients

265

266 3.5.1. Approach

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

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

278

$$279 \quad D_{X(Cc)} = \frac{X/Ca_{Cc}}{X/Ca_{Solution}} \quad (2)$$

280

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

282

$$283 \quad D_{X(Ar)} = \frac{X/Ca_{Ar}}{X/Ca_{Solution}} \quad (3)$$

284

285 $D_{X(Cc)}$ is available from previous studies (Day and Henderson, 2013), and $X/Ca_{(Cc)}$ and
286 $X/Ca_{(Ar)}$ are measured values. Using the assumption that the dripwater trace element/Ca ratio
287 was similar for precipitation of calcite and aragonite (see below for a critical discussion),
288 $X/Ca_{Solution}$ can be calculated from equation (2). Inserting this value in Eq. (3), $D_{X(Ar)}$ can be
289 calculated. In summary, $D_{X(Ar)}$ is given by:

290

291

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

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

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

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3.5.2. Error propagation

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Because assessing potential past changes in dripwater trace element composition is challenging, speleothem trace element data variability must be considered carefully. In order to solve this, we included the standard deviation of the trace element data in the error propagation of the aragonite distribution coefficients. In addition, the uncertainty of the trace element analysis and the uncertainty related to the published calcite trace element distribution coefficients (Day and Henderson, 2013) are included. The error bars on the calculated aragonite distribution coefficients are, thus, very conservative. We used the following equation to calculate the absolute error of the speleothem aragonite D_X values:

321

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

322

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

331

332 3.5.3. Boundary conditions for aragonite precipitation

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

350

351 3.6. Sample and trace element data selection

352 The samples and trace element/Ca ratios selected for the calculations are subject to strict
353 criteria. Post-depositional diagenesis may alter the trace element composition of both aragonite
354 (Lachniet et al., 2012; Ortega et al., 2005) and calcite speleothems (Scholz et al., 2014).
355 Consequently, data derived from diagenetically altered sections were avoided. In addition, only

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

378

379 **4. Results and interpretation**

380

381 4.1. Petrography and degree of preservation

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

386

387 4.1.1. Stalagmite MAW4

388 The calcite portion of stalagmite MAW4 (Fig. 3a-c) shows discontinuous, inclusion-
389 rich layers composed of non-ordered, relatively small (10-100 μm wide) calcite crystals

390 (Fig. 3b). In between these layers, columnar, radiaxial calcite crystals occur (Neuser and
391 Richter, 2007; Richter et al., 2011) (Fig. 3b). Directly beneath an aragonite interval, calcite
392 fabrics consisting of fan-like structures with a sweeping extinction over several crystals exist
393 (Figs. 3a and 4d).

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

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

407

408 4.1.2. Stalagmite KRUM11

409 The calcite fabric of stalagmite KRUM11 appears as mosaic-like in thin sections (Figs.
410 3d-f) (Frisia and Borsato, 2010), whereas the aragonite directly above the calcite shows an
411 acicular fabric (Frisia and Borsato, 2010) (Fig. 3e). Under plane polarized light, darker, non-
412 translucent zones alternate with translucent crystals within the aragonite (Fig. 3f).

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

420

421 4.1.3. Stalagmite HBSH1

422 The calcite layers within stalagmite HBSH1 are 5-10 mm thick and consist of columnar
423 calcite crystals. The aragonite has an acicular fabric characterised by a sweeping extinction

424 pattern across several crystals (Fig. 3g). The individual crystals are somewhat longer and wider
425 compared to those from stalagmite MAW4 (Fig. 2), and individual needle-like aragonite
426 crystals and spherulites are distributed between the relatively long and wide aragonite crystals
427 (Fig. 3g). No diagnostic features of diagenesis (e.g., micritization, dissolution or calcite-to-
428 aragonite transformation) are apparent, and the fabrics are therefore considered primary.

429

430 4.1.4. Flowstone MO

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

435

436 4.2. Conditions of formation

437

438 4.2.1. Timing of calcite-to-aragonite transitions and determination of speleothem growth rates

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

441 The calcite phase of stalagmite KRUM11 occurred between 16.89 ± 0.11 and
442 16.42 ± 0.12 ka (Fig. 2; Table 3). The mean growth rate for this section is ca. $35 \mu\text{m/a}$.

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

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

452

453 4.2.2. Temperature at time of deposition

454 Day and Henderson (2013) documented that calcite D_{Mg} and D_{U} in precipitation
455 experiments depend on temperature. In particular, $D_{\text{U}(\text{Cc})}$ is 0.11 at 7°C and 0.12 at 15°C ,
456 whereas $D_{\text{Mg}(\text{Cc})} = 0.01 * e^{0.02 * T}$. Although the temperature dependency of $D_{\text{Mg}(\text{Cc})}$ is relatively

457 small in comparison to cave site temperature variations, an approximate assessment of cave
458 temperatures is considered important here.

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

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

478

479 4.3. Distribution coefficients

480

481 4.3.1. Trace element data

482 Trace element data across the Cc-Ar transitions from the different speleothems are
483 presented in Fig. 5. The line scan data reproduce the single spot analyses very well indicating
484 sample homogeneity at the sub-millimeter scale. The Cc-Ar transitions are clearly visible in
485 Mg/Ca, Sr/Ca, Ba/Ca and U/Ca ratios (Fig. 5). As expected, Sr/Ca, Ba/Ca and U/Ca ratios are
486 higher in aragonite, whereas Mg/Ca is higher in calcite. For sample MAW4, a stepwise increase
487 (decrease) in Sr/Ca and U/Ca (Mg/Ca) is apparent starting ca. 3 mm below the Cc-Ar transition
488 and is followed by the actual Cc-Ar transition. A more detailed discussion is required to clarify
489 which data are most useful for the calculations of the aragonite distribution coefficients.

490 Stalagmite MAW4 shows a fan-like calcite fabric (Fig. 3a-c), which is interpreted as the
491 result of aragonite-to-calcite transformation. It is possible that the intermediate values of Sr/Ca,
492 U/Ca and Mg/Ca are associated with this fabric because it is common that secondary calcite
493 may preserve the trace element signature of the precursor aragonite (Niggemann and Richter,
494 2006). However, the thin section was taken from another portion of stalagmite MAW4, thus
495 preventing establishing a direct link with the trace element data. Therefore, an area close to the
496 trace element transect was mapped with Raman spectroscopy, which indicated that both phases
497 with the intermediate (Cc1) and high (Cc2) Mg/Ca ratios are indeed calcite with negligible
498 aragonite (Fig. 4). Sr/Ca and U/Ca ratios are higher, and the Mg/Ca ratios are lower in Cc1 than
499 in Cc2, suggesting that aragonite-to-calcite diagenesis may have affected Cc1. Consequently,
500 only the trace element data derived from Cc2 are used to calculate distribution coefficients.

501

502 4.3.2. Speleothem aragonite distribution coefficients

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

512 The calculated aragonite distribution coefficients with associated uncertainties are
513 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
514 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
515 stalagmite HBSH1 are higher for all elements examined and increase standard deviations
516 significantly (Table 6). This is especially the case for $D_{Ba(Ar)}$, which changes from 0.91 ± 0.88
517 to 0.46 ± 0.18 if the values calculated from stalagmite HBSH1 are excluded (Table 6). Despite
518 the uncertainty, the results demonstrate for the first time that under karst environmental
519 conditions $D_{Mg(Ar)}$ is considerably smaller than one, $D_{Sr(Ar)}$ is above one or close to unity, and
520 $D_{U(Ar)}$ is larger than one. As noted earlier, we used the trace element datasets covering two
521 lateral Cc-Ar transitions from stalagmite HK1 (Wassenburg et al., 2012) to verify the $D_{Sr(Ar)}$,
522 $D_{Ba(Ar)}$ and $D_{U(Ar)}$ derived from stratigraphical Cc-Ar transitions. The corresponding $D_{X(Ar)}$
523 values are indistinguishable from those derived using stratigraphic Cc-Ar transitions adding

524 confidence to the validity of our estimates (Fig. 6). The large difference in growth rate between
525 the aragonite (295 $\mu\text{m/a}$) and the calcite (24 $\mu\text{m/a}$) sections of stalagmite MAW4 does not seem
526 to affect the calculated aragonite $D_{X(\text{Ar})}$ value because the results are consistent with the other
527 values.

528

529 **5. Discussion**

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

544

545 5.1. Sensitivity analysis

546 Although only the best available speleothem samples with calcite-aragonite transitions
547 were used, the calculated aragonite $D_{X(\text{Ar})}$ values of course depend on the data selected for the
548 calculations. To assess any selection bias, all calculations were repeated with trace element data
549 representing only 2-155 years of stalagmite growth instead of 2-771 years. This transect
550 consisting of 2-155 years of data comprises the part of the original trace element transect of 2-
551 771 years closest to the Cc-Ar transition. This sensitivity analysis was performed on each
552 sample (input parameters used for the corresponding calculations are given in supplemental
553 Table EA1). The median $D_{X(\text{Ar})}$ values of both datasets are comparable (Table 6), indicating
554 that the calculated $D_{X(\text{Ar})}$ values do not strongly depend on the selected trace element transect.
555 Nevertheless, the mean X/Ca ratio calculated using the longer dataset should be statistically
556 more robust, and is thus the preferred value.

557 In addition to varying the number of trace element data points, the results were tested
 558 using an aragonite-to-calcite transition from stalagmite HK3 (Wassenburg et al., 2012). We
 559 applied the same approach to the data from the Ar-Cc transition to calculate the calcite
 560 distribution coefficient by using the aragonite distribution coefficient. Using the same error
 561 propagation as for the calculated aragonite distribution coefficients, the calculated calcite
 562 distribution coefficients are 0.019 ± 0.004 , 0.14 ± 0.02 , 0.13 ± 0.02 and 0.13 ± 0.05 for $D_{Mg(Cc)}$,
 563 $D_{Sr(Cc)}$, $D_{Ba(Cc)}$ and $D_{U(Cc)}$, respectively. Although this transition was interpreted as a hiatus
 564 (Wassenburg et al. 2012), $D_{X(Cc)}$ values calculated across this transition are, with exception of
 565 $D_{Mg(Cc)}$, within error of the $D_{X(Cc)}$ values reported by Day and Henderson (2013). We refer to
 566 section 5.5 for a detailed discussion of D_{Mg} . These cross-validations provide further support
 567 that our approach yields reliable results.

568

569 5.2. Rayleigh distillation effects

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

584

$$585 \quad r = \frac{v \cdot \sigma \cdot 9.48151 \cdot 10^{-4}}{31536000}, \quad (6)$$

586

587 where r is the average $CaCO_3$ deposition rate ($mmol/cm^2/s$), v is the speleothem growth rate
 588 ($\mu m/year$), and σ is the density of aragonite (g/cm^3). With assumptions for drip rate, initial

589 dripwater Ca^{2+} concentration and film thickness, the amount of Ca removed from the dripwater
590 per drip can be calculated for every Cc-Ar transition using the equation from Stoll et al. (2012):
591

$$592 \quad Ca - excess = \frac{r \cdot \Delta t / \delta}{Ca_i}, \quad (7)$$

593
594 where δ is the thickness of the water film (cm), Δt is drip interval (s), and Ca_i is initial Ca
595 concentration (mmol/cm^3). The boundary conditions were chosen relatively conservative, such
596 that the calculated excess Ca^{2+} represents an overestimation rather than an underestimation. In
597 particular, we assumed a very long drip-interval of 600 s (10 min), a low initial dripwater Ca
598 concentration of 20 mg/l and a realistic film thickness of 0.01 cm (Baker et al., 2014; Hansen
599 et al., 2013). The estimated amount of excess Ca^{2+} precipitation ranges from 0.08 to 3.9%
600 (Table 5), except for stalagmite MAW4 aragonite, for which a value of 19% is estimated. With
601 only 0.08 to 3.9% of excess Ca^{2+} precipitation during one drip interval, Rayleigh distillation
602 effects are minimal and within the range of our analytical uncertainties. For MAW4, an
603 influence of Rayleigh distillation on the calculated aragonite $D_{\text{X(Ar)}}$ values cannot be excluded.
604 However, we emphasize that an initial dripwater Ca concentration of 20 mg/l for the dripwater
605 is very low, and typical values range from 30 to 90 mg/l (Frisia et al., 2002; Karmann et al.,
606 2007; Riechelmann et al., 2011; Tremaine and Froelich, 2013). Drip sites with lower dripwater
607 Ca^{2+} concentrations are usually associated with low CaCO_3 saturation indices and low
608 precipitation rates.

609

610 5.3. Speleothem aragonite $D_{\text{Sr(Ar)}}$

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

617 The calculated aragonite $D_{\text{Sr(Ar)}}$ values depend on the value used for $D_{\text{Sr(Cc)}}$ of calcite.
618 Calcite $D_{\text{Sr(Cc)}}$ is known to be dependent on solution composition (Mucci and Morse, 1983;
619 Pingitore and Eastman, 1986), precipitation rate (Gabitov and Watson, 2006; Treble et al.,
620 2005), and possibly competition effects (Borsato et al., 2007). The latter may be related to the
621 availability of impurities in the crystal lattice, which in turn may be controlled by the

622 incorporation of Mg. The application of a universal $D_{Sr(Cc)}$ for all Cc-Ar transitions may
623 therefore not be appropriate.

624 Precipitation experiments from Mucci and Morse (1983) showed that the incorporation
625 of small sized Mg-ions is accompanied by increasing incorporation of larger Sr-ions. This
626 relationship appeared to be linear and is expressed by $D_{Sr(Cc)} = 0.146 + 0.01833 * \%MgCO_3$.
627 Although it is tempting to use this relationship to correct the calcite $D_{Sr(Cc)}$ values used for the
628 calculations, we do not consider this as a suitable approach since the precipitation experiments
629 from Mucci and Morse (1983) reflect marine conditions. In addition, a calcite $D_{Sr(Cc)}$ value of
630 0.146 in absence of Mg seems high in comparison to the values reported from cave precipitation
631 experiments (Tremaine and Froelich, 2013). However, the laboratory precipitation experiments
632 of Day and Henderson (2013) were specifically designed to mimic the solution composition of
633 caves with a limestone host rock, and used dripwater Mg/Ca ratios of 0.047. In our study, the
634 calculated dripwater Mg/Ca ratios of all samples are between 0.6 and 2.8, reflecting the high
635 Mg content of the corresponding host rock (Table 1). Therefore, calcite $D_{Sr(Cc)}$ may have been
636 generally underestimated resulting in an underestimated value of aragonite $D_{Sr(Ar)}$. Since the
637 calcite of HBSH1 is characterized by the lowest Mg/Ca ratios, the aragonite $D_{Sr(Ar)}$ value
638 calculated from HBSH1 may be least affected by the underestimation of calcite $D_{Sr(Cc)}$.

639 Stalagmite CL26 provided aragonite D_{Sr} values <1 (0.70; Fig. 6, Table 5). Even
640 considering a calcite $D_{Sr(Cc)}$ value of 0.15 (McMillan et al., 2005) results in an aragonite $D_{Sr(Ar)}$
641 value of 0.87. This value is still lower than the mean value calculated from the four Cc-Ar
642 transitions from stalagmite HBSH1 (1.83 ± 0.46). Considering the relatively similar growth
643 rates of 50 $\mu\text{m/a}$ for stalagmite CL26 and 10 $\mu\text{m/a}$ for HBSH1, a large growth rate effect on
644 calcite $D_{Sr(Cc)}$ is unlikely. Furthermore, Pingitore and Eastman (1986) showed that calcite
645 $D_{Sr(Cc)}$ increases with lower calcite Sr/Ca ratios. However, the calcite Sr/Ca ratios of stalagmite
646 HBSH1 are comparable to those of the other samples (Table 4). Thus, the different values
647 obtained from the different stalagmites may be realistic and explicable by differing factors
648 controlling aragonite $D_{Sr(Ar)}$.

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

656 Gabitov et al. (2006) reported that Sr incorporation into aragonite shows little
657 dependency on growth rate. However, their experiments were conducted at precipitation rates
658 of 2-117 $\mu\text{m}/\text{day}$, which is not comparable to the slow growth rates of the speleothem samples
659 examined here. Figure 7 suggests a growth rate dependency of aragonite $D_{\text{Sr}(\text{Ar})}$, but only for
660 (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
661 converge to values around 1.01 (± 0.18), a value that overlaps with the results reported from
662 marine analogue precipitation experiments (Table 6). We emphasize that calcite $D_{\text{Sr}(\text{Cc})}$ has not
663 been corrected with respect to its Mg/Ca ratio and that the relationship is only based on a small
664 number of data points. In addition, uncertainties in the calculated speleothem growth rate
665 related to dating uncertainties indicate that this suggestion should be considered with caution.
666 Nonetheless, growth rate could be a potential factor, which may be important when interpreting
667 Sr signals of slowly growing aragonite speleothems. Lower growth rates may be associated
668 with higher aragonite $D_{\text{Sr}(\text{Ar})}$, contrasting the relationship between growth rate and calcite
669 $D_{\text{Sr}(\text{Cc})}$.

670

671 5.4. Speleothem aragonite $D_{\text{Ba}(\text{Ar})}$

672 Both Ba and Sr are characterized by large ionic radii and have similar chemical
673 properties. Therefore, their partitioning into aragonite and calcite is similar. Indeed,
674 precipitation experiments indicate that calcite $D_{\text{Ba}(\text{Cc})}$ and calcite $D_{\text{Sr}(\text{Cc})}$ are similar (Day and
675 Henderson, 2013) and increase with increasing growth rates (Tesoriero and Pankow, 1996).
676 Aragonite $D_{\text{Ba}(\text{Ar})}$ and $D_{\text{Sr}(\text{Ar})}$ respond in a similar manner to temperature changes, i.e., both Ba
677 and Sr incorporation decrease with increasing temperature (Dietzel et al., 2004; Gaetani and
678 Cohen, 2006). Similarly as for Sr, the relatively large ionic radius of Ba results in preferential
679 incorporation into the aragonite crystal lattice, and aragonite $D_{\text{Ba}(\text{Ar})}$ is (as $D_{\text{Sr}(\text{Ar})}$) expected to
680 be >1 , at least for temperatures below 40°C (Dietzel et al., 2004; Gaetani and Cohen, 2006)
681 (Table 6). However, only two of our aragonite $D_{\text{Ba}(\text{Ar})}$ values calculated from Cc-Ar transitions
682 in stalagmite HBSH1 meet this expectation, all other values have a mean of 0.46 ± 0.18 (Table
683 6; Fig. 6).

684 Values of aragonite $D_{\text{Ba}} < 1$ have been reported for temperatures of 40°C and higher
685 (Dietzel et al., 2004; Gaetani and Cohen, 2006). Such temperatures are not expected for cave
686 environments unless they are strongly affected by hydrothermal fluids. Furthermore, aragonite
687 $D_{\text{Ba}(\text{Ar})}$ seems to be independent of growth rate. As for Sr, solution composition (i.e., high
688 Mg/Ca ratios) and an underestimation of calcite $D_{\text{Ba}(\text{Cc})}$ may explain this potential
689 underestimation of aragonite $D_{\text{Ba}(\text{Ar})}$. The ionic radii of Ca, Sr and Ba in sixfold coordination

690 are 1.08, 1.21 and 1.44 Å, respectively. Because Ba has the largest ionic radius, increased Mg
691 incorporation may affect calcite $D_{\text{Ba}(\text{Cc})}$ more strongly than calcite $D_{\text{Sr}(\text{Cc})}$, although this idea
692 has not been tested yet. Thus, it remains unclear whether this effect would be sufficient to
693 explain the observed difference with published aragonite $D_{\text{Ba}(\text{Ar})}$ values derived from
694 precipitation experiments mimicking marine environments. It is possible that in cave
695 environments, Ba incorporation into aragonite is prohibited through competition effects with
696 other large cations. Alternatively, Ba may also be incorporated to a substantial extent through
697 adsorption to colloidal or particulate matter. In summary, our results show that aragonite $D_{\text{Ba}(\text{Ar})}$
698 values derived from precipitation experiments reflecting marine environments should be
699 considered with caution when applied to cave environments. Additional work is needed to
700 clarify the incorporation mechanisms in detail.

701

702 5.5. Speleothem aragonite $D_{\text{Mg}(\text{Ar})}$

703 Our calculated aragonite $D_{\text{Mg}(\text{Ar})}$ values agree with the values reported by Gabitov et al.
704 (2008) and Zhong and Mucci (1989) (Table 6), but Gaetani and Cohen (2006) found higher
705 values (Table 6). The discrepancy between Gaetani and Cohen (2006) and other estimates may
706 reflect different experimental setups and analytical techniques (Gabitov et al., 2008). The
707 variability of our calculated speleothem aragonite D_{Mg} values is relatively large (Fig. 6), which
708 is most likely related to the incorporation mechanism of Mg into aragonite because its ionic
709 radius in six-fold coordination is only 0.80 Å. Therefore, it is very unlikely to substitute for Ca
710 within the aragonite crystal lattice. Gabitov et al. (2008) found a strong precipitation rate effect
711 and explained it by the growth entrapment model (Watson, 1996, 2004). According to this
712 model, Mg incorporation approaches equilibrium with the solution below a precipitation rate
713 of 0.09 $\mu\text{m}/\text{day}$ (i.e., 33 $\mu\text{m}/\text{a}$) (Gabitov et al., 2008), leading to Mg concentrations close to zero
714 ppm. However, the aragonite sections of stalagmite HBSH1 are characterized by growth rates
715 lower than 17 $\mu\text{m}/\text{a}$ and contain 8 ppm Mg. Some studies showed that part of the Mg in
716 aragonite speleothems is associated with Al, Si, and Th, which was interpreted as detrital
717 material (Yang et al., 2015; Wassenburg et al., 2013).

718

719 5.6. Speleothem aragonite $D_{\text{U}(\text{Ar})}$

720 Our calculated aragonite $D_{\text{U}(\text{Ar})}$ values are in a similar range as the relatively high values
721 reported by Meece and Benninger (1993) (Table 6). Furthermore, Jamieson et al. (in revision)
722 also uses speleothem calcite-to-aragonite transitions to calculate $D_{\text{U}(\text{Ar})}$ and report a value of
723 3.74 ± 1.13 , confirming our values. In contrast, Gabitov et al. (2008) found significantly lower

724 aragonite $D_{U(Ar)}$ values, whereas Kitano and Oomori (1971) reported intermediate values (Table
725 6). As discussed by Gabitov et al. (2008), U is mostly incorporated into $CaCO_3$ as $UO_2(CO_3)_3$
726 (Reeder et al., 2000), which is most abundant at solution pH-values between 7.5 and 8 (Djogic
727 et al., 1986). For pH-values in this range, high aragonite $D_{U(Ar)}$ values can thus be expected.
728 However, Meece and Benninger (1993) performed experiments with pH-values between 8 and
729 8.8, which consequently should result in relatively low $D_{U(Ar)}$ values. As a consequence, U-
730 incorporation into aragonite must be governed by multiple factors.

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

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

747

748 **6. Conclusions**

749 Aragonite speleothems may serve as excellent climate archives due to their amenability
750 to $^{230}Th/U$ dating, provided that potential environmental proxies (i.e., stable isotopes, trace
751 elements) contained within them can be well understood. This study represents a significant
752 improvement towards quantifying and understanding trace element partitioning in speleothem
753 aragonite, which is a prerequisite to assessing the extent to which prior aragonite precipitation
754 (PAP) has affected speleothem aragonite trace element variability. Of special interest is whether
755 $D_{X(Ar)}$ is above or below one because this determines whether enhanced PAP is associated with
756 lower or higher speleothem trace element concentrations.

757 We derive mean speleothem aragonite values for $D_{Mg(Ar)}$, $D_{Sr(Ar)}$, $D_{Ba(Ar)}$, and $D_{U(Ar)}$ of
758 $9.7 \cdot 10^{-5} \pm 9.01 \cdot 10^{-5}$, 1.38 ± 0.53 , 0.91 ± 0.88 , and 6.26 ± 4.54 , respectively. All estimated
759 values indicate that $D_{Mg(Ar)} \ll 1$ and $D_{U(Ar)} > 1$ (with the exception of one value), and $D_{Sr(Ar)} >$
760 1 or around unity. For $D_{Ba(Ar)}$, the majority of our samples suggest values < 1 , although a few
761 values are > 1 . Our values show considerable variability, which may be due to variable
762 precipitation rates (particularly important for $D_{Sr(Ar)}$ and $D_{Mg(Ar)}$), pH (important for $D_{U(Ar)}$),
763 and uncertainties in the calcite $D_{X(Cc)}$ used for the calculations. An effect of temperature on
764 $D_{Sr(Ar)}$ and $D_{Ba(Ar)}$ could not be identified in this study. Furthermore, our data suggest that
765 speleothem aragonite $D_{Sr(Ar)}$ may be affected by precipitation rate if the speleothem growth rate
766 is below $20 \mu\text{m/a}$. Lower precipitation rates seem associated with higher $D_{Sr(Ar)}$, although this
767 should be confirmed by additional work.

768 Even though the calculated $D_{X(Ar)}$ are associated with considerable uncertainties, this
769 study provides the foundation for interpreting trace element concentrations in speleothem
770 aragonite in terms of climate change. In particular, dry climate conditions may lead to lower
771 karst recharge and enhanced prior aragonite precipitation, which results in lower speleothem U
772 but higher Mg concentrations if prior aragonite precipitation is indeed the dominating process
773 (for example, Jamieson et al., in revision). If $D_{Sr(Ar)}$ is above one, then dry climate conditions
774 may also lead to lower speleothem Sr concentrations, although this remains to be confirmed by
775 additional research.

776

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793

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1013 **Figure captions**

1014

1015 Figure 1. Sampling locations of the speleothems used in this study. 1) Grotte Prison de Chien,
1016 north-west Middle Atlas, Morocco. 2) Grotte de Piste, north-west Middle Atlas, Morocco. 3)
1017 Unnamed cave 8 km south of Treveles, Alpujaras, southern Spain. 4) Grotte de Clamouse,
1018 southern France. 5) Hüttenbläuserschachthöhle, central Germany. 6) Krem Mawmluh Cave,
1019 Meghalaya plateau, north-east India. 7) Krem Umsynrang Cave, Meghalaya plateau, north-east
1020 India.

1021

1022 Figure 2. Slabs showing Cc-Ar transitions with the corresponding trace element transects and
1023 the positions of ²³⁰Th/U-sampling. Blue dashed lines indicate boundaries between calcite and
1024 aragonite. Yellow and black arrows indicate speleothem growth direction. a-c) Stalagmite
1025 KRUM11. d-e) Stalagmite MAW4. f-g) Flowstone MO. h-i) Stalagmite HBSH1 part 4.

1026

1027 Figure 3. Thin section petrography of calcite and aragonite fabrics. a) Stalagmite MAW4,
1028 transition from undulose columnar calcite to calcite fans with sweeping extinction to acicular
1029 aragonite. The two calcite fabrics are separated by detrital material (cross-polarised light). b)
1030 Stalagmite MAW4, columnar undulose calcite (cross-polarised light). c) Stalagmite MAW4,
1031 undulose columnar calcite interbedded by two detrital layers. d) Stalagmite KRUM11, calcite
1032 (cross-polarised light). e) Stalagmite KRUM11, Cc-Ar transition with acicular aragonite.
1033 (cross-polarised light). f) Same as (e), but with plain polarized light. Arrows indicate primary
1034 aragonite (Ar-p) and potentially micritized aragonite (Ar-m). g) Stalagmite HBSH1, part 4,
1035 columnar calcite crystals and acicular aragonite (cross-polarised light). h) Same as (g), but with
1036 plain polarized light. i) Flowstone MO, undulose columnar calcite crystals and acicular
1037 aragonite (cross-polarised light). j) Same as (i), but with plain polarized light.

1038

1039 Figure 4. Results of Raman spectroscopy of stalagmite MAW4. Blue dashed lines indicate the
1040 main transition from calcite to aragonite. a) Scan from MAW4 with positions of linescan and
1041 spots indicated (red); Cc1 and Cc2 (separated by yellow dashed line) are also indicated. b) 5
1042 µm resolution Raman spectroscopy map covering the aragonite, Cc1 and Cc2. The image is
1043 stretched in horizontal direction. c) 2 µm resolution Raman spectroscopy map covering Cc1
1044 with very limited aragonite. Dark red represents aragonite, green represents calcite. d) Thin
1045 section of stalagmite MAW4 with Cc-Ar transition (cross-polarised light). e) 2 µm resolution

1046 Raman spectroscopy map covering fan-like calcite and aragonite. Blue represents aragonite,
1047 pink represents calcite.

1048

1049 Figure 5. Molar trace element Mg/Ca, U/Ca, Sr/Ca and Ba/Ca ratios across the investigated Cc-
1050 Ar transitions. a) Flowstone MO, b) Stalagmite MAW4. c) Stalagmite HBSH1 part 4. Linescan
1051 (grey) and single spot (black) analyses, respectively, are indicated. For stalagmite HBSH1, only
1052 spot analyses are available. Linescan data are shown as 5-point running medians. Data marked
1053 by the red shaded bar represent the data from the calcite section that have been used for the
1054 calculations. Data marked by the brown shaded bar represents the data from the aragonite
1055 section that have been used for the calculations.

1056

1057 Figure 6. Compilation of the speleothem aragonite distribution coefficients calculated from the
1058 Cc-Ar transitions studied. Diamonds (squares) indicate values derived from stratigraphic
1059 (lateral) Cc-Ar transitions. Shaded error bars include an additional uncertainty of 50% on the
1060 trace element to Ca ratio of the dripwater. Note that the y-axis has a logarithmic scale. For
1061 reference, the black horizontal line indicates a distribution coefficient value of 1 for the
1062 elements Sr, Ba, and U.

1063

1064 Figure 7. Relation between speleothem aragonite D_{Sr} and growth rate. Linear regression for the
1065 five data points corresponding to growth rates $< 20 \mu\text{m}/\text{year}$ and associated correlation
1066 coefficient and p-value is shown.

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