

# Northumbria Research Link

Citation: Jamieson, Robert, Baldini, James U.L., Brett, Marianne J., Tylor, Jessica, Ridley, Harriet E., Ottley, Chris J., Prufer, Keith M., Wassenburg, Jasper A., Scholz, Denis and Breitenbach, Sebastian (2016) Intra- and inter-annual uranium concentration variability in a Belizean stalagmite controlled by prior aragonite precipitation: A new tool for reconstructing hydro-climate using aragonitic speleothems. *Geochimica et Cosmochimica Acta*, 190. pp. 332-346. ISSN 0016-7037

Published by: UNSPECIFIED

URL:

This version was downloaded from Northumbria Research Link: <http://northumbria-test.eprints-hosting.org/id/eprint/53419/>

Northumbria University has developed Northumbria Research Link (NRL) to enable users to access the University's research output. Copyright © and moral rights for items on NRL are retained by the individual author(s) and/or other copyright owners. Single copies of full items can be reproduced, displayed or performed, and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided the authors, title and full bibliographic details are given, as well as a hyperlink and/or URL to the original metadata page. The content must not be changed in any way. Full items must not be sold commercially in any format or medium without formal permission of the copyright holder. The full policy is available online: <http://nrl.northumbria.ac.uk/policies.html>

This document may differ from the final, published version of the research and has been made available online in accordance with publisher policies. To read and/or cite from the published version of the research, please visit the publisher's website (a subscription may be required.)



**Northumbria  
University**  
NEWCASTLE



University**Library**

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**

4 Robert A. Jamieson <sup>a,\*</sup>, James U.L. Baldini <sup>a</sup>, Marianne J. Brett <sup>a,b</sup>, Jessica Taylor <sup>a</sup>, Harriet E. Ridley <sup>a</sup>,  
5 Chris J. Ottley <sup>a</sup>, Keith M. Prufer <sup>c</sup>, Jasper A. Wassenburg <sup>d</sup>, Denis Scholz <sup>d</sup>, Sebastian F. M.  
6 Breitenbach <sup>e</sup>

7 <sup>a</sup> Department of Earth Sciences, Durham University, United Kingdom

8 <sup>b</sup> Royal Holloway University, London, United Kingdom

9 <sup>c</sup> Department of Anthropology, University of New Mexico, United States of America

10 <sup>d</sup> Institute for Geosciences, Johannes Gutenberg University, Mainz, Germany

11 <sup>e</sup> Department of Earth Sciences, University of Cambridge, United Kingdom

12

13 \* Corresponding author at: Department of Earth Sciences, Durham University, United Kingdom. E-  
14 mail address: [r.a.jamieson@durham.ac.uk](mailto:r.a.jamieson@durham.ac.uk)

15 Keywords: speleothem, trace elements, prior aragonite precipitation, uranium, seasonality, Belize

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  $\text{CO}_2$   
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  $2 \times 10^{-5}$  to  $1 \times 10^{-5}$  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  $0.2 \times 10^{-5}$ - $0.5 \times 10^{-5}$ . 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  $3.74 \pm 1.13$ , 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 ( $6.26 \pm 4.54$ ). 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  $D_{\text{U}}^{\text{a}}$   
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  $D_{\text{U}}^{\text{a}}$  values. Alternatively, they may be truly different  $D_{\text{U}}^{\text{a}}$   
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  $3.74 \pm 1.13$  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 ( $r > 0.5$ ). 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  $\sim 1850$ , 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  $3.74 \pm 1.13$ , 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.

#### 424 Acknowledgements

425 The authors thank Silvia Frisia and Ian Fairchild for productive discussion at the 2015 Summer School  
426 on Speleothem Science. Instrumental rainfall records are courtesy of Hydromet Belize.

427 YOK-G stalagmite was sampled with permission from the Belize Institute of Archaeology.

428 This work was funded by the ERC (240167) to JULB, NSF (HSD 0827305) and Alphawood Foundation  
429 to KP, and DFG (WA3532/1-1) to JAW.

430

#### 431 References

- 432 Amiel, A.J., Miller, D.S., Friedman, G.M., 1973. Incorporation of uranium in modern corals.  
433 *Sedimentology* 20, 523-528.
- 434 Borsato, A., Frisia, S., Fairchild, I.J., Somogyi, A., Susini, J., 2007. Trace element distribution in annual  
435 stalagmite laminae mapped by micrometer-resolution X-ray fluorescence: implications for  
436 incorporation of environmentally significant species. *Geochimica et Cosmochimica Acta* 71, 1494-  
437 1512.
- 438 Borsato, A., Frisia, S., Wynn, P.M., Fairchild, I.J., Miorandi, R., 2015. Sulphate concentration in cave  
439 dripwater and speleothems: long-term trends and overview of its significance as proxy for  
440 environmental processes and climate changes. *Quaternary Science Reviews* 127, 48-60.
- 441 Bourdin, C., Douville, E., Genty, D., 2011. Alkaline-earth metal and rare-earth element incorporation  
442 control by ionic radius and growth rate on a stalagmite from the Chauvet Cave, Southeastern France.  
443 *Chemical Geology* 290, 1-11.
- 444 Busenburg, E., Plummer, L.N., 1985. Kinetic and thermodynamic factors controlling the distribution  
445 of  $\text{SO}_4^{2-}$  and  $\text{Na}^{+}$  in calcites and selected aragonites. *Geochimica et Cosmochimica Acta* 49, 713-  
446 725.
- 447 Day, C.C., Henderson, G.M., 2013. Controls on trace-element partitioning in cave-analogue calcite.  
448 *Geochimica et Cosmochimica Acta* 120, 612-627.



449 DeCarlo, T.M., Gaetani, G.A., Holcomb, M., Cohen, A.L., 2015. Experimental determination of factors  
450 controlling U/Ca of aragonite precipitated from seawater: Implications for interpreting coral  
451 skeleton. *Geochimica et Cosmochimica Acta* 162, 151-165.

452 Denniston, R.F., Wyrwoll, K.-H., Polyak, V.J., Brown, J.R., Asmerom, Y., Wanamaker Jr, A.D., LaPointe,  
453 Z., Ellerbroek, R., Barthelmes, M., Cleary, D., Cugley, J., Woods, D., Humphreys, W.F., 2013. A  
454 Stalagmite record of Holocene Indonesian–Australian summer monsoon variability from the  
455 Australian tropics. *Quaternary Science Reviews* 78, 155-168.

456 Esper, J., Cook, E.R., Schweingruber, F.H., 2002. Low-Frequency Signals in Long Tree-Ring  
457 Chronologies for Reconstructing Past Temperature Variability. *Science* 295, 2250-2253.

458 Etiégni, L., Campbell, A.G., 1991. Physical and chemical characteristics of wood ash. *Bioresource*  
459 *Technology* 37, 173-178.

460 Fairchild, I.J., Baker, A., Borsato, A., Frisia, S., Hinton, R.W., McDermott, F., Tooth, A.F., 2001. Annual  
461 to sub-annual resolution of multiple trace-element trends in speleothems. *Journal of the Geological*  
462 *Society* 158, 831-841.

463 Fairchild, I.J., Borsato, A., Tooth, A.F., Frisia, S., Hawkesworth, C.J., Huang, Y., McDermott, F., Spiro,  
464 B., 2000. Controls on trace element (Sr–Mg) compositions of carbonate cave waters: implications for  
465 speleothem climatic records. *Chemical Geology* 166, 255-269.

466 Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spötl, C., Matthey, D., McDermott, F., E.I.M.F., 2006.  
467 Modification and preservation of environmental signals in speleothems. *Earth-Science Reviews* 75,  
468 105-153.

469 Fairchild, I.J., Spötl, C., Frisia, S., Borsato, A., Susini, J., Wynn, P.M., Cauzid, J., 2010. Petrology and  
470 geochemistry of annually laminated stalagmites from an Alpine cave (Obir, Austria): seasonal cave  
471 physiology. *Geological Society, London, Special Publications* 336, 295-321.

472 Fairchild, I.J., Treble, P.C., 2009. Trace elements in speleothems as recorders of environmental  
473 change. *Quaternary Science Reviews* 28, 449-468.

474 Finch, A.A., Shaw, P.A., Holmgren, K., Lee-Thorp, J., 2003. Corroborated rainfall records from  
475 aragonitic stalagmites. *Earth and Planetary Science Letters* 215, 265-273.

476 Flor, T.H., Moore, W.S., 1977. Radium/calcium and uranium/calcium determinations for western  
477 Atlantic reef corals, *Proc 3rd Int Coral Reef Symp*, pp. 555-561.

478 Friedman, G.M., 1968. Geology and geochemistry of reefs, carbonate sediments, and waters, Gulf of  
479 Aqaba (Elat), Red Sea. *Journal of Sedimentary Research* 38, 895-919.

480 Frisia, S., Borsato, A., Fairchild, I.J., Susini, J., 2005. Variations in atmospheric sulphate recorded in  
481 stalagmites by synchrotron micro-XRF and XANES analyses. *Earth and Planetary Science Letters* 235,  
482 729-740.

483 Frumkin, A., Stein, M., 2004. The Sahara–East Mediterranean dust and climate connection revealed  
484 by strontium and uranium isotopes in a Jerusalem speleothem. *Earth and Planetary Science Letters*  
485 217, 451-464.

486 Gabitov, R.I., Gaetani, G.A., Watson, E.B., Cohen, A.L., Ehrlich, H.L., 2008. Experimental  
487 determination of growth rate effect on U<sup>6+</sup> and Mg<sup>2+</sup> partitioning between aragonite and fluid at  
488 elevated U<sup>6+</sup> concentration. *Geochimica et Cosmochimica Acta* 72, 4058-4068.

489 Gabitov, R.I., Sadekov, A., Leinweber, A., 2014. Crystal growth rate effect on Mg/Ca and Sr/Ca  
490 partitioning between calcite and fluid: An in situ approach. *Chemical Geology* 367, 70-82.

491 Gaetani, G.A., Cohen, A.L., 2006. Element partitioning during precipitation of aragonite from  
492 seawater: A framework for understanding paleoproxies. *Geochimica et Cosmochimica Acta* 70, 4617-  
493 4634.

494 Green, H., Pickering, R., Drysdale, R., Johnson, B.C., Hellstrom, J., Wallace, M., 2015. Evidence for  
495 global teleconnections in a late Pleistocene speleothem record of water balance and vegetation  
496 change at Sudwala Cave, South Africa. *Quaternary Science Reviews* 110, 114-130.

497 Gvirtzman, G., Friedman, G.M., Miller, D.S., 1973. Control and distribution of uranium in coral reefs  
498 during diagenesis. *Journal of Sedimentary Research* 43, 985-997.

499 Hartland, A., Fairchild, I.J., Lead, J.R., Borsato, A., Baker, A., Frisia, S., Baalousha, M., 2012. From soil  
500 to cave: Transport of trace metals by natural organic matter in karst dripwaters. *Chemical Geology*  
501 304-305, 68-82.

502 Huang, Y., Fairchild, I.J., 2001. Partitioning of Sr<sup>2+</sup> and Mg<sup>2+</sup> into calcite under karst-analogue  
503 experimental conditions. *Geochimica et Cosmochimica Acta* 65, 47-62.

504 Jamieson, R.A., Baldini, J.U.L., Frappier, A.B., Müller, W., 2015. Volcanic ash fall events identified  
505 using principal component analysis of a high-resolution speleothem trace element dataset. *Earth*  
506 *and Planetary Science Letters* 426, 36-45.

507 Johnson, K.R., Hu, C., Belshaw, N.S., Henderson, G.M., 2006. Seasonal trace-element and stable-  
508 isotope variations in a Chinese speleothem: The potential for high-resolution paleomonsoon  
509 reconstruction. *Earth and Planetary Science Letters* 244, 394-407.

510 Kennett, D.J., Breitenbach, S.F., Aquino, V.V., Asmerom, Y., Awe, J., Baldini, J.U., Bartlein, P.,  
511 Culleton, B.J., Ebert, C., Jazwa, C., Macri, M.J., Marwan, N., Polyak, V., Pruffer, K.M., Ridley, H.E.,  
512 Sodemann, H., Winterhalder, B., Haug, G.H., 2012. Development and disintegration of Maya political  
513 systems in response to climate change. *Science* 338, 788-791.

514 McDermott, F., Frisia, S., Huang, Y., Longinelli, A., Spiro, B., Heaton, T.H.E., Hawkesworth, C.J.,  
515 Borsato, A., Keppens, E., Fairchild, I.J., van der Borg, K., Verheyden, S., Selmo, E., 1999. Holocene  
516 climate variability in Europe: Evidence from  $\delta^{18}\text{O}$ , textural and extension-rate variations in three  
517 speleothems. *Quaternary Science Reviews* 18, 1021-1038.

518 McDonald, J., Drysdale, R., Hill, D., Chisari, R., Wong, H., 2007. The hydrochemical response of cave  
519 drip waters to sub-annual and inter-annual climate variability, Wombeyan Caves, SE Australia.  
520 *Chemical Geology* 244, 605-623.

521 Meece, D.E., Benninger, L.K., 1993. The coprecipitation of Pu and other radionuclides with CaCO<sub>3</sub>.  
522 *Geochimica et Cosmochimica Acta* 57, 1447-1458.

523 Mucci, A., Morse, J.W., 1983. The incorporation of Mg<sup>2+</sup> and Sr<sup>2+</sup> into calcite overgrowths:  
524 influences of growth rate and solution composition. *Geochimica et Cosmochimica Acta* 47, 217-233.

525 Perrin, C., Prestimonaco, L., Servelle, G., Tilhac, R., Maury, M., Cabrol, P., 2014. Aragonite-Calcite  
526 Speleothems: Identifying Original and Diagenetic Features. *Journal of Sedimentary Research* 84, 245-  
527 269.

528 Polag, D., Scholz, D., Mühlinghaus, C., Spötl, C., Schröder-Ritzrau, A., Segl, M., Mangini, A., 2010.  
529 Stable isotope fractionation in speleothems: Laboratory experiments. *Chemical Geology* 279, 31-39.

530 Railsback, L.B., Liang, F., Vidal Romaní, J.R., Grandal-d'Anglade, A., Vaquero Rodríguez, M., Santos  
531 Fidalgo, L., Fernández Mosquera, D., Cheng, H., Edwards, R.L., 2011. Petrographic and isotopic  
532 evidence for Holocene long-term climate change and shorter-term environmental shifts from a  
533 stalagmite from the Serra do Courel of northwestern Spain, and implications for climatic history  
534 across Europe and the Mediterranean. *Palaeogeography, Palaeoclimatology, Palaeoecology* 305,  
535 172-184.

536 Reeder, R.J., Nugent, M., Lambie, G.M., Tait, C.D., Morris, D.E., 2000. Uranyl Incorporation into  
537 Calcite and Aragonite: XAFS and Luminescence Studies. *Environmental Science & Technology* 34,  
538 638-644.

539 Ridley, H.E., Asmerom, Y., Baldini, J.U.L., Breitenbach, S.F.M., Aquino, V.V., Pruffer, K.M., Culleton,  
540 B.J., Polyak, V., Lechleitner, F.A., Kennett, D.J., Zhang, M.H., Marwan, N., Macpherson, C.G., Baldini,  
541 L.M., Xiao, T.Y., Peterkin, J.L., Awe, J., Haug, G.H., 2015a. Aerosol forcing of the position of the  
542 intertropical convergence zone since AD 1550. *Nature Geoscience* 8, 195-200.

543 Ridley, H.E., Baldini, J.U.L., Pruffer, K.M., Walczak, I.W., Breitenbach, S.F.M., 2015b. High-resolution  
544 monitoring of Yok Balum Cave, Belize: An investigation of seasonal ventilation regimes and the  
545 atmospheric and drip-flow response to a local earthquake. *Journal of Cave and Karst Studies* 77, 183-  
546 199.

547 Rutledge, H., Baker, A., Marjo, C.E., Andersen, M.S., Graham, P.W., Cuthbert, M.O., Rau, G.C., Roshan,  
548 H., Markowska, M., Mariethoz, G., Jex, C.N., 2014. Dripwater organic matter and trace element

549 geochemistry in a semi-arid karst environment: Implications for speleothem paleoclimatology.  
550 *Geochimica Et Cosmochimica Acta* 135, 217-230.

551 Sackett, W., Potratz, H., 1963. Dating of carbonate rocks by ionium-uranium ratios. *Subsurface*  
552 *geology of Eniwetok Atoll* 260, 1053-1065.

553 Schroeder, J.H., Miller, D.S., Friedman, G.M., 1970. Uranium distributions in recent skeletal  
554 carbonates. *Journal of Sedimentary Research* 40, 672-681.

555 Siklosy, Z., Kern, Z., Demeny, A., Pilet, S., Leel-Ossy, S., Lin, K., Shen, C.-C., Szeles, E., Breitner, D.,  
556 2011. Speleothems and pine trees as sensitive indicators of environmental pollution – A case study  
557 of the effect of uranium-ore mining in Hungary. *Applied Geochemistry* 26, 666-678.

558 Swart, P.K., Hubbard, J.A.E.B., 1982. Uranium in Scleractinian Coral Skeletons. *Coral Reefs* 1, 13-19.

559 Tan, L., Shen, C.-C., Cai, Y., Lo, L., Cheng, H., An, Z., 2014. Trace-element variations in an annually  
560 layered stalagmite as recorders of climatic changes and anthropogenic pollution in Central China.  
561 *Quaternary Research* 81, 181-188.

562 Thompson, G., Livingston, H.D., 1970. Strontium and uranium concentrations in aragonite  
563 precipitated by some modern corals. *Earth and Planetary Science Letters* 8, 439-442.

564 Treble, P.C., Fairchild, I.J., Griffiths, A., Baker, A., Meredith, K.T., Wood, A., McGuire, E., 2015.  
565 Impacts of cave air ventilation and in-cave prior calcite precipitation on Golgotha Cave dripwater  
566 chemistry, southwest Australia. *Quaternary Science Reviews* 127, 61-72.

567 Tremaine, D.M., Froelich, P.N., 2013. Speleothem trace element signatures: A hydrologic  
568 geochemical study of modern cave dripwaters and farmed calcite. *Geochimica Et Cosmochimica Acta*  
569 121, 522-545.

570 Veeh, H.H., Turekian, K.K., 1968. Cobalt, silver and uranium concentrations of reef building corals in  
571 the Pacific Ocean. *Limnology and Oceanography* 13, 304-308.

572 Wassenburg, J.A., 2013. Holocene climate evolution in NW Morocco as recorded in aragonitic  
573 speleothems: Significance of the North Atlantic Oscillation, Fakultät für Geowissenschaften. Ruhr-  
574 Universität Bochum.

575 Wassenburg, J.A., Immenhauser, A., Richter, D.K., Jochum, K.P., Fietzke, J., Deininger, M., Goos, M.,  
576 Scholz, D., Sabaoui, A., 2012. Climate and cave control on Pleistocene/Holocene calcite-to-aragonite  
577 transitions in speleothems from Morocco: Elemental and isotopic evidence. *Geochimica et*  
578 *Cosmochimica Acta* 92, 23-47.

579 Wassenburg, J.A., Immenhauser, A., Richter, D.K., Niedermayr, A., Riechelmann, S., Fietzke, J.,  
580 Scholz, D., Jochum, K.P., Fohlmeister, J., Schroder-Ritzrau, A., Sabaoui, A., Riechelmann, D.F.C.,  
581 Schneider, L., Esper, J., 2013. Moroccan speleothem and tree ring records suggest a variable positive  
582 state of the North Atlantic Oscillation during the Medieval Warm Period. *Earth and Planetary Science*  
583 *Letters* 375, 291-302.

584 Wassenburg, J.A., Scholz, D., Jochum, K.P., Cheng, H., Oster, J., Immenhauser, A., Richter, D.K.,  
585 Häger, T., Jamieson, R.A., Baldini, J.U.L., Hoffmann, D., Breitenbach, S.F.M., In Revision.  
586 Determination of aragonite trace element distribution coefficients from speleothem calcite-  
587 aragonite transitions. *Geochimica et Cosmochimica Acta*.

588 Woodhead, J., Hellstrom, J., Pickering, R., Drysdale, R., Paul, B., Bajo, P., 2012. U and Pb variability in  
589 older speleothems and strategies for their chronology. *Quaternary Geochronology*.

590 Wynn, P.M., Fairchild, I.J., Baker, A., Baldini, J.U.L., McDermott, F., 2008. Isotopic archives of  
591 sulphate in speleothems. *Geochimica et Cosmochimica Acta* 72, 2465-2477.

592 Wynn, P.M., Fairchild, I.J., Frisia, S., Spötl, C., Baker, A., Borsato, A., 2010. High-resolution sulphur  
593 isotope analysis of speleothem carbonate by secondary ionisation mass spectrometry. *Chemical*  
594 *Geology* 271, 101-107.

595 Wynn, P.M., Fairchild, I.J., Spötl, C., Hartland, A., Matthey, D., Fayard, B., Cotte, M., 2014. Synchrotron  
596 X-ray distinction of seasonal hydrological and temperature patterns in speleothem carbonate.  
597 *Environmental Chemistry* 11, 28.

598 Yang, Q., Scholz, D., Jochum, K.P., Hoffmann, D.L., Stoll, B., Weis, U., Schwager, B., Andreae, M.O.,  
599 2015. Lead isotope variability in speleothems - a promising new proxy for hydrological change? First  
600 results from a stalagmite from western Germany. *Chemical Geology*.  
601 Zhou, J., Lundstrom, C.C., Fouke, B., Panno, S., Hackley, K., Curry, B., 2005. Geochemistry of  
602 speleothem records from southern Illinois: Development of  $(^{234}\text{U})/(^{238}\text{U})$  as a proxy for  
603 paleoprecipitation. *Chemical Geology* 221, 1-20.

604

605

606

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  $3.74 \pm 1.13$  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).

648

649

650

Source	Type	n	$D_{\text{U}}^{\alpha}$	$D_{\text{U}}^{\alpha}$	$D_{\text{U}}^{\alpha}$
			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 <sup>6+</sup> laboratory experiment, inorganic precipitation with ammonium	8	0.04	0.15	0.12
			8	0	

	carbonate				
Meece and Benninger (1993)	Seawater, high pCO <sub>2</sub> to saturate with CaCO <sub>3</sub>	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  $D_{\text{U}}^{\text{C}}$  used in Figure 1.

652

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

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).

655