

1 **Intra- and inter-annual uranium concentration variability in a Belizean stalagmite controlled by**
2 **prior aragonite precipitation: a new tool for reconstructing hydro-climate using aragonitic**
3 **speleothems**

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16

17 Abstract

18 Aragonitic speleothems are increasingly utilised as palaeoclimate archives due to their amenability
19 to high precision U-Th dating. Proxy records from fast-growing aragonitic stalagmites, precisely
20 dated to annual timescales, can allow investigation of climatic events occurring on annual or even
21 sub-annual timescales with minimal chronological uncertainty. However, the behaviour of many
22 trace elements, such as uranium, in aragonitic speleothems has not thus far been as well constrained
23 as in calcitic speleothems. Here, we use uranium concentration shifts measured across primary
24 calcite-to-aragonite mineralogical transitions in speleothems to calculate the distribution coefficient
25 of uranium in aragonitic speleothems (derived $D_U = 3.74 \pm 1.13$). Because our calculated D_U is
26 considerably above 1 increased prior aragonite precipitation due to increased karst water residence
27 time should strongly control stalagmite aragonite U/Ca values. Consequently, uranium
28 concentrations in aragonitic speleothems should act as excellent proxies for effective rainfall.

29 We test this using a high-resolution ICP-MS derived trace element dataset from a Belizean
30 stalagmite. YOK-G is an aragonitic stalagmite from Yok Balum cave in Belize with an extremely robust
31 monthly-resolved chronology built using annual $\delta^{13}\text{C}$ cycles. We interpret seasonal U/Ca variations in
32 YOK-G as reflecting changes in the amount and seasonality of prior aragonite precipitation driven by
33 variable rainfall amounts. The U/Ca record strongly suggests that modern drying has occurred in
34 Belize, and that this drying was primarily caused by a reduction in wet season rainfall. This is
35 consistent with published stable isotope data from YOK-G also very strongly suggesting modern
36 rainfall reductions, previously interpreted as the result of southward ITCZ displacement. Our results
37 strongly suggest that U/Ca values in aragonitic speleothems are excellent proxies for rainfall
38 variability. This new tool, combined with the exceptional chronological control characteristic of
39 aragonitic stalagmites and the high spatial resolution afforded by modern microanalytical
40 techniques, should facilitate the construction of new exquisitely resolved rainfall records, providing
41 rare insights into seasonality changes as well as long-term changes in local recharge conditions.

42 1.1 Introduction

43 Speleothems are invaluable continental paleoclimate archives that are amenable to precise and
44 accurate U-Th dating, and can yield high-resolution proxy records. Speleothem-based climate
45 reconstructions are particularly useful for reconstructing effective rainfall, and can provide diverse
46 information about rainfall, including moisture source and trajectory, rainfall amount, seasonality,
47 and karst residence time (Fairchild et al., 2006). Well-established stable isotope proxies retain each
48 of these variables to varying degrees in different stalagmites. Disentangling these effects in a given
49 sample is challenging, with individual proxies such as $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ potentially reflecting multiple
50 climatological and environmental factors in a single proxy record. Therefore, considering multi-proxy
51 approaches when attempting to reconstruct effective rainfall from speleothem records is critical.
52 Trace element proxies for prior carbonate precipitation and/or residence time reflect the volume of
53 water infiltrating through the karst and can help deconvolve these separate signals. In calcite
54 speleothems, the most commonly used trace element proxy for prior calcite precipitation (PCP) is
55 Mg/Ca (Fairchild and Treble, 2009), due to its abundance and strong partitioning between fluid and
56 solid phases (Fairchild et al., 2000). Other element ratios such as Sr/Ca or Ba/Ca also produce
57 complementary information about hydrology (McDonald et al., 2007). In addition, sulphate
58 concentrations in speleothems have been used as tracers of volcanic or anthropogenic inputs to the
59 karst system (Borsato et al., 2015; Frisia et al., 2005; Wynn et al., 2008; Wynn et al., 2010; Wynn et
60 al., 2014). Elements that are less water soluble or less easily incorporated into the calcite crystal
61 lattice, although utilised more rarely, are useful proxies for volcanic or anthropogenic inputs into the

62 karst system (Jamieson et al., 2015) or as chronological markers of seasonal flushing of associated
63 organic material (Borsato et al., 2007; Hartland et al., 2012). Similar mechanisms control trace
64 elements in aragonitic speleothems, although the differing crystal structure of aragonite compared
65 to that of calcite means that elements are incorporated differently between the two minerals.
66 Aragonitic speleothems are particularly useful in paleoclimatic research because their generally high
67 uranium content allows very high U-Th dating precision (Denniston et al., 2013; Kennett et al., 2012;
68 Woodhead et al., 2012). Despite this potential, the relative scarcity of published aragonitic
69 stalagmite trace element records (Finch et al., 2003; Tan et al., 2014; Wassenburg, 2013) means that
70 trace element partitioning behaviour into their structure remains poorly understood. Research
71 constraining uncertainties in elemental behaviour in aragonitic stalagmite is therefore crucial.

72 1.2 Prior Aragonite Precipitation

73 Prior calcite precipitation is a significant control on drip water element concentrations before trace
74 element incorporation in speleothems (Fairchild et al., 2001; Fairchild et al., 2000; Fairchild and
75 Treble, 2009; Treble et al., 2015). Precipitation of calcium carbonate up-flow from the speleothem
76 will either increase or decrease the concentrations of various trace elements in dripwaters (and thus
77 speleothems) depending on the value of their distribution coefficients. This mechanism controls a
78 significant proportion of variability in water-soluble alkaline earth metal concentrations due to their
79 abundance and predictable behaviour. PCP is not a primary control on other elemental variations
80 due to the dominance of other processes such as supply, transport, and/or growth/crystal structure
81 dependencies for incorporation (e.g. pH Wynn et al. (2014) or growth rate Fairchild et al. (2001)). Far
82 less is known about the effects of prior aragonite precipitation (PAP) on speleothem geochemistry.
83 However, PAP probably significantly influences speleothem geochemistry in environments where
84 aragonite precipitation is favoured, though currently very few studies have considered PAP controls
85 on speleothem geochemistry. Fairchild and Treble (2009) discussed the potential of PAP as an
86 influence on Sr/Ca, but concluded that it would have a minimal effect on strontium concentrations.
87 Wassenburg et al. (2012) highlighted the potential for PAP to increase dripwater Mg/Ca, and a lack
88 of PCP as an explanation for the decoupling of Sr, Mg and Ba within speleothem aragonite.
89 Wassenburg et al. (2013) identified PAP from monitored drip waters by observing a negative
90 correlation between Mg and Sr concentrations. These studies established PAP as a process that can
91 affect dripwater and/or speleothem trace element concentrations, but did not propose a diagnostic
92 elemental proxy for PAP. The potential of PAP to function as an important hydrologically mediated
93 control on speleothem geochemistry merits further consideration, especially considering that the
94 differing crystal structure of aragonite compared to calcite may favour the incorporation of elements

95 with larger ionic radii, thereby providing proxies for environmental changes that are not available in
96 calcite speleothems. One element incorporated in greater concentrations in aragonite because of
97 the aforementioned reasons is uranium, which is mostly incorporated as $\text{UO}_2(\text{CO}_3)_3$ (Reeder et al.,
98 2000) and readily substitutes for Ca within the aragonite crystal structure but less so in that of
99 calcite.

100 U/Ca has not previously been used extensively in speleothem studies as a proxy for
101 paleoenvironmental information, however several groups have measured U/Ca or $^{234}\text{U}/^{238}\text{U}$ activity
102 ratios in calcite speleothems and discussed the source and mechanisms of incorporation. Bourdin et
103 al. (2011) suggested that uranium in dripwaters is primarily derived from limestone dissolution at
104 their study site, with its incorporation in calcite depending on crystallographic factors such as the
105 presence of kinks or lattice defects. Other groups have suggested that uranium can be derived from
106 an external source such as Saharan dust (Frumkin and Stein, 2004), overlying sediments (Zhou et al.,
107 2005), or anthropogenic sources/disruption (Siklosy et al., 2011). In addition, PCP has been discussed
108 as a possible influence on drip water U/Ca (Johnson et al., 2006). In summary, very few studies have
109 discussed uranium in detail as a proxy and, to our knowledge, none in aragonitic speleothems.

110 1.3 Distribution Coefficients in Speleothem Aragonite and Calcite

111 One of the key limitations in quantitative speleothem trace element research is imprecise
112 knowledge of the distribution coefficients (D_{TE}) controlling the incorporation of elements in
113 speleothems. Existing studies of distribution coefficients in both calcite and aragonite are often non-
114 speleothem specific, and can include biological effects not present in stalagmites (corals), non-
115 comparable fluids (seawater, or other high ionic strength solutions), or implausible growth rates or
116 temperatures (Busenburg and Plummer, 1985; DeCarlo et al., 2015; Meece and Benninger, 1993;
117 Swart and Hubbard, 1982). As such, the applicability of these values to speleothem science is
118 extremely limited.

119 Recent studies have determined distribution coefficients for speleothem calcite based on karst
120 analogue experiments (Day and Henderson, 2013), or using in-situ measurements of dripwaters and
121 precipitates (Tremaine and Froelich, 2013). These values are more applicable to speleothem studies
122 than earlier efforts, but distribution coefficients are not absolute constants. Instead, distribution
123 coefficients depend on a variety of factors including: temperature, growth rate, competition effects
124 (i.e., solution composition), pH, biological factors, elemental form (e.g., valence state, complexation,
125 etc.), crystallography, and many others (Gabitov et al., 2008; Gabitov et al., 2014; Huang and
126 Fairchild, 2001; Meece and Benninger, 1993; Mucci and Morse, 1983). It is thus likely that cave- or

127 drip-specific distribution coefficient values exist. The concept of a distribution coefficient does have
128 value for understanding trace element partitioning in a general sense, but is not an absolute
129 constraint on trace element variability in speleothems.

130 In practice, the key piece of information for interpreting speleothem trace element data in terms of
131 PCP and/or PAP is whether the distribution coefficient is greater than or less than one, that is,
132 whether it is preferentially included or excluded from the mineral phase. Even this binary distinction
133 is within the range of estimates for some elements in aragonite within the previously published
134 literature (Figure 1); therefore defining clear ranges for these values in speleothems is critical.
135 Without better estimates of these values, it is not possible to determine whether elemental
136 concentrations would increase or decrease in response to increasing amounts of PAP.

137 Uranium is abundant in aragonitic speleothems but lacks a well-constrained distribution coefficient
138 value. Existing studies generally suggest that uranium is preferentially incorporated into aragonitic
139 stalagmites ($D_U > 1$) and excluded from calcitic stalagmites ($D_U < 1$) (Denniston et al., 2013). If the
140 values of D_U are indeed either side of one in the two mineral phases then uranium represents an
141 ideal geochemical parameter to diagnose the presence, dominance, or variability of PAP as a control
142 on stalagmite geochemistry. PAP variability is (like PCP variability) likely controlled by recharge
143 variability, and may therefore allow U/Ca to function as a palaeorainfall proxy in karst environments
144 where aragonite precipitation occurs. This study is the first to investigate the systematics of U/Ca in
145 an aragonitic speleothem as a proxy for PAP and, in conjunction with $\delta^{13}\text{C}$, to use these geochemical
146 indicators to reconstruct past rainfall variability and seasonality.

147 2.0 Yok Balum cave site description

148 Yok Balum cave in southern Belize (16° 12' 30.78" N, 89° 40' 24.42"W; 366m above sea level) is a
149 well monitored tropical cave developed in a SW-to-NE trending karst ridge composed of Campur
150 Formation limestone in the Toledo district of southern Belize. The cave is well studied, with cave
151 monitoring records (Ridley et al., 2015b) as well as stable isotope records from two stalagmites
152 already published (Kennett et al., 2012; Ridley et al., 2015a). Here, we supplement these existing
153 records, particularly the YOK-G $\delta^{13}\text{C}$ record of Ridley et al. (2015a), with complementary trace
154 element data.

155 The cave consists of a single main trunk passage approximately 540m in length with two entrances.
156 These entrances are a small eastern opening and a larger, higher opening to the southwest formed
157 by a cave roof collapse. The cave ventilates daily through these two entrances, ensuring that CO_2
158 concentrations in the cave never rise to a level where dissolution of carbonate speleothems would

159 occur. The cave is developed in a tectonically active area, and field observations suggest that it may
160 have formed tracking a local fault. The stalagmite YOK-G was collected in 2006 from an actively
161 dripping area of the cave approximately 80m from the smaller eastern entrance.

162 Southern Belize has a tropical climate, with seasonal temperatures only ranging approximately 4°C
163 about the annual mean of 22.8°C. Latitude and elevation control rainfall distribution in Belize, with
164 total annual rainfall ranging from 1300mm in the north to 4500mm in the south. Rainfall in the
165 region exhibits a strong seasonality with >80% of the annual rainfall occurring between June and
166 September in the peak of the May-January wet season. February to April receives significantly less
167 rainfall, with evaporation greatly reducing soil and karst infiltration (Kennett et al., 2012).

168 3.0 Methods

169 3.1 Sample preparation and analysis

170 For analyses approximately 250µg of speleothem material was milled at 100µm resolution using a
171 computer-controlled ESI/New Wave Micromill, equipped with a 0.8mm tungsten carbide drill bit.
172 Powders were dissolved in 1% Nitric Acid (PWR 67% Nitric Acid Ultrapure Normatom for trace
173 element analysis, diluted with Milli-Q water) and a suite of elements measured using a Thermo
174 Scientific X Series II inductively-coupled plasma mass spectrometer (ICP-MS) at Durham University.
175 The milled analyte used in this analysis is an aliquot of the larger milled volume; the remainder was
176 used for stable isotope measurements (Ridley et al., 2015a), thereby allowing direct comparison
177 with no chronological error between the proxies.

178 A set of multi-elemental Romil standards and blanks re-run throughout the sequence of samples
179 allow precise quantification and correction for machine drift. Analytical precision on individual
180 samples was <5% RSD for Ca, Mg and U, with Ca precision generally <2% RSD (3 repeat
181 measurements). Detection limits varied by run, but were generally <0.1ppb for Mg and Ca, and
182 <1ppt for U.

183 Stable isotope analyses were conducted at Durham University using a Thermo-Finnigan MAT 253
184 Isotope-Ratio Mass Spectrometer coupled with a Gasbench II, external precision of 0.05-0.1‰ as
185 detailed in Ridley et al. (2015a). Each batch of fifty sample aliquots was run alongside 14 standard
186 powders; NBS18 (carbonatite), NBS19 (limestone), LS VEC (lithium carbonate) and an internal
187 laboratory standard DCSO1. Normalisations and corrections were made to NBS19 and LS VEC.
188 Random samples were re-run to ensure reproducibility between the runs and lend confidence to the
189 results. Values reported are relative to the international VPDB standard.

190 Clear annual cycles in the monthly resolved $\delta^{13}\text{C}$ dataset, anchored to 1955 by detecting the
191 radiocarbon 'bomb spike', were used to construct the monthly-resolution stalagmite age model.
192 Eighteen high-precision U-Th dates produced at the University of New Mexico Radiogenic Isotope
193 Laboratory fall within error of the cycle counting age model confirming the independent chronology.
194 Specifics of the dating and age model construction are detailed in Ridley et al. (2015a). The
195 stalagmite was actively dripping at the time of collection; however, reliable $\delta^{13}\text{C}$ cycles are only
196 present until 1982 (approximately 8mm from the stalagmite top). The reasons for this are unclear,
197 and may reflect a cessation or slowdown in growth after 1982, possibly linked to the proximal El
198 Chichón eruption, which is approximately synchronous with this change. Therefore, post-1982
199 measurements are not considered because of lack of adequate chronological control.

200 3.2 Empirical calculation of distribution coefficients in speleothems

201 We present a method to calculate D_{ij}^a from speleothem calcite to aragonite transitions. Our
202 approach is similar to the method described by Wassenburg et al. (In Revision), who also provide
203 speleothem aragonite distribution coefficients for Mg, Sr and Ba. Wassenburg et al. (In Revision) also
204 provide and discuss in detail the uncertainty of the resulting aragonite distribution coefficient taking
205 into account , among other factors, potential changes in the chemical composition of the dripwater
206 through time.

207 The calculations of the aragonite distribution coefficients involves two-steps: Firstly, a fluid
208 concentration is calculated using the known uranium distribution coefficient for calcite together with
209 the measured uranium concentration in a calcite layer. Secondly, the calculated fluid value, together
210 with the measured uranium concentration in the aragonite layer, is then used to calculate the
211 distribution coefficient between the fluid and aragonite (Figure 2). The uranium distribution
212 coefficient for calcite used here is calculated from the temperature dependent equation of Day and
213 Henderson (2013) ($D_{ij}^c = 0.14e^{(-0.025*T)}$) and mean annual temperature within each studied cave.

214 This approach operates on the assumption that the U/Ca in the fluid have not changed significantly
215 between the precipitation of the two mineral phases. To minimise the potential effect of variable
216 fluid concentrations we have used values from as close together as are available in the stalagmite,
217 but this does not preclude the possibility of small changes in concentration because of hydrological
218 or climatological variations. This concern can be somewhat ameliorated by examining layers with
219 lateral changes in mineralogy such as those documented by Wassenburg et al. (2012). This approach
220 is more robust as the mineral phases precipitated from the same drip, with only very small changes
221 in fluid chemistry occurring laterally as the minerals precipitate. We calculate several uranium

222 distribution coefficient values in aragonite (D_{ij}^a) using this method from speleothems with both
223 lateral and vertical transitions between mineral phases (McDermott et al., 1999; Railsback et al.,
224 2011; Wassenburg, 2013; Wassenburg et al., 2012; Wassenburg et al., 2013). Any speleothems for
225 which petrographic analysis suggests diagenetic alteration (e.g. Green et al. (2015)) are omitted from
226 this analysis due to the recrystallized phase potentially precipitating from a markedly different fluid
227 composition (Perrin et al., 2014).

228 4.0 Results

229 4.1 Stable Isotope and Trace Element Results

230 From 1669-1983 AD, the YOK-G $\delta^{13}\text{C}$ record shows a long term trend towards more positive values,
231 with a shift of approximately 0.5-1‰ in the long term mean over that interval (Figure 3).

232 Superimposed on this trend are decadal-scale $\delta^{13}\text{C}$ fluctuations of between 0.5-1‰, as well as
233 cyclical intra-annual (seasonal) variability of up to 1‰. U/Ca shows a decrease in the long-term
234 mean from approximately 2×10^{-5} to 1×10^{-5} from 1669-1983 AD, with several decadal scale
235 fluctuations of similar magnitude. Like $\delta^{13}\text{C}$, U/Ca shows annual cycles, with U/Ca cycle amplitudes
236 of approximately 0.2×10^{-5} - 0.5×10^{-5} . Annual U/Ca cycles are generally anti-correlated with those of
237 $\delta^{13}\text{C}$, although not exclusively so. The mean annual values of $\delta^{13}\text{C}$ and U/Ca anti-correlate
238 throughout the record (1669-1983; $r = -0.70$, $p < 0.0001$).

239 Mg/Ca values in YOK-G show a very low magnitude long-term decrease in baseline values. Annual
240 spikes of up to 0.0007 above the 0.0001 baseline occur during the wet season, anti-correlated with
241 the annual cycles in $\delta^{13}\text{C}$.

242 4.2 Uranium Distribution Coefficients

243 The calculated values for D_{ij}^a are summarised in Figure 2 and Table 1, where calculations using both
244 vertical and lateral transitions show similar value ranges for D_{ij}^a of 1.8-4.5. Our preferred value for
245 D_{ij}^a calculated from this study is 3.74 ± 1.13 , as the mean value \pm one standard deviation of the two
246 lateral calcite-aragonite transitions used. This value should not be considered an absolute value for
247 the reasons discussed in section 1.3. However, it provides a useful approximation for modelling and
248 confirms that the value in aragonitic speleothems is greater than one. Wassenburg et al. (in review)
249 use a similar approach using additional speleothem transitions and report a similar range of
250 distribution coefficients (6.26 ± 4.54). As our calculated values also fall within this range, we can
251 confidently assert that the D_{ij}^a value in speleothem aragonite is greater than one.

252 5.0 Discussion

253 5.1 General Trends in U/Ca and $\delta^{13}\text{C}$

254 In general, $\delta^{13}\text{C}$ in aragonitic speleothems and in systems where PAP is occurring will behave very
255 similarly to the calcite equivalents. Whilst the exact value of the fractionation factor between
256 precipitated aragonite and bicarbonate in solution may vary slightly from that of calcite, progressive
257 precipitation will still act to increase the $\delta^{13}\text{C}$ of the solution (Fairchild et al., 2006; Polag et al.,
258 2010). As a result, PAP and PCP will both lead to higher $\delta^{13}\text{C}$ values in speleothems. Ridley et al.
259 (2015a) interpreted $\delta^{13}\text{C}$ values in YOK-G as a palaeorainfall proxy, and noted both a strong intra-
260 annual signal corresponding to seasonality as well as long-term variations resulting from
261 intertropical convergence zone position (ITCZ) shifts linked to anthropogenic and natural (volcanic)
262 aerosol forcing. The $\delta^{13}\text{C}$ record shows an increasing drying trend post-1850, which is expressed in
263 both the overall $\delta^{13}\text{C}$ signal and particularly in the wet season $\delta^{13}\text{C}$ values. This multi-proxy inferred
264 drying trend mirrors the observed decrease in annual rainfall in several meteorological stations near
265 Yok Balum cave (Ridley et al., 2015a).

266 5.2 Uranium Distribution Coefficients

267 Lateral transition values are the basis for our preferred value as they result from small changes in
268 dripwater concentrations due to mineral precipitation rather than potentially large shifts vertically
269 due to changes in climate or flow path, which may result in competition effects modifying the D_{U}^{α}
270 value. The range of these values may result from variations in U/Ca in the dripwaters between the
271 precipitation of the two phases (e.g. due to prior carbonate precipitation or varying dissolution)
272 producing variable errors in the calculated D_{U}^{α} values. Alternatively, they may be truly different D_{U}^{α}
273 values in each stalagmite stemming from the various other factors which influence distribution
274 coefficients (e.g. growth rates Gabitov et al. (2008) or dripwater pH Wassenburg et al. (In Revision)).
275 Similarly high values have been found experimentally (Meece and Benninger, 1993) and in
276 speleothem samples (Wassenburg et al., in review). However, because these values are all greater
277 than one they indicate that uranium is preferentially incorporated into speleothem aragonite. This is
278 consistent with the general understanding of the uranium incorporation mechanism into the crystal
279 lattice. In aragonite the most common aqueous uranium species, $\text{UO}_2(\text{CO}_3)_3^{4-}$, is incorporated into
280 the crystal structure intact, whilst to be incorporated into calcite the co-ordination of this unit has to
281 change (Reeder et al., 2000). This suggests that the distribution coefficients established here are
282 consistent with both the known crystallographic incorporation mechanism, and the generally higher
283 observed concentrations of uranium in aragonitic speleothems. We can conclude that PAP would
284 result in lowered U/Ca values in dripwater, and thus lower stalagmite concentrations, during drier
285 conditions.

286 5.3 Intra-annual variations and inferred controls on U/Ca

287 Mean monthly U/Ca values demonstrate the presence of a clear annual cyclicity in YOK-G, which is
288 overall anti-correlated with annual $\delta^{13}\text{C}$ cycles (Figure 4). A mechanism must therefore operate at
289 the YOK-G site that increases dripwater U/Ca values during wetter months of the year. Prior calcite
290 precipitation would have the opposite effect, lowering U/Ca values during wetter months and
291 increasing U/Ca during drier months as uranium is excluded from calcite and dripwater
292 concentrations increase with intensified PCP. Increased residence times of infiltrating water in drier
293 months would also tend to increase uranium concentrations as percolating waters have more time
294 to leach trace elements from the karst rock. The D_U value of 3.74 ± 1.13 calculated above,
295 definitively greater than one (Figure 1), confirms that PAP would result in increased U/Ca values
296 during the wet season. As both PCP and/or increased residence times would have the opposite
297 effect to the observed variability, we infer that PAP is the dominant control on seasonal variations in
298 U/Ca concentrations throughout YOK-G (Figure 5).

299 The mean annual values of $\delta^{13}\text{C}$ and U/Ca anti-correlate throughout the record (1669-1983; $r = -0.70$,
300 $p < 0.0001$), consistent with PAP as a dominant control on YOK-G U/Ca on inter-annual timescales.
301 The strength of the anti-correlation between $\delta^{13}\text{C}$ and U/Ca varies interannually with some years
302 displaying a very strong anti-correlation but others exhibiting a weaker anti-correlation or
303 occasionally even a positive correlation (Figure 6). Overall, U and $\delta^{13}\text{C}$ are strongly anti-correlated in
304 121 years ($r < -0.5$), weakly anti-correlated in 76 years ($-0.5 < r < 0$), weakly positively correlated in
305 71 years ($0 < r < 0.5$), and strongly positively correlated in 45 years ($r < 1$). Positively correlated years
306 are characterised by greatly reduced rainfall seasonality inferred by using both U/Ca and $\delta^{13}\text{C}$ (Figure
307 7). This suggests that in years where $\delta^{13}\text{C}$ and U/Ca are positively correlated, PAP is no longer the
308 dominant control on the intra-annual U/Ca variability of the speleothem. Monthly and mean annual
309 $\delta^{13}\text{C}$ and U/Ca values suggest that these years are drier than the overall mean, as well as exhibiting
310 reduced seasonality. This reflects decreased rainfall, largely in the wet season, where $\delta^{13}\text{C}$ and U/Ca
311 are markedly less negative and lower respectively. Therefore, we can infer that in years with
312 reduced wet season rainfall, the dominance of seasonal PAP control on YOK-G geochemistry breaks
313 down because of increased residence time (and thus bedrock dissolution) becoming a more
314 dominant control or simply because of reduced seasonal rainfall contrasts. During drier years
315 increased PAP is still occurring, resulting in lower U/Ca values in those years, it simply does not
316 display the strong seasonal pattern observed in wetter/more seasonal years.

317 The variability of this seasonal (anti)-correlation varies through time in the stalagmite record (Figure
318 8), and is linked to the inferred amount of summer rainfall. Prior to ~ 1850 , strongly seasonal, wetter,

319 anti-correlated years dominate the record, suggesting that in the pre-industrial period most years in
320 Belize were characterised by strongly seasonal rainfall controlled by the earlier arrival of ITCZ
321 rainfall. Following the mid-1800s, the frequency of years when $\delta^{13}\text{C}$ and U/Ca are positively
322 correlated increases, reflecting reduced wet season rainfall, consistent with a more southerly ITCZ
323 (Ridley et al., 2015a).

324 5.4 Comparison with meteorological records

325 Comparison with Punta Gorda rainfall station records (1906-1983) from approximately 30km to the
326 southeast further supports the link between the annual $\delta^{13}\text{C}$ versus U/Ca correlation with
327 seasonality. Maximum monthly rainfall and the difference between maximum and minimum
328 monthly rainfall (both measures of rainfall seasonality, because minimum monthly rainfall is
329 reasonably consistent through the record) both anti-correlate with the U/Ca vs $\delta^{13}\text{C}$ annual
330 correlation value ($r = -0.26$, $p = 0.03$ and $r = -0.27$, $p = 0.02$ respectively). In other words, years with
331 greater wet season rainfall and increased seasonality resulted in a stronger negative correlation
332 between U/Ca and $\delta^{13}\text{C}$, and years with less wet season rainfall and reduced seasonality exhibit a
333 positive correlation because seasonal PAP shifts are muted and consequently is no longer a
334 dominant control on seasonal U/Ca variability. We suggest that this diminished seasonality is enough
335 that residence time and bedrock interaction effects (which positively correlate with $\delta^{13}\text{C}$) overwhelm
336 the lower amplitude seasonal U/Ca variability signal. PAP is still occurring, and indeed is likely
337 intensified in these drier years, however it exhibits reduced variability on intra-annual timescales
338 due to the reduced seasonality. Consequently, dry years have a lower mean U/Ca value due to
339 increased PAP, but positively correlate intra-annually with $\delta^{13}\text{C}$ due to reduced variability in PAP
340 (Figure 9).

341 5.5 Comparison of proxies with long-term climate records

342 In the Industrial Period (post-1850), $\delta^{13}\text{C}$ and U/Ca both indicate a trend of overall drying and
343 reduced seasonality. As outlined by Ridley et al. (2015a) these variables (annual means, peak wet
344 values, peak dry values and seasonal differences of both proxies) all correlate with increasing
345 Northern Hemisphere Temperature (NHT) (see Table 2). Indeed U/Ca displays a stronger and more
346 significant relationship with NHT over this period perhaps suggesting that this proxy is even more
347 sensitive to rainfall shifts than $\delta^{13}\text{C}$.

348 This shift in both proxies towards drier and less seasonally variable conditions post-1850 supports
349 the interpretation of Ridley et al. (2015a) that the northern maximum extent of the ITCZ has shifted
350 southwards in response to increased anthropogenic sulphate aerosol emissions in the Northern

351 Hemisphere and changing hemispheric temperature contrasts, consequently resulting in drier wet
352 seasons in Belize and reduced hydrological seasonality.

353 For the pre-industrial period the relationship with NHT is less clear, with only dry season U/Ca
354 showing a weak ($r = -0.16$, $p = 0.003$) anti-correlation to NHT. This suggests that NHT had an
355 influence on dry season moisture balance, possibly in the form of increased dry season
356 evapotranspiration, but did not strongly influence wet season rainfall.

357 In summary, on inter-annual timescales U/Ca in YOK-G is a proxy for overall dryness in Belize, whilst
358 the annual correlation or anti-correlation of U/Ca and $\delta^{13}\text{C}$ reflects changes in intra-annual rainfall
359 seasonality.

360 5.6 Mg/Ca variability in YOK-G

361 Mg/Ca is a more commonly used proxy for prior carbonate precipitation in speleothems, due to its
362 strong partitioning behaviour and abundance in karst environments. We therefore also examine the
363 behaviour of Mg/Ca in YOK-G over the same period of the $\delta^{13}\text{C}$ and U/Ca datasets. Having
364 established that PAP is a significant control on the geochemistry of YOK-G, this is a unique
365 opportunity to improve our understanding of magnesium behaviour in aragonitic stalagmites.

366 Prior carbonate precipitation does not appear to control intra-annual Mg/Ca variability in this
367 speleothem. Distribution coefficients for magnesium quoted in the literature are generally below
368 one in both calcite (e.g., $D_{\text{Mg}}^{\text{c}} = 0.012\text{-}0.029$ (Day and Henderson, 2013), $D_{\text{Mg}}^{\text{c}} = 0.015\text{-}0.020$ (Fairchild
369 et al., 2010)) and aragonite (e.g., $D_{\text{Mg}}^{\text{a}} = 0.000097 \pm 0.00009$ (Wassenburg et al., In Revision) $D_{\text{Mg}}^{\text{a}} =$
370 $0.00002 - 0.00008$ (Gabitov et al., 2008), $D_{\text{Mg}}^{\text{a}} = 0.00053 - 0.0149$ (Gaetani and Cohen, 2006)),
371 therefore drier intervals should lead to increased stalagmite Mg concentrations, and a positive
372 seasonal correlation with $\delta^{13}\text{C}$. However, YOK-G Mg/Ca generally peaks in the wet season, anti-
373 correlating with $\delta^{13}\text{C}$, opposite to the predicted relationship if either PCP or PAP were the dominant
374 controls on Mg/Ca in this stalagmite (Figure 10). We propose three possible mechanisms for this
375 observation:

376 1) Elevated wet season Mg/Ca values could result from influx of magnesium rich material from the
377 soil and epikarst during periods of increased rainfall. One candidate for this material is wood ash
378 produced by biomass burning from slash and burn agriculture as practiced in the region. Magnesium
379 is a significant component of wood ash (Etiégni and Campbell, 1991), and could potentially be
380 washed in as either magnesium bearing minerals found in wood ash or as leached ions in dripwaters.

381 2) Times of higher rainfall and increased water volume in the karst may activate flowpaths sampling
382 from areas of less chemically mature dolomitised limestone material where increased amounts of
383 magnesium are dissolved from the host rock. This overflow pathway, only active during periods of
384 increased rainfall, potentially passes through rocks with elevated magnesium content and/or less
385 weathered surfaces. This explanation, whilst plausible, is extremely difficult to test without extensive
386 additional site hydrology characterisation and country rock sampling within the karst.

387 3) Because the aragonite crystal lattice strongly excludes magnesium ($D_{Mg}^a = 0.00002 - 0.00008$
388 (Gabitov et al., 2008)) organic colloidal transport, clay mineral incorporation or the presence of fluid
389 inclusions may overprint any hydrological controls on the Mg signal (Wassenburg, 2013; Wassenburg
390 et al., 2012; Yang et al., 2015). This is consistent with the timing of the increased Mg/Ca values, as
391 wet season rainfall would result in both increased flushing of material and potentially increased
392 growth rates. The nature of the long-term Mg dataset, with large amplitude, but short-lived, spikes
393 in Mg concentration superimposed on a relatively low concentration baseline supports sporadic
394 inputs of colloidally associated Mg associated with flush events.

395 Regardless of the specific mechanism, Mg/Ca is clearly not an effective hydrological proxy in this
396 stalagmite. This further reinforces the concept that the interpretation of proxy records in stalagmites
397 as rainfall variability often requires more information than a single proxy record. Multi-proxy
398 approaches using trace elements in conjunction with stable isotopes (this study), other trace
399 element proxies (Wassenburg et al., 2012) , or dripwater monitoring (Rutledge et al., 2014), are vital
400 to support any palaeoclimatic interpretation.

401 6.0 Conclusions

402 We calculate a distribution coefficient of uranium in aragonitic speleothems of 3.74 ± 1.13 , which is
403 in agreement within error with the value derived by Wassenburg et al. (In review). We infer that
404 prior aragonite precipitation results in lower U/Ca in speleothems. Aragonitic speleothems contain
405 relatively high concentrations of uranium and thus have great potential to provide exceptionally
406 precise U-Th ages. In addition, they grow in environments where varying aragonite precipitation
407 along the flow pathway can exert a strong control on dripwater uranium content with little
408 additional noise in the signal from varying external inputs. We therefore suggest that in aragonitic
409 speleothems uranium concentrations are a powerful proxy for rainfall variability.

410 The unusually high temporal resolution of the YOK-G trace element record enables an examination
411 of seasonal geochemical variations in aragonitic stalagmites and the development of a new proxy for
412 rainfall. U/Ca hydrological variations occur on both intra- and inter-annual timescales, and are

413 therefore useful for assessing seasonal changes in rainfall patterns. We demonstrate that U/Ca
414 correlates with other rainfall proxies such as $\delta^{13}\text{C}$, can be linked to instrumental rainfall records,
415 correlates with other climatic variables (e.g., NHT), and reflects previously inferred trends in Belizean
416 paleo-rainfall. Mg/Ca in YOK-G does not appear to be a viable paleo-rainfall proxy, emphasising the
417 importance of considering multiple proxies.

418 The development of an additional hydrological proxy in aragonitic speleothems, which is easily
419 measured at extremely high spatial resolution and appears extremely sensitive to rainfall amount
420 and seasonality, is an important addition to the set of tools available with which to reconstruct
421 climate. Aragonitic speleothems, with their precise age controls, are ideal for this purpose as they
422 minimise age uncertainty. This study presents a valuable new method for estimating palaeo-rainfall
423 in low-latitude regions where few high quality rainfall proxy archives are available.

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607 Figure Captions and Tables

608 Figure 1: A selection of published and newly calculated distribution coefficients for uranium in
609 aragonite. From left to right: published values for aragonite corals in seawater (orange) and
610 inorganic laboratory precipitation experiments (blue), calculated values for vertical transitions in
611 speleothems (brown) and lateral transitions in speleothems (green) calculated as described in
612 Section 4.2 (Amiel et al., 1973; DeCarlo et al., 2015; Flor and Moore, 1977; Friedman, 1968; Gabitov
613 et al., 2008; Gvirtzman et al., 1973; McDermott et al., 1999; Meece and Benninger, 1993; Railsback
614 et al., 2011; Sackett and Potratz, 1963; Schroeder et al., 1970; Swart and Hubbard, 1982; Thompson
615 and Livingston, 1970; Veeh and Turekian, 1968; Wassenburg, 2013; Wassenburg et al., 2012).
616 Published coral and experimental values are shown with the range of values reported, calculated
617 values (this study) are shown with \pm one standard deviation of the mean of the calculated values
618 (black). The mean value of 3.74 ± 1.13 for lateral transitions (bold circle) is our preferred value (see
619 section 4.2).

620 Figure 2: Examples of vertical and lateral calcite-aragonite transitions from Wassenburg (2013) (left).
621 Distribution coefficient calculation method used in this paper (right).

622 Figure 3: A: Time series plot of long-term trends in $\delta^{13}\text{C}$ (blue), U/Ca (red), Mg/Ca (green) and $\delta^{18}\text{O}$
623 (black). B: Expanded time series (1790-1810) showing annual cyclicity in proxy values.

624 Figure 4: Mean monthly variations of U/Ca (red) and $\delta^{13}\text{C}$ (blue) in stalagmite YOK-G (means over
625 1669-1983). Mean monthly rainfall at the Punta Gorda meteorological station from 1966-1985 (grey
626 bars).

627 Figure 5: Influence of rainfall on $\delta^{13}\text{C}$ and factors influencing U/Ca ratios in speleothems.

628 Figure 6: Comparison of mean monthly fluctuations in U/Ca and $\delta^{13}\text{C}$ in years with varying levels of
629 correlation between the two variables. The dataset is divided into six separate groups based on the
630 correlation between U/Ca and $\delta^{13}\text{C}$, then the mean values for each calendar month plotted above.
631 January and December months are labelled, with months joined sequentially.

632 Figure 7: Comparison of selected decades where $\delta^{13}\text{C}$ and U/Ca are A) seasonally anti-correlated
633 (1790-1800) and B) seasonally correlated (1950-1960). Dashed lines show decadal mean values, with
634 range bars representing \pm one standard deviation. Decadal means suggest that, based on both
635 proxies, the seasonally correlated decades are drier overall, with smaller amplitude seasonal
636 variations.

637 Figure 8: A) Mean annual $\delta^{13}\text{C}$ vs. seasonal correlation between U/Ca and $\delta^{13}\text{C}$ and B) U/Ca vs.
 638 seasonal correlation between U/Ca and $\delta^{13}\text{C}$. C) U/Ca vs. $\delta^{13}\text{C}$ seasonal correlations as an annual
 639 time series with 15-year running average. Correlation values shift from negatively correlated
 640 towards more positively correlated in recent years.

641 Figure 9: Competing controls on U/Ca during wet and dry years. During wet years (A, B) PAP is highly
 642 variable seasonally (A), dominating the U/Ca intra-annual variability and anti-correlating with $\delta^{13}\text{C}$
 643 (B). During dry years (C, D) PAP is less variable seasonally and the signal is subsumed by bedrock
 644 interaction (C), resulting in a seasonal correlation with $\delta^{13}\text{C}$ (D).

645 Figure 10: Mean monthly variations of Mg/Ca (green) and $\delta^{13}\text{C}$ (blue) in stalagmite YOK-G (means
 646 over 1669-1983). Mean monthly rainfall at the Punta Gorda meteorological station from 1966-1985
 647 (grey bars).

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Source	Type	n	D_{U}^{α}	D_{U}^{α}	D_{U}^{α}
			Min	Max	Mean
Sackett and Potratz (1963)	Aragonitic Corals in Seawater	2	0.62	0.81	0.72
Veeh and Turekian (1968)	Aragonitic Corals in Seawater	8	0.51	0.95	0.72
Friedman (1968)	Aragonitic Corals in Seawater	2	0.76	0.83	0.80
Schroeder et al. (1970)	Aragonitic Corals in Seawater	6	0.64	1.42	1.02
Thompson and Livingston (1970)	Aragonitic Corals in Seawater	4	0.97	1.46	1.30
Gvirtzman et al. (1973)	Aragonitic Corals in Seawater	3	0.61	0.67	0.64
Amiel et al. (1973)	Aragonitic Corals in Seawater	3	1.01	1.01	1.01
Flor and Moore (1977)	Aragonitic Corals in Seawater	4	0.91	1.3	1.05
Swart and Hubbard (1982)	Aragonitic Corals in Seawater	9	0.53	0.87	0.65
DeCarlo et al. (2015)	Abiogenic Seawater Lab Experiment	27	0.15	0.38	0.31
			4		
Gabitov et al. (2008)	U ⁶⁺ laboratory experiment, inorganic precipitation with ammonium	8	0.04	0.15	0.12
			8	0	

	carbonate				
Meece and Benninger (1993)	Seawater, high pCO ₂ to saturate with CaCO ₃	11	1.77	9.85	4.11
McDermott et al. (1999)	Vertical Transition				3.52
Railsback et al. (2011)	Vertical Transition				1.95
Wassenburg et al. (2012)	Vertical Transition				1.85
Wassenburg et al. (2012)	Vertical Transition				2.62
Wassenburg et al. (2012)	Vertical Transition				3.09
Mean Value (Vertical Transition)					2.60 ± 0.72
Wassenburg (2013)	Lateral Change				4.55
Wassenburg (2013)	Lateral Change				2.94
Mean Value (Lateral Transition)					3.74 ± 1.13

651 Table 1: Values of D_{U}^{C} used in Figure 1.

652

	r value	p value
Peak Wet $\delta^{13}\text{C}$	0.42	4.3×10^{-7}
Peak Dry $\delta^{13}\text{C}$	0.40	1.4×10^{-6}
Mean Annual $\delta^{13}\text{C}$	0.46	1.8×10^{-8}
Seasonal Difference in $\delta^{13}\text{C}$	-0.15	0.08
Peak Wet U/Ca	-0.59	2.5×10^{-14}
Peak Dry U/Ca	-0.65	1.3×10^{-17}
Mean Annual U/Ca	-0.68	8.1×10^{-20}
Seasonal Difference in U/Ca	-0.19	0.030
$\delta^{13}\text{C}$ vs U/Ca Correlation	0.34	4.52×10^{-5}

653 Table 2: Industrial period (1850-1983) correlations and significance of hydrological proxies with the
654 Northern Hemisphere Temperature reconstruction of Esper et al. (2002).

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