Hydrological and climatological controls on radiocarbon concentrations in a tropical stalagmite

Franziska A. Lechleitner[1,2]*, James U.L. Baldini[2], Sebastian F.M. Breitenbach[3], Jens Fohlmeister[4,5], Cameron McIntyre[1,6,7], Bedartha Goswami[8,9], Robert A. Jamieson[2], Tessa S. van der Voort[1], Keith Prufer[10], Norbert Marwan[8], Brendan J. Culleton[11], Douglas J. Kennett[11], Yemane Asmerom[12], Victor Polyak[12], Timothy I. Eglinton[1]

(1) Department of Earth Sciences, ETH Zurich, Sonneggstrasse 5, 8092 Zurich, Switzerland
(2) Department of Earth Sciences, Durham University, Durham, DH1 3LE, UK
(3) Department of Earth Sciences, Cambridge University, Downing Street, Cambridge, CB2 3EQ, UK
(4) Institute of Environmental Physics, University of Heidelberg, Im Neuenheimer Feld 229, 69129 Heidelberg, Germany
(5) Institute of Earth and Environmental Science, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany
(6) Department of Physics, Laboratory of Ion Beam Physics, ETH Zurich, 8093 Zurich, Switzerland
(7) Scottish Universities Environmental Research Centre (SUERC), East Kilbride, UK
(8) Potsdam-Institute for Climate Impact Research, Transdisciplinary Concepts & Methods, Telegraphenberg A 31, 14473 Potsdam
(9) Department of Physics, Universität Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany
(10) Dept. of Anthropology, University of New Mexico, Albuquerque, NM 87106, USA
(11) Dept. of Anthropology, Institute for Energy and the Environment, The Pennsylvania State University, PA 16802, USA
(12) Dept. of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA

*Corresponding author: franziska.lechleitner@erdw.ethz.ch

Abstract

Precisely-dated stalagmites are increasingly important archives for the reconstruction of terrestrial paleoclimate at very high temporal resolution. In-depth understanding of local conditions at the cave site and of the processes driving stalagmite deposition is of paramount importance for interpreting proxy signals incorporated in stalagmite carbonate. Here we present a sub-decadally resolved dead carbon fraction (DCF) record for a stalagmite from Yok Balum Cave (southern Belize). The record is coupled to parallel stable carbon isotope

($\delta^{13}C$) and U/Ca measurements, as well as radiocarbon (^{14}C) measurements from soils overlying the cave system. Using a karst carbon cycle model we disentangle the importance of soil and karst processes on stalagmite DCF incorporation, revealing a dominant host rock dissolution control on total DCF. Covariation between DCF, $\delta^{13}C$, and U/Ca indicates that karst processes are a common driver of all three parameters, suggesting possible use of $\delta^{13}C$ and trace element ratios to independently quantify DCF variability. A statistically significant multi-decadal lag of variable length exists between DCF and reconstructed solar activity, suggesting that solar activity influenced regional precipitation in Mesoamerica over the past 1500 years, but that the relationship was non-static. Although the precise nature of the observed lag is unclear, solar-induced changes in North Atlantic oceanic and atmospheric dynamics may play a role.

1. Introduction

Stalagmites are critical archives for the reconstruction of terrestrial paleoclimate. They are dateable with exceptional precision, and provide high-resolution time series data that reflect past climatic and environmental conditions (e.g., Ridley et al., 2015a; Vaks et al., 2013). However, because local conditions that influence proxy signals can vary between cave sites, careful interpretation of stalagmite paleoclimate records is necessary. A robust interpretation of stalagmite paleoclimate proxies therefore requires detailed knowledge of surface and cave conditions, including cave monitoring studies (Breitenbach et al., 2015), and assessments of hydrological and carbon cycle processes within the karst system (Frisia et al., 2011; Noronha et al., 2015; Rudzka-Phillips et al., 2013).

Combined analyses of stable carbon isotopes and ^{14}C in stalagmite carbonate can be particularly informative because the two proxies reflect carbon inputs from different surface environment sources (atmosphere, soil and vegetation), and from the host rock (Genty et al., 2001; Hendy, 1971; Oster et al., 2010). Meteoric water encounters high CO_2 levels in the soil, epikarst, and bedrock atmosphere (Baldini, 2010; Breecker et al., 2012; Noronha et al., 2015). Due to the biological nature of the processes involved in the production of soil CO_2 (microbial decomposition of soil organic matter (SOM) and root respiration), the $\delta^{13}C$ is strongly depleted (around -26‰ for areas dominated by C_3-type plants), whereas ^{14}C is often slightly to moderately depleted compared to the contemporaneous atmosphere through the decomposition of older residual SOM (Suppl. Fig. 1) (Genty and Massault, 1999). Dissolution of the ancient (i.e., ^{14}C-free) carbonate host rock by the acidic aqueous solution results in higher $\delta^{13}C$ values but a further reduction in ^{14}C contents in the water solution (Suppl. Fig. 1) (Genty et al., 2001). Carbonate speleothems form when dripwater saturated with respect to $CaCO_3$ enters a cave, where CO_2 levels are generally much lower than in the dripwater solution (McDermott, 2004). CO_2 degassing leads to supersaturation in the solution with respect to $CaCO_3$ and subsequent carbonate precipitation. Rapid degassing, for example in well-ventilated caves or under slow drip rates, promotes kinetic isotopic fractionation effects, leading to substantially higher $\delta^{13}C$ values (Breitenbach et al., 2015; Frisia et al., 2011).

Early studies attempting to date groundwater using ^{14}C concluded that the composite origin of groundwater carbon leads to large age offsets compared to the contemporaneous atmosphere (Fontes and Garnier, 1979; Wigley, 1975), which is then transferred to stalagmite carbonate. The difference between the

91 stalagmite and the contemporaneous atmosphere ^{14}C content at the time of
92 carbonate deposition is called the 'dead carbon fraction' (DCF), and can be highly
93 variable depending on karst and soil conditions, such as the thickness of bedrock
94 overlying the cave and SOM age spectrum (Genty et al., 2001; Griffiths et al.,
95 2012; Noronha et al., 2014; Rudzka et al., 2011). Detailed understanding of
96 carbon cycle controls is therefore paramount for understanding specific karst
97 systems and for the correct interpretation of stalagmite proxy records.
98 Well-dated stalagmite ^{14}C time series have extended the IntCal calibration curve,
99 taking into account DCF as a constant offset between stalagmite ^{14}C
100 measurements and IntCal (Hoffmann et al., 2010; Southon et al., 2012). These
101 studies led to significant improvements in our ability to date natural and
102 archaeological samples in the absence of direct atmospheric ^{14}C records such as
103 tree rings (i.e., beyond 13.9 kyr BP) (Reimer et al., 2013). However, DCF
104 variations beyond the tree-ring based interval of the calibration curve are
105 difficult to account for and to distinguish from variations in atmospheric ^{14}C
106 activity, requiring a method independent from the calibration curve for the
107 detection of DCF variations in stalagmites. Although DCF may be relatively
108 constant in a cave environment over long periods of time (e.g., in stalagmite H-82
109 from Hulu Cave; Southon et al., 2012), significant short-term variations can occur
110 (Griffiths et al., 2012; Noronha et al., 2014), especially during climatic extremes
111 (e.g., the last deglaciation; Oster et al., 2010; Rudzka et al., 2011). Understanding
112 the factors driving DCF variations would not only be important for calibration
113 purposes, but might also open the door to ^{14}C dating of stalagmites using
114 conventional calibration approaches.
115

Here we present a sub-decadally resolved stalagmite ^{14}C record from the tropical Yok Balum Cave, Belize. The exceptional resolution and chronological precision of our ^{14}C record allows direct comparison to atmospheric ^{14}C activity over the past 1500 years, and provides valuable insights into how hydrology and the karst pathways respond to climatic changes at the site. We use $\delta^{13}C$ and U/Ca to infer the importance of kinetic fractionation and prior calcite precipitation (PCP) and/or prior aragonite precipitation (PAP) occurring at the site. Carbon cycle modeling and the analysis of soil samples from above the cave help disentangle the main processes influencing ^{14}C and $\delta^{13}C$ at our site and strengthen the proxy interpretation. We compare our high-resolution ^{14}C record to atmospheric ^{14}C from IntCal13 (Reimer et al., 2013) and solar activity proxies to detect similarities and infer driving mechanisms.

2. Cave setting and climate

Yok Balum Cave is located in southern Belize in the district of Toledo (16°12'30.780 N, 89°4'24.420 W, 366 m above sea level) (Fig. 1). The cave developed in a steep and remote hill in a SW-NE trending karst ridge composed of limestone of Cretaceous age of the Campur Formation (Kennett et al., 2012; Miller, 1996). The vegetation above the cave consists of dense subtropical forest, composed primarily of C3 plants. Soil thickness above Yok Balum Cave varies considerably; it is generally very thin (< 30 cm) but occasionally forms deeper (up to 60 cm) pockets in the strongly karstified limestone. The soil is a leptosol (WRB, 2006) and has poorly developed horizons. Due to the generally inaccessible location of the hilltop above Yok Balum Cave, it is unlikely that the vegetation and cave hydrology was ever disturbed by farming activities in the

141 past, although the area has been populated for millennia (Kennett et al., 2012;
142 Walsh et al., 2014).
143 Yok Balum Cave consists of a single main trunk conduit overlain by ~ 14 m of
144 karstified bedrock with one entrance at each end at different elevations,
145 resulting in constant airflow and a dynamic diurnal and seasonal ventilation
146 regime (Ridley et al., 2015a, 2015b) (Fig. 1). Detailed cave microclimate
147 monitoring, including logging of temperature, cave air CO_2, radon, and drip rates,
148 has been carried out since 2011 (Kennett et al., 2012; Ridley et al., 2015b). The
149 cave has a nearly constant temperature of 22.9 ± 0.5°C (Ridley et al., 2015b) that
150 closely reflects the outside mean annual air temperature. Belize is located at the
151 northernmost extent of the present-day boreal summer Intertropical
152 Convergence Zone (ITCZ), whose annual migration dominates local climate
153 (Ridley et al., 2015a) (Fig. 1). Precipitation is heavily biased towards the boreal
154 summer months, when 400-700 mm of monthly rainfall can be registered,
155 whereas winters are generally very dry (< 70 mm/month; Poveda et al., 2006).
156

157 **3. Materials and methods**

158 **3.1. Stalagmite YOK-I**

159 Stalagmite YOK-I was collected in 2006 and is 606.9 mm long. The upper 415
160 mm are entirely composed of aragonite and were analyzed previously for high
161 resolution stable isotopes of oxygen ($\delta^{18}O$) and $\delta^{13}C$ (Kennett et al., 2012) (Fig.
162 2). YOK-I was actively growing at the time of collection, and detailed U-Th
163 measurements indicate that the aragonitic section spans the last 2000 years
164 (Kennett et al., 2012). In this study, the top 285.5 mm of YOK-I were resampled
165 for ^{14}C, $\delta^{13}C$, and U/Ca.

3.2. Stalagmite ^{14}C measurements

Samples for high-precision graphite ^{14}C analysis were milled continuously along the growth axis, following the previous stable isotope sampling transect, using a semi-automated high-precision drill (Sherline 5400 Deluxe) at ETH Zürich. The resultant transect produced 198 high-precision ^{14}C measurements, taken at a resolution between 0.5 – 3.3 mm. Contamination from sample and equipment handling was minimized by cleaning all surfaces with methanol and drying using compressed air between each sample. Additionally, the top 0.1 mm of stalagmite surface was discarded after milling. Graphitization and ^{14}C analysis were performed at the Laboratory for Ion Beam Physics (LIP) at ETH Zürich. 8-12 mg aliquots of carbonate powder were graphitized using an automatic graphitization system fitted with a carbonate handling system (CHS-AGE, Ionplus) and ^{14}C content was measured with an accelerator mass spectrometer (MICADAS, Ionplus). Oxalic acid II (NIST SRM 4990C) was used as the normalizing standard and was measured to a precision better that 2‰. IAEA-C1 was used as blank while IAEA-C2 and a modern coral standard where used as secondary standards. A ^{14}C-free stalagmite sample was used as a processing control.

3.3. Stable isotope and trace element analysis

YOK-I was previously sampled at 100 μm resolution for $\delta^{13}C$ and $\delta^{18}O$ analysis, published in Kennett et al (2012). To avoid any depth bias during the re-sampling for the current study, stable isotope measurements were performed on aliquots from some of the same powders. This was especially important because

191 the age model based on the stable isotopes was applied to this study. Samples
192 were analyzed for $\delta^{18}O$ and $\delta^{13}C$ on a Thermo Delta V Plus mass spectrometer
193 coupled with a ThermoFinnigan GasBench II carbonate preparation device at the
194 Geological Institute, ETH Zürich, following the procedure described in
195 Breitenbach and Bernasconi (2011).
196 U/Ca ratios were measured on aliquots of the same powders used for ^{14}C and
197 $\delta^{13}C$. The powders were dissolved in 1% Nitric Acid (PWR 67% Nitric Acid
198 Ultrapure Normatom for trace element analysis, diluted with ultrapure water)
199 and measured using a Thermo Scientific X-Series II inductively-coupled plasma
200 mass spectrometer (ICP-MS) at Durham University. Multi-elemental Romil
201 standards and blanks were run throughout the sequence to allow precise
202 quantification and correction for machine drift. Analytical precision for U was
203 <5% RSD for individual measurements, and detection limits were generally <1
204 ppt. Ca measurement precision was generally <2% RSD, with all analyses well
205 above detection limits of ~<0.1ppb.
206
207 **3.4. Soil samples**
208 A ca. 60 cm deep soil profile, extending to the top of the bedrock, was collected in
209 June 2013. Because of the extreme karstification of the bedrock, soil thickness is
210 very variable above the cave, and a deeper pocket was chosen to capture the
211 maximum extent of the soil. The profile was sampled at 4-5 cm per sampled
212 depth for a total of 13 samples. All samples were stored in dark and cool
213 conditions whenever possible, and freeze-dried upon arrival to the laboratory.
214 Smaller aliquots of the soil samples were homogenized and larger plant
215 fragments particles (> 5 mm) were removed manually.

The amount of organic carbon and ^{14}C content in the soil profile was determined at LIP, ETH Zürich. To remove carbonates prior to analysis, aliquots of homogenized soil samples were transferred to silver capsules and fumigated over three days at 60°C using 37% HCl (puriss. p.a. grade, Sigma Aldrich) (Komada et al., 2008) and neutralized for 24 hrs over solid NaOH. Samples were then wrapped in a second tin capsule and pressed. The % organic carbon was determined using an elemental analyzer (Vario MICRO cube, Elementar) calibrated using atropine as the standard (Säntis, product SA990746B). ^{14}C content was determined on a second aliquot of carbonate-free soil containing 1 mg carbon using an automated graphitization system and an accelerator mass spectrometer (AGE-MICADAS, Ionplus). Oxalic acid II (NIST SRM 4990C) was the normalizing standard measured to 4‰ precision. Ancient anthracite coal was used as the blank and processing control and IAEA-C7 and -C8 were used as secondary standards. Samples where corrected for constant contamination by extraneous carbon using the anthracite processing control and secondary standards.

Water extractable organic carbon (WEOC) of the soil samples was characterized to infer the nature of SOM transported through the karst. ^{14}C content of WEOC was determined by extracting 5 g of soil with 20 ml of 0.5 wt% NaCl (in ultrapure water) in pre-combusted glass centrifuge tubes (similar to Hagedorn et al., 2004). The tubes were centrifuged three times for 15 min, and the solution was re-homogenized using a vortex mixer in between. The supernatant was decanted using combusted glass pipettes, filtered through a column containing a small amount of pre-combusted glass fibre to remove solid particles, and freeze-dried using a Christ Alpha 1-2 LD plus freeze-dryer equipped with an oil-free pump to

241 prevent contamination. The extracts were then transferred to pre-combusted 12
242 ml borosilicate Exetainer vials (Labco) using 5 ml of ultrapure water at pH 2. The
243 ^{14}C content was measured following the method described in Lang et al. (2016)
244 using wet chemical oxidation and accelerator mass spectrometry using a Gas Ion
245 Source (GIS) interface (Ionplus).
246
247 **3.5. Carbon isotope models**
248 DCF in stalagmite YOK-I (DCF_{YOK-I}) reflects various sources, mainly soil and
249 vegetation, carbonate host rock, and fractionation effects (Griffiths et al., 2012).
250 In order to separate and infer the relative importance of each contributing
251 source to DCF_{YOK-I}, a modified version of a soil-karst carbon isotope model,
252 described in Fohlmeister et al. (2011) and Griffiths et al. (2012), was applied to
253 the dataset (Suppl. Fig. 2). Briefly, the model first calculates the SOM spectrum
254 that best fits the measured stalagmite bomb spike. Three SOM pools with
255 different mean ages and turnover times were calculated, and optimized to find
256 the best fit with the measured stalagmite bomb spike via a Monte Carlo approach
257 (30,000 runs). The SOM spectrum was applied to the entire dataset to reveal the
258 ^{14}C content of the soil gas. This assumes that vegetation and soil composition
259 have remained constant over the period of stalagmite growth. Fractionation
260 effects between CO_2 and HCO_3^- when entering the groundwater DIC solution are
261 taken into account using the fractionation factor for ^{14}C $^{14}\varepsilon = 2 \times {}^{13}\varepsilon/10$
262 (Southon, 2011), resulting in approximately +1.8 fraction modern ($F^{14}C$; Reimer
263 et al., 2004) at 25°C. The remaining DCF signal is divided into host rock
264 dissolution and in-cave kinetic fractionation effects. In-cave kinetic fractionation
265 ($\Delta\delta^{13}C$), including the effects of PCP/PAP, is calculated as the difference between

stalagmite $\delta^{13}C$ and $\delta^{13}C$ estimated for the drip water solution after carbonate dissolution, when water is saturated with respect to Ca^{2+} (Griffiths et al., 2012). Dripwater $\delta^{13}C$ can be calculated iteratively, by considering the host rock $\delta^{13}C$ and the soil-water DIC $\delta^{13}C$ (in our case 0‰ and -17‰, respectively). Using the DCF value at that point in time permits calculation of the relative contribution of the host rock and DIC to the total dripwater $\delta^{13}C$ (as described in Griffiths et al, 2012). Kinetic fractionation effects on ^{14}C are readily quantifiable, because a 1‰ change in $\delta^{13}C$ equals a shift of ca. 0.2 $F^{14}C$ in ^{14}C (Southon, 2011). After removing the effects of vegetation/SOM and kinetic fractionation, the residual DCF is attributed to host rock dissolution processes.

4. Results

4.1. YOK-I ^{14}C record

The YOK-I ^{14}C record extends from ~ -54 back to 1400 years BP (i.e., 2004 to 555 C.E.), based on the U/Th age model constructed by Kennett et al. (2012) (Table 1, Fig. 2). A gap is present between 1341 and 1400 C.E., due to sampling difficulties at the transition between two slabs of stalagmite YOK-I. The mean temporal resolution is 5 years, and the maximum resolution is 0.7 years. A general decay trend is visible between 555 and 1950 C.E., with superimposed deviations in the range of ±0.2 $F^{14}C$. The modern part of the ^{14}C record (1950-present, top 9.3 mm) shows a clear imprint of bomb carbon, with maximum values of 1.14 $F^{14}C$ (at 1990 C.E.) (Fig. 2B).

Conversion of ^{14}C activity to DCF reveals significant variability over the entire interval studied (Table 1, Fig. 3A). Errors in $DCF_{YOK\text{-}I}$ are between 0.23 and 0.67%, and were calculated using error propagation following Noronha et al.

(2014). DCF_{YOK-I} values range between 9.04 and 16.7% (mean: 12.9%). The lowest DCF values occur during the period ca. 700-1100 C.E., concurrent with the most enriched $\delta^{13}C$ values (Fig. 3C).

4.2. Stable isotopes and U/Ca

The new $\delta^{13}C$ record measured on aliquots of the samples used for ^{14}C and U/Ca analyses, is of a lower resolution but shows excellent agreement with the previous high-resolution profile published in Kennett et al. (2012), confirming that no spatial error occurred during the resampling (Table 1, Fig. 3C). Several pronounced positive excursions in $\delta^{13}C$ are apparent throughout the record, e.g., at ca. 1780, 1500, 940, 620, and most notably, between 1040-1100 C.E.

184 aliquots of powders drilled for ^{14}C analysis were also used for U/Ca measurements. Values (expressed as U/Ca in ppm/ppm × 1000) vary from 0.00068 to 0.02952, with a pronounced minimum during the period 1040-1100 C.E. and highest values at the beginning of the record (550-700 C.E.) (Table 1, Fig. 3B). A large gap in U/Ca measurements exists between ~ 1250-1600 C.E., due to the transition between two stalagmite slabs (as in the ^{14}C record), as well as lack of availability of sufficient sample powder for analysis. The early part of the record (550-1180 C.E.) is generally characterized by pronounced variability in U/Ca with several rapid (sub-decadal) large excursions synchronous with shifts in $\delta^{13}C$, whereas the more recent part (1600-1950 C.E.) shows much more uniform values.

4.3. Soil samples

315 Soil organic carbon (SOC) content was measured twice with similar results
316 (Table 2, Fig. 4, series A and B). The highest values are found in the top sample
317 (~20% organic carbon), mainly composed of plant litter in the organic horizon,
318 followed by a steady decrease towards the bottom of the profile, with the lowest
319 sample (at ~60 cm depth) only containing ~2% organic carbon.
320 $F^{14}C$ values from the bulk SOC are generally quite high (0.85 to 1.1 $F^{14}C$), with
321 systematically decreasing values towards the bottom of the profile (Table 2, Fig.
322 4). The presence of bomb carbon is suggested at the top of the profile, where the
323 highest values are found between 5-15 cm below the surface, whereas in the
324 topmost sample, $F^{14}C$ is slightly lower. The WEOC $F^{14}C$ shows a similar pattern as
325 the bulk soil, with a steady decrease in $F^{14}C$ from the top to the bottom of the
326 profile (0.93 to 1.09 $F^{14}C$). There is a bifurcation in WEOC and bulk SOC $F^{14}C$
327 values with increasing depth, with the WEOC fraction decreasing less rapidly and
328 implying younger carbon than in the bulk SOC (Table 2, Fig. 4).
329
330 **4.4. Karst carbon isotope modeling**
331 The model with the best fit to the bomb spike data from YOK-I (Fig. 5A) produces
332 a SOM spectrum with the following parameters:
333 y_1 = 6 years; c_1 = 34%
334 y_2 = 37 years; c_2 = 62%
335 y_3 = 580 years; c_3 = 4%
336 where y_i denotes the mean age of the SOM pools and c_i the relative contribution
337 of the SOM pools to the respired soil gas CO_2. Applying this spectrum to the
338 entire record shows that most of the atmospheric variation is expressed in the
339 soil gas, due to the young SOM spectrum (Fig. 5B). Nevertheless, soil gas ^{14}C

activity is ~0.01 $F^{14}C$ lower than the contemporaneous atmospheric ^{14}C activity, and lagging the latter by ~15 years (Fig. 5B), due to the integrating nature of SOM. A slight enrichment occurs due to fractionation effects between CO_2 and DIC in the soil. The average contribution from vegetation and SOM to DCF_{YOK-I} is 0.015 $F^{14}C$, whereas the average enrichment from in-cave fractionation is -0.027 $F^{14}C$. The host rock contribution is therefore dominant, amounting to 0.139 $F^{14}C$ on average (Fig. 5C).

5. Discussion

5.1. Sources of carbon in stalagmite YOK-I

We disentangle the influence of soil and karst processes on stalagmite carbon isotopes by combining high-precision isotope measurements on stalagmites, bulk SOC and soil WEOC, and karst carbon isotope modeling.

The trend towards lower ^{14}C activities in the soil profile (Fig. 4) reflects general ageing of the SOM related to gradual soil buildup, and the slow downward cycling of dissolved organic matter (DOM), as described in a conceptual model by Kaiser and Kalbitz (2012). In this model, temporary storage of DOM through sorption mechanisms and microbial degradation result in an increasing trend in SOM ^{14}C ages with depth. The WEOC represents the most labile pool of SOM that is readily dissolved in water (Hagedorn et al., 2004) and reflects the same trend as the bulk soil samples, but with a less pronounced decrease in ^{14}C content. This is likely related to the preferential extraction of smaller, and thus more labile, compounds from the soil, including those from living microbial biomass (Hagedorn et al., 2004; Jones and Willett, 2006).

364 The analysis of bulk soil and WEOC samples shows that the SOM spectrum from
365 the soil above Yok Balum is quite young, and that the DOM leached from the soil
366 matrix (WEOC) echoes this trend. Backward modeling of SOM from the bomb
367 spike in YOK-I corroborates a very young SOM contribution to the karst system
368 (96% <50 years old) (Fig. 5). Although the model assumes constant vegetation
369 type and density above Yok Balum Cave over the past 1500 years, vegetation
370 shifts may have occurred because of severe droughts recorded between 700-
371 1100 C.E. (Kennett et al., 2012). Less dense vegetation and reduced soil microbial
372 activity during dry periods or under sustained deforestation would result in
373 older apparent ages of the SOM and lead to stronger smoothing of the
374 atmospheric ^{14}C signal delivered to the cave and increased stalagmite DCF
375 (Fohlmeister et al., 2011a). However, this signal would be opposite than that
376 observed in $DCF_{YOK\text{-}I}$ during the 700-1100 C.E. period, where DCF is at its
377 minimum. We attribute this to the minor influence of SOM to $DCF_{YOK\text{-}I}$ (Fig. 5C),
378 and therefore we conclude that large changes in DCF cannot originate from SOM
379 variability.
380 Young and fast cycling soils are often observed at tropical sites (Trumbore,
381 1993), where high temperature and humidity promote biological activity and
382 consequently result in high SOM turnover rates (Davidson and Janssens, 2006).
383 On the other hand, studies from (sub-)tropical karst settings have suggested that
384 a substantial contribution from pools of pre-aged SOM must influence the carbon
385 cycle at these locations: at Liang Luar Cave, on the Indonesian island of Flores,
386 the modeled SOM was dominated by a multi-centennial carbon pool (Griffiths et
387 al., 2012). A very old SOM spectrum was also observed in a recent study on soils
388 from above Heshang Cave, China (Noronha et al., 2015). It is likely that

389 differences in local conditions, soil depth, and microbial activity, and the
390 magnitude of pre-aged organic carbon reservoirs in the deep vadose zone, are
391 responsible for the contrasting characteristics of the Yok Balum Cave
392 speleothem.
393 The overall modeled contribution of SOM to the DCF_{YOK-I} is found to be small
394 (max. 2.5%), and the largest contributions to DCF_{YOK-I} appear to come from
395 carbonate dissolution in the karst and from changes in karst hydrology (Fig. 6C).
396 Measured DCF_{YOK-I} shows substantial and rapid transitions of up to 4%, with
397 lower DCF values correlating with less negative $\delta^{13}C$ and $\delta^{18}O$ values and vice-
398 versa (Fig. 3). This suggests lower/higher DCF_{YOK-I} occurred during drier/wetter
399 conditions, corroborating studies where stalagmite DCF was observed to co-vary
400 with other hydroclimate proxies (Griffiths et al., 2012; Noronha et al., 2014). The
401 hydrological imprint on DCF appears to be related to shifts between the open
402 and closed end-members of the karst system (Hendy, 1971). More open system
403 conditions prevail during periods of lower recharge, i.e. drier periods. This
404 promotes lower DCF values as the karst aqueous solution constantly re-
405 equilibrates with the soil CO_2 reservoir through air-filled voids and pores,
406 resulting in higher water (and stalagmite) ^{14}C activities. Conversely, during
407 wetter periods, the karst system is more often waterlogged and the aqueous
408 solution becomes isolated from the contemporaneous soil CO_2 reservoir (closed
409 system), resulting in much higher amounts of dead carbon from carbonate
410 dissolution being added to the solution (Fohlmeister et al., 2011b).
411 The importance of kinetic fractionation and PCP/PAP with respect to carbon
412 isotopic signatures in YOK-I are investigated using both $\delta^{13}C$ and U/Ca, coupled
413 to modeling. We consider both processes; although YOK-I is aragonitic, PCP

414 could occur in the karst overlying the cave, increasing the Mg/Ca ratio in the
415 aqueous solution, and consequently resulting in aragonite precipitation in the
416 cave (Wassenburg et al., 2012). U sourced from the overlying soil and the host
417 rock itself can be modulated by PCP/PAP (Johnson et al., 2006). Because U is
418 incorporated in the carbonate lattice, PAP should effectively scavenge U from the
419 drip water solution, resulting in lower stalagmite U contents during drier
420 periods (Jamieson et al., *in press*; Wassenburg et al., *in press*). $\delta^{13}C$ is strongly
421 altered by kinetic in-cave fractionation and PCP/PAP, as forced degassing by low
422 CO_2 partial pressure enriches the solution in ^{13}C (Frisia et al., 2011; Hendy,
423 1971). Modeling of kinetic fractionation effects between DIC and $CaCO_3$ (both in-
424 cave fractionation and PCP/PAP) in stalagmite YOK-I shows that most of the
425 variation in $\delta^{13}C$ is attributable to this process, whereas the soil and carbonate
426 host rock signatures are only responsible for the overall range in $\delta^{13}C$ (Fig. 6).
427 Despite the fact that mass-dependent fractionation with respect to ^{12}C is about
428 twice as strong for ^{14}C than ^{13}C, fractionation effects are generally not as strongly
429 expressed in ^{14}C as in $\delta^{13}C$, due to the difference in unit of the two parameters (%
430 in ^{14}C vs. ‰ in $\delta^{13}C$) (Fohlmeister et al., 2011b; Southon, 2011). Most of the
431 variability in $\delta^{13}C$ attributed to fractionation by the karst model is also present in
432 the U/Ca record (Fig. 6B). Several large and rapid positive excursions are found
433 both in $\delta^{13}C$ and U/Ca, most notably between 1040 and 1100 C.E., and all
434 coincide with periods of increased in-cave kinetic fractionation as calculated
435 with $\Delta\delta^{13}C$. U/Ca ratios in YOK-I therefore are interpreted to reflect local
436 hydrological conditions and the amount of PAP occurring at the site, providing
437 additional evidence for kinetic fractionation as the main driver of $\delta^{13}C$ in this
438 stalagmite.

Previous studies have highlighted the potential of hydrological proxies for detecting past stalagmite DCF shifts: Rudzka et al. (2011) showed that shifts in DCF during the last deglaciation were matched by synchronous shifts in $\delta^{13}C$, implying a common forcing mechanism on the two proxies (e.g., effective infiltration or changes in mean SOM age). Another study combined DCF and Mg/Ca data measured on a tropical stalagmite and highlighted the importance of host rock dissolution processes for stalagmite DCF (Griffiths et al., 2012).

In YOK-I, both $\delta^{13}C$ and U/Ca values show remarkable similarities ($r = -0.83$, $p < 0.001$), suggesting a strong imprint of PCP/PAP and in-cave kinetic fractionation on both proxies. Comparison with $DCF_{YOK\text{-}I}$ reveals a significant correlation with respect to U/Ca ($r = 0.49$, $p < 0.001$) and $\delta^{13}C$ ($r = -0.5$, $p < 0.001$), suggesting a common forcing on all three proxies (Fig. 7). Since kinetic fractionation is not a strong component of $DCF_{YOK\text{-}I}$ (Fig. 5), another mechanism driven by the same forcing that controls U/Ca and $\delta^{13}C$ must exist. The modeling results confirm that, similar to previous studies, the dominant control on $DCF_{YOK\text{-}I}$ is the dissolution of host rock carbonate, driven by open vs. closed system conditions. All three processes (host rock dissolution, kinetic fractionation and PCP/PAP) are sensitive to effective infiltration within the karst, and thus ultimately driven by climatic conditions. Increasing aridity leads to more open-system conditions and enhanced PAP and kinetic fractionation, resulting in strong covariance between DCF, U/Ca and $\delta^{13}C$ (Fig. 7). This relationship highlights the potential usefulness of combined $\delta^{13}C$, trace element and ^{14}C records to infer past DCF variability. It may also be possibile to detect changing infiltration even when DCF cannot be readily calculated, i.e., during time intervals beyond the tree-ring based interval of the ^{14}C calibration curve or for ^{14}C dating applications. U/Ca

ratios are increasingly recognized as sensitive tracers for PAP in aragonitic stalagmites (Jamieson et al., *in press*), and other trace elements have successfully been used in calcitic samples (e.g., Mg/Ca, Griffiths et al., 2012).

Detailed analysis of the sources of carbon in YOK-I reveals a strong dependency on both hydroclimate and the amount of effective infiltration into the karst system. DCF, $\delta^{13}C$ and U/Ca all show a trend towards drier conditions during the period 700-1100 C.E., a time interval previously described in conjunction with the disintegration of Classic Maya political systems (Douglas et al., 2015; Haug et al., 2003; Hodell et al., 1995; Kennett et al., 2012). Whereas $\delta^{18}O$ reflects the amount of precipitation, moisture source and storm path length, $\delta^{13}C$ is a useful local indicator of effective infiltration into the karst (Ridley et al., 2015a). All factors driving $\delta^{13}C$ result in its enrichment during dry periods: reduced vegetation density and soil microbial activity result in higher $\delta^{13}C$ values of the soil water; more open-system conditions in the karst promote PCP/PAP and kinetic fractionation, progressively enriching $\delta^{13}C$ in the aqueous solution. Therefore, although the kinetic nature of the processes acting on $\delta^{13}C$ prevent quantification of the hydrological deficit, $\delta^{13}C$ in YOK-I is a sensitive recorder of infiltration dynamics.

5.2. 'Bomb' radiocarbon signals YOK-I

The young SOM contribution to the drip water at Yok Balum Cave is reflected in the pronounced bomb spike in stalagmite YOK-I, which reaches its peak at 1.14 $F^{14}C$, with an overall spike of 0.27 $F^{14}C$ (Fig. 2B). Comparing this value to the maximum $F^{14}C$ in the atmospheric Northern Hemisphere zone 2 record (1.98 $F^{14}C$ in 1963; Hua et al., 2013) confirms that YOK-I is a highly responsive

489 stalagmite in terms of carbon transfer, with a damping ratio, D, of 66.1%. D is
490 calculated as the difference between the highest and lowest bomb-^{14}C value in
491 the stalagmite, compared to the atmospheric value. In comparison to an
492 extensive study of a number of stalagmites by Rudzka-Phillips et al. (2013), YOK-
493 I shows one of the least dampened bomb spikes. The rapid increase in $F^{14}C$,
494 synchronous with the beginning of the bomb spike rise, also highlights the rapid
495 fluid transfer in the karst at Yok Balum Cave. These features could be related to
496 the much higher sampling resolution in YOK-I compared to other studies;
497 however, the strong similarity between the bomb spike recorded in YOK-I and
498 YOK-G, another stalagmite from the same cave (Ridley et al., 2015a), suggests
499 that the amplitude of the perturbation is real. The YOK-I bomb spike does not
500 show a pronounced maximum, but rather a rapid increase in ^{14}C activity until ca.
501 1970 C.E., followed by a plateau, until decrease slowly starts after ca. 1990 C.E,
502 very similar to YOK-G (Fig. 2B). It is worth noting that the measured drip rate for
503 stalagmite YOK-G was 30 times higher than for YOK-I, likely attributable to
504 different hydrological pathways in the karst overlying the cave (Ridley et al.,
505 2015a). This corroborates the notion that processes related to the turnover of
506 soil organic matter are responsible for the modulation of the bomb spike in
507 stalagmites (Genty and Massault, 1999; Rudzka-Phillips et al., 2013), rather than
508 changes in karst hydrology. The two stalagmite bomb spikes from Yok Balum
509 Cave and the resultant modeled SOM spectra support the results from the
510 analysis of soil and WEOC samples, indicating only minor contributions of old
511 recalcitrant carbon from the soil to the karst system. Compared again with the
512 study by Rudzka-Phillips et al. (2013), the stalagmites from Yok Balum Cave
513 show similar behavior to the samples from arid and warm sites, with sparse

514 vegetation and thin soils. Although southern Belize is not characterized by year-
515 round aridity, the boreal winter months are very dry, and infiltration in the karst
516 is significantly reduced (Ridley et al., 2015b). Together with the low carbon
517 storage potential of the soils overlying Yok Balum Cave, this may explain the
518 apparent similarity to the arid sites described in Rudzka-Phillips et al. (2013).
519
520 **5.3. Lagged solar influence on DCF**
521 Similarities are apparent when comparing DCF_{YOK-I} to proxies for solar activity
522 (which modulates the production rate of atmospheric ^{14}C; Abreu et al., 2013),
523 such as the total solar irradiance (dTSI) record by Steinhilber et al. (2009) (Fig.
524 8). A lag-correlation analysis was performed between YOK-I and the Steinhilber
525 dTSI record. The YOK-I DCF and $\delta^{13}C$ records were first estimated on the same
526 (uniformly sampled) time scale as that of the Steinhilber dTSI using a Bayesian
527 proxy estimation approach presented in Goswami et al. (2014). All records were
528 normalized to mean zero and unit standard deviation, following which a
529 millennial trend was removed and the resulting residuals were smoothed with a
530 Gaussian kernel of 5 years width. Pearson's cross correlation was then estimated
531 between the resulting smoothed residuals at different lags by shifting the YOK-I
532 datasets ahead of the dTSI data appropriately. Using a window of 450 years over
533 the data, the evolution of lagged correlation was obtained which helped
534 demarcate distinct time periods based on the behavior of the lagged correlation
535 values over time (Fig. 8B).
536 The analysis reveals the presence of statistically significant correlations with a
537 persistent lag between 30 and 50 years of DCF_{YOK-I} with respect to dTSI during
538 the period 900-1250 C.E. However, for the period after ~1250 C.E., we fail to

539 detect similar statistically significant correlations. The same analysis was also
540 performed on $\delta^{13}C$, yielding very similar results as $DCF_{YOK\text{-}I}$ (although the lag
541 extends between 10-50 years in this case) (Fig. 8B). These observations strongly
542 suggest that hydrologic change at Yok Balum Cave occurred several decades
543 after shifts in atmospheric ^{14}C content, induced by solar irradiance, and were not
544 a direct reflection of contemporaneous atmospheric ^{14}C. Rainfall at Yok Balum
545 Cave is largely controlled by the seasonal migration of the ITCZ, and due to the
546 cave's location at the present-day northern boundary of the annual ITCZ range,
547 stalagmites from the site are very sensitive to subtle southward ITCZ migration
548 (Ridley et al., 2015a). Because the ITCZ tracks the Earth's thermal equator, it
549 migrates in response to hemispheric and global temperature shifts (Schneider et
550 al., 2014), controlled by the strength of the Sun, which also modulates
551 atmospheric ^{14}C content. Two possible processes could induce a lagged response
552 to the atmospheric records in $DCF_{YOK\text{-}I}$:
553 i) The stalagmite DCF is influenced by a large pool of 'old' organic carbon derived
554 from the soil or deep vadose zone, or
555 ii) The lag is an actual reflection of a delayed response of rainfall patterns at Yok
556 Balum Cave to solar forcing on climate.
557 The presence of large amounts of old carbon in the karst system is unlikely,
558 because the model results (based on the YOK-I bomb spike) suggest otherwise.
559 In addition, the fact that the lagged response to solar forcing is detectable in both
560 DCF and $\delta^{13}C$ (and U/Ca) suggests that there is another factor influencing both
561 proxies. Numerous studies have found decadal-scale lags (on the order of 10-40
562 years) in the response of rainfall patterns to solar forcing (Kobashi et al., 2015;
563 Moffa-Sanchez et al., 2014; Shindell et al., 2001; Swingedouw et al., 2011; Waple

et al., 2002). It is possible that a similar delayed response of Mesoamerican rainfall to solar forcing results in the lag observed in DCF_{YOK-I}, especially prior to 1250 C.E. Although the precise nature of the observed lag is unclear, solar-induced changes in the amount of freshwater and/or sea ice delivered to the North Atlantic basin and subsequent feedbacks in oceanic and atmospheric dynamics (e.g., in the state of the North Atlantic Oscillation) may play a role (Kobashi et al., 2015; Swingedouw et al., 2011; Waple et al., 2002). A possible solar influence on drought occurrence in the Yucatan has previously been suggested by Hodell et al. (2001). The apparent weakening of the solar influence on the YOK-I record after 1250 C.E. suggests a shift in the mechanism responsible for the observed lag between solar activity and rainfall at Yok Balum Cave. Although the causes for the lagged response between DCF_{YOK-I} and solar activity remain unclear, we note that the breaking down of the lagged proxy-Sun relationship (potentially a complete decoupling between rainfall and solar activity) is broadly synchronous with the beginning of the Little Ice Age (LIA), a period of extensive cooling in the Northern Hemisphere (Mann et al., 2009). This could therefore reflect a decreased influence of solar activity on hydroclimate (at least in Mesoamerica) during the LIA, and emergence of a different dominant forcing on ITCZ position (e.g., volcanism, Miller et al., 2012). However, other climate reconstructions and more extensive research are required to verify this interpretation.

6. Conclusions

We present a comprehensive study of carbon cycling and the controls on stalagmite DCF at the tropical Yok Balum Cave, southern Belize. Subdecadal-scale

589 DCF, $\delta^{13}C$, and U/Ca records from stalagmite YOK-I covering the last 1500 years,
590 combined with bulk SOC, WEOC, and modeling analysis of ^{14}C, reveal the sources
591 of carbon incorporated in stalagmite YOK-I, and on the factors and processes that
592 give rise to variations in DCF:

593 • Overall, the largest contribution to total DCF_{YOK-I} is carbonate bedrock
594 dissolution in the karst, significantly modulated by hydrological
595 conditions. Contributions of SOM to the total DCF_{YOK-I} are relatively small,
596 due to the fast SOM turnover and low carbon storage potential of the soil.
597 Dynamic ventilation of the cave system and seasonal aridity in the region
598 results in strong kinetic fractionation effects and PAP acting on $\delta^{13}C$ and
599 U/Ca. We acknowledge, however, that our approach of using constant
600 vegetation and SOM parameters in the model might bear some
601 weaknesses and should be refined by future studies.

602 • We find a strong relationship between DCF, $\delta^{13}C$, and U/Ca, suggesting a
603 common forcing factor on all three proxies (i.e., hydroclimate conditions
604 above the cave). These results highlight the potential usefulness of $\delta^{13}C$
605 and trace element ratios to track changes in stalagmite DCF, and could
606 help detecting past shifts in DCF when no independent age control is
607 available (e.g., for periods beyond the tree-ring based interval of the
608 atmospheric ^{14}C calibration curve) or for stalagmite ^{14}C dating purposes.

609 • Comparison of the high-resolution DCF_{YOK-I} and $\delta^{13}C$ records to IntCal13
610 and solar records shows compelling similarity with a variable lag (10-50
611 years) in the response of YOK-I to the solar forcing. We suggest that
612 rainfall above the site was driven by solar forcing but with a lagged
613 response, and raise the possibility that solar forcing of ITCZ position

varies temporally, and becomes much less prominent after the transition into the LIA.

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Tables:

Table 1: Results of the proxy study on stalagmite YOK-I. DCF was calculated using the formula: $\boldsymbol{DCF = 1 - \left({}^{\boldsymbol{a^{14}C_{stal.init.}}}\!\!\diagup\!\!_{\boldsymbol{a^{14}\,C_{atm.init.}}} \right)}$ where $a^{14}C_{stal.\,init.}$ and $a^{14}C_{atm.\,init.}$ represent stalagmite and atmosphere ^{14}C activity (respectively) at the time of carbonate deposition.

Table 2: Analysis of soil samples. A profile consisting of 13 samples was collected above Yok Balum Cave, and both bulk SOC and WEOC ^{14}C were measured.

Figures:

Fig. 1. Maps of Yok Balum cave, southern Belize: A - Cave map showing the location of stalagmite YOK-I (red dot), and the approximate position of the soil profile collected above the cave (yellow circle) (Map A is adapted from a map by Tom Miller). B - Topographic map of the study site, with indication of the location of Yok Balum cave. C - Overview map of Central America and the general setting of the cave. (Maps in B and C are by A.E. Thompson, courtesy of the Uxbenká Archaeological Project).

862 Fig. 2: A - Photoscan of the section of stalagmite YOK-I that was analysed for ^{14}C
863 together with results from ^{14}C analysis (U/Th ages are shown for comparison). A
864 pronounced bomb spike appears at the top of the stalagmite. B - Bomb spike
865 recorded in stalagmite YOK-I (red dots), compared to the atmospheric record
866 from the northern Hemisphere zone 2 (Hua et al. (2013), black line), and to the
867 bomb spike recorded in stalagmite YOK-G from the same cave (grey dots, Ridley
868 et al. (2015a)). Signal damping due to the age spectrum of SOM results in the
869 lower amplitude and slightly delayed response of stalagmites YOK-I and YOK-G
870 with respect to the atmosphere.
871
872 Fig. 3: Results of the analysis of geochemical proxies in stalagmite YOK-I: A - DCF
873 calculated from ^{14}C measurements (purple line, including 1σ errors); B - U/Ca in
874 ppm/ppm x 1000 (green line); C - $\delta^{13}C$ measured on the same aliquots as used
875 for ^{14}C analysis (dark red diamonds) show that no sampling bias occurred with
876 respect to the original high-resolution $\delta^{13}C$ time series (light red line); D - $\delta^{18}O$
877 from the original high-resolution time series (both high resolution stable isotope
878 records were previously published in Kennett et al., 2012).
879
880 Fig. 4: Results from the analysis of the soil profile collected above Yok Balum
881 cave. Amount of carbon present in the samples was determined twice, showing
882 very reproducible results (grey and black dots). $F^{14}C$ shows regularly decreasing
883 values through the bulk SOC profile with bomb carbon imprint in the top 10 cm
884 (red dots), and a slower decrease in the WEOC (blue dots).
885

886 Fig. 5: Results of the modeling procedure on stalagmite YOK-I: A - The best fit of
887 the model with the bomb spike data (black symbols) is shown by the red dashed
888 line, the atmospheric bomb spike is shown for comparison in blue. B - The
889 calculated soil air ^{14}C activity, after applying the SOM spectrum derived from the
890 bomb spike on the entire time series, is shown in green. Fractionation between
891 gaseous CO_2 and DIC results in slight enrichment (orange line). The atmospheric
892 activity is shown in black for comparison. C - Results of the deconvolution of
893 DCF: the black line shows the total DCF as measured on the stalagmite. The DCF
894 contribution from vegetation/SOM is shown by the green line, and in-cave
895 fractionation effects result in the orange line. DCF derived from host rock
896 dissolution is shown in purple.
897
898 Fig. 6: Evolution of $\delta^{13}C$ in the Yok Balum karst system, determined by modeling.
899 A - $\delta^{13}C$ of the drip water (blue line), calculated using the measured total DCF,
900 indicating the degree of open vs. closed system and consequently soil CO_2
901 exchange with the aqueous solution in the karst. B - U/Ca (green line) is
902 modulated by PAP, and shows remarkable similarity with stalagmite $\delta^{13}C$. C -
903 $\Delta\delta^{13}C$ (black line) is calculated as the difference between $\delta^{13}C$ of the drip water
904 and the stalagmite, and reflects the amount of kinetic fractionation affecting the
905 sample (as described in Griffiths et al. (2012)). D - $\delta^{13}C$ in YOK-I (red line),
906 underlain by the high resolution profile presented in Kennett et al. (2012).
907
908 Fig. 7: Relationship between $\delta^{13}C$, U/Ca and DCF in stalagmite YOK-I: A -
909 Relationship between $\delta^{13}C$ and U/Ca. A significant linear correlation (black line, r
910 = -0.83, $p<0.001$; 95% confidence interval as grey dashed line) exists between

911 $\delta^{13}C$ and U/Ca ratios. DCF values are color-coded. B - Scatterplots showing the
912 relationship between DCF and $\delta^{13}C$ (upper), and DCF and U/Ca (lower), with
913 associated correlation coefficients. All proxies are influenced by karst
914 infiltration: $\delta^{13}C$ reflects the amount of PCP/PAP and kinetic fractionation in the
915 cave, whereas U/Ca is influenced by PAP. DCF responds to the degree of open-vs-
916 closed system conditions in the karst, modulated by changes in effective
917 infiltration.
918
919 Fig. 8: External forcing on YOK-I carbon isotopic records: A - Comparison of YOK-
920 I DCF and $\delta^{13}C$ to total solar irradiance (dTSI) calculated from ^{10}Be (blue curve)
921 (Steinhilber et al., 2009) and atmospheric $\Delta^{14}C$ from IntCal13 (grey curve)
922 (Reimer et al., 2013). Dashed lines indicate features present in all records
923 suggesting solar forcing with a variable lag on precipitation at Yok Balum Cave.
924 U/Th ages for stalagmite YOK-I are shown to highlight the excellent age control
925 of the record. B - Lag-correlation plots quantifying the lag between DCF and $\delta^{13}C$
926 at Yok Balum Cave and dTSI (Steinhilber et al., 2009). The test was done with
927 5000 randomized surrogates for each lag. Dashed lines indicate significant
928 values (two-sided at 0.05 significance level with Bonferroni correction). A band
929 of high correlations lagging the solar forcing by ~30-50 years for DCF, and ~10-
930 50 for $\delta^{13}C$ is visible between ~900-1250 C.E., but the relationship breaks down
931 in the younger part of the record (1300-1700 C.E.). Note that $\delta^{13}C$ is plotted on
932 an inverse colorbar compared to DCF since the two proxies have the opposite
933 response to hydrological changes (wetter: DCF increases, $\delta^{13}C$ decreases).
934

Suppl. Fig. 1: Conceptual diagram of carbon cycle processes occurring in a karst system and the associated response in the hydrological proxies (^{14}C, $\delta^{13}C$ and U/Ca) used in this study.

Suppl. Fig. 2: Schematic of the modeling process (as in Griffiths et al., 2012) as applied to the dataset from stalagmite YOK-I. The model is composed of two parts: in a first step, the stalagmite bomb spike is used to calculate the best fitting SOM spectrum, by using a Monte Carlo optimization process. In the second part, the SOM spectrum is applied to the remaining stalagmite dataset and the contributions to DCF from vegetation, in-cave fractionation and host rock dissolution can be separated and quantified.