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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 ± 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 $\delta^{13}C$ 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 $\delta^{18}O$ or $\delta^{13}C$ 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 $UO_2(CO_3)_3$ (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 $^{234}U/^{238}U$ 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 δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}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_U^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) ($D_U^c = 0.14e^{(-0.025*T)}$) 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_U^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 δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}C, although not exclusively so. The mean annual values of δ^{13}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 δ^{13}C.

242 4.2 Uranium Distribution Coefficients

243 The calculated values for D_U^a are summarised in Figure 2 and Table 1, where calculations using both

244 vertical and lateral transitions show similar value ranges for D_U^a of 1.8-4.5. Our preferred value for

245 D_U^a calculated from this study is 3.74 ± 1.13, as the mean value ± 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_U^a value in speleothem aragonite is greater than one.

252 5.0 Discussion

253   5.1 General Trends in U/Ca and δ^{13}C

254   In general, δ^{13}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 δ^{13}C of the solution (Fairchild et al., 2006; Polag et al.,

258   2010). As a result, PAP and PCP will both lead to higher δ^{13}C values in speleothems. Ridley et al.

259   (2015a) interpreted δ^{13}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 δ^{13}C record shows an increasing drying trend post-1850, which is expressed in

263   both the overall δ^{13}C signal and particularly in the wet season δ^{13}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^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_U^a values. Alternatively, they may be truly different D_U^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, $UO_2(CO_3)_3{}^{4-}$, 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 δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}C (Figure

307   7). This suggests that in years where δ^{13}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   δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}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), δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}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_{Mg}^{c} = 0.012-0.029 (Day and Henderson, 2013), D_{Mg}^{c} = 0.015-0.020 (Fairchild

369 et al., 2010)) and aragonite (e.g., D_{Mg}^{a} = 0.000097 ± 0.00009 (Wassenburg et al., In Revision) D_{Mg}^{a} =

370 0.00002 − 0.00008 (Gabitov et al., 2008), D_{Mg}^{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 δ^{13}C. However, YOK-G Mg/Ca generally peaks in the wet season, anti-

373 correlating with δ^{13}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 (Rutlidge 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 δ^{13}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.

430

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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 ± 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 δ^{13}C (blue), U/Ca (red), Mg/Ca (green) and δ^{18}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 δ^{13}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 δ^{13}C and factors influencing U/Ca ratios in speleothems.

628   Figure 6: Comparison of mean monthly fluctuations in U/Ca and δ^{13}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 δ^{13}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 δ^{13}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 ± 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 $\delta^{13}C$ vs. seasonal correlation between U/Ca and $\delta^{13}C$ and B) U/Ca vs.

638 seasonal correlation between U/Ca and $\delta^{13}C$. C) U/Ca vs. $\delta^{13}C$ 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 $\delta^{13}C$

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 $\delta^{13}C$ (D).

645 Figure 10: Mean monthly variations of Mg/Ca (green) and $\delta^{13}C$ (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^a Min	D_U^a Max	D_U^a 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	0.154	0.38	0.31
Gabitov et al. (2008)	U^{6+} laboratory experiment, inorganic precipitation with ammonium	8	0.048	0.150	0.12

	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^a used in Figure 1.

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	r value	p value
Peak Wet $\delta^{13}C$	0.42	4.3×10^{-7}
Peak Dry $\delta^{13}C$	0.40	1.4×10^{-6}
Mean Annual $\delta^{13}C$	0.46	1.8×10^{-8}
Seasonal Difference in $\delta^{13}C$	-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
$\delta^{13}C$ 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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