1   A novel approach for construction of radiocarbon-based chronologies

2   for speleothems

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23   **Abstract**

24   **Robust chronologies are crucial for the correct interpretation of climate**

25   **proxy records and for detailed reconstructions of palaeoclimate.**

26   **Stalagmites have garnered strong interest as recorders of past climate in**

27   **part due to their amenability to U-series dating. However, many**

28   **stalagmites are not dateable using this technique due to low ^{238}U and/or**

29   **high detrital Th concentrations (e.g., many tropical cave systems (Adkins et**

30   **al., 2013)), and occasionally these issues affect stalagmites across wide**

31   **geographical regions (e.g., large parts of Australia (Green et al. 2013))**

32   **complicating the use of stalagmites in these areas. Radiocarbon (^{14}C) offers**

33   **an alternative method of dating stalagmites, but issues associated with the**

34   **'dead carbon fraction' (DCF) have historically hindered this approach.**

35   **Here, a novel ^{14}C-based method for dating stalagmites is presented and**

36   **discussed. The technique calculates a best-fit growth rate between a time-**

37   **series of stalagmite ^{14}C data and known atmospheric ^{14}C variability. The**

38   **new method produces excellent results for stalagmites that satisfy four**

39   **requirements: *i)* the absence of long-term secular variability in DCF (i.e.,**

stalagmite DCF varies around a mean value with no long-term trend), *ii)* stalagmite growth rate does not vary significantly (the technique identifies stalagmites with substantial growth rate variability), *iii)* the stalagmite record is long enough that measurable ^{14}C decay has occurred, and *iv)* one 'anchor' point exists where the calendar age is known. The model produces good results for a previously U-Th dated stalagmite from Heshang Cave, China, and is then applied to an undated stalagmite from southern Poland. The new method will not replace high-precision U-Th measurements, because the precision of the technique is difficult to quantify. However, it provides a means for dating certain stalagmites undateable by conventional U-Th methods and for refining coarse U-Th chronologies.

1. Introduction

Stalagmites are becoming increasingly important climate archives, and have yielded numerous iconic records of past terrestrial climate (e.g., Cheng et al., 2009; Wang et al., 2001; Fairchild et al., 2006). Generally, stalagmites are amenable to very precise absolute dating using the U-Th method (Cheng et al., 2013; Dorale et al., 2007). The distinctly different behavior of U and Th in drip waters means that stalagmite carbonate theoretically contains almost no ^{230}Th when deposited, and that subsequent ^{230}Th accumulation results purely from radioactive decay of ^{238}U and ^{234}U, allowing precise determination of carbonate precipitation age (van Calsteren and Thomas, 2006). Additionally, the development of powerful analytical techniques, initially Thermal Ionisation Mass Spectrometry (TIMS) (Edwards et al., 1987; Li et al., 1989) and subsequently Multi-Collector Inductively Coupled Plasma Mass Spectrometery (MC-ICPMS) (Hoffmann et al., 2007), have greatly improved chronological precision. However, stalagmites either with high detrital Th (not derived from in situ radioactive decay) or with extremely low uranium concentrations have proven problematic, and are occasionally not dateable using this approach (González-Lemos et al., 2015; Urban et al., 2015). Young stalagmites (< 300 years), where the U-Th method has its largest uncertainties, are most susceptible to these issues (Hodge et al., 2011; Mattey et al., 2008).

73   The first method proposed to develop chronologies for stalagmite-based climate

74   records was ^{14}C dating (Broecker et al., 1960; Hendy and Wilson, 1968), due to

75   its already widespread application to other terrestrial archives such as tree rings

76   and lake sediments (e.g., Reimer et al., 2013; Street and Grove, 1979; Suess,

77   1980) and in groundwater research (Wigley, 1975). However, ^{14}C in

78   groundwater and consequently stalagmite carbonate reflects contemporaneous

79   atmospheric ^{14}C combined with variable amounts of ^{14}C-depleted carbon from

80   the soil and host rock. This reservoir effect, termed the "dead carbon fraction"

81   (DCF, used hereafter in this text), or "dead carbon proportion" (dcp, DCP), if not

82   properly constrained, results in stalagmite ages that are too old (Genty and

83   Massault, 1999; Genty et al., 2001; Holmgren et al., 1994). Formally, DCF is

84   expressed as:

85    $$DCF = 1 - \left(a^{14}C_{stal.init.} \Big/ a^{14}C_{atm.init.} \right) \qquad (1)$$

86   where $a^{14}C_{stal.\ init.}$ and $a^{14}C_{atm.\ init.}$ represent stalagmite and atmosphere ^{14}C activity

87   (respectively) at the time of carbonate deposition. Potentially unquantifiable

88   DCF variability, combined with contemporaneous analytical advances involving

89   the U-Th method, resulted in the dismissal of ^{14}C-dating of stalagmites as a viable

90   approach (Gascoyne, 1992; Genty et al., 2001). The issues with absolute [14]C

91   dating of stalagmites revolve around accurate quantification of DCF. Solving this

92   problem would thus open the door to the application of the technique to

93   speleothems. Over the past two decades, numerous studies have attempted to

94   identify mechanisms governing DCF and its variability, largely with the aim of

95   using DCF as tracer for hydrological and carbon cycle processes (Fohlmeister et

96   al., 2011, 2010; Genty and Massault, 1999; Genty et al., 2001; Griffiths et al.,

97   2012; Noronha et al., 2014). This past research strongly suggests that host rock

98   dissolution processes and the degree of open- versus closed-system behavior

99   within the karst (Fohlmeister et al., 2010; Griffiths et al., 2012; Noronha et al.,

100   2014), as well as contributions from soil organic matter (Oster et al., 2010;

101   Scholz et al., 2012), exert primary control on DCF variability. All these processes

102   are dependent on hydrological conditions, and consequently several recent

103   papers have proposed that changes in DCF reflect past hydroclimate variability

104 (Griffiths et al., 2012; Noronha et al., 2014; Oster et al., 2010). Additionally, the
105 location of the atmospheric 'bomb spike' (resulting from widespread nuclear
106 testing in the 1950s and 1960s) within stalagmite stratigraphy represents a
107 potentially useful chronological tool. For example, Mattey et al. (2008) and
108 Hodge et al. (2011) used the bomb spike imprint to date stalagmites by inverse
109 modelling of their ^{14}C uptake, providing a method for development of robust
110 chronologies for very recent deposits (~1950-present) where U-Th techniques
111 are less precise. Hua et al. (2012) constructed additional chronologies for two of
112 the stalagmites used by Hodge et al. (2011) using the ^{14}C bomb spike combined
113 with high-resolution δ^{18}O and δ^{13}C measurements. Another approach is
114 illustrated in González-Lemos et al. (2015), who used δ^{13}C values to define
115 periods of similar DCF, assuming a comparable hydrological influence on both
116 parameters. These studies have applied ^{14}C dating to stalagmites using very
117 different approaches to constrain DCF, illustrating the potential applicability of
118 the technique to stalagmites. For most samples, U-Th dating produces the best
119 dates, but for samples not amenable to U-Th dating, the ^{14}C method provides an
120 alternate chronological tool. Additionally, high precision ^{14}C dating typically
121 requires only 8-10 mg powered sample, compared to up to several 100 mg for U-
122 Th, which is advantageous in many situations.

123

124 Here we present a new method for the construction of accurate stalagmite
125 chronologies using ^{14}C. The method determines the mean stalagmite growth rate
126 by comparing a long stalagmite ^{14}C time-series to atmospheric ^{14}C over the same
127 time interval. The technique is not yet applicable to all stalagmites, but highlights
128 promising aspects of stalagmite ^{14}C records that could be refined to fit a wide
129 variety of samples.

130

131 2. Sample description
132 Stalagmite NIED08-05 was collected in 2008 from Niedźwiedzia Cave in Kletno,
133 Poland (Fig. 1). The cave has been a closed system since the Early Holocene, with
134 access to the surface only through ponors (Don, 1989; Pflitsch and Piasecki,
135 2003). However, the presence of cave bear skulls and entire skeletons in the cave
136 indicate that there must always have been a relatively large opening to the

137 outside world (Bieronski et al., 2009). The first 200 m of cave passage were
138 discovered in 1966 during marble mining followed by an additional ~2 km in
139 1982.

140 The cave's isolation from the outside atmosphere would have minimized
141 external influences, and encouraged slow calcite growth. NIED08-05 grew in the
142 upper level of Niedźwiedzia Cave, approximately 10 meters below the surface
143 (Fig. 1), where air temperature is very stable (<1.0°C variation around the multi-
144 annual average), and relative humidity (RH) is almost 100% (Piasecki and
145 Sawinski, 2009). The mean annual temperature within the cave is 6°C, reflecting
146 the mean annual outside temperature. To ensure active stalagmite growth, the
147 drip feeding NIED08-05 was monitored for ~three months (04 April - 20 June
148 2008) using a Stalagmate drip counter. After removal from the cave, NIED08-05
149 was sectioned along its growth axis and polished at Durham University. The
150 stalagmite is 12.5 cm long and composed of very dense, coarse crystalline calcite
151 (Fig. 2a). No regular visible laminae exist, except for a few white microcrystalline
152 layers that may reflect growth hiatuses. Very low concentrations of ^{238}U (mean
153 concentrations = ~14 ppb) prevented high-precision U-Th dating, as typical
154 dating errors over the Holocene were between 190 and 4065 years, with
155 numerous stratigraphic inversions. Because the stalagmite was otherwise an
156 excellent sample (free from detrital contamination, appropriate crystal
157 morphology, from a region with few long palaeoclimate records), it was decided
158 to date the sample using ^{14}C.

159

160 3. Analytical methods

161 3.1. ^{14}C measurements

162 Samples for high-precision graphite ^{14}C analysis were drilled at 5 mm resolution
163 along the growth axis using a semi-automatic high precision drill (Sherline 5400
164 Deluxe) at ETH Zurich. To minimise potential contamination, all the equipment
165 and the stalagmite were cleaned with methanol and dried using compressed air
166 prior to sampling, and the top 0.1 mm of stalagmite surface powder was
167 discarded. Aliquots of ~8 mg of carbonate powder were dissolved in 1 ml of 85%
168 H_3PO_4. Fast carbonate dissolution and a complete conversion to CO_2 were
169 ensured by heating the sample vials to 85°C for one hour. Graphitisation was

170 performed using an Automatic Graphitization Equipment (AGE) system (Wacker
171 et al., 2010) via iron-catalysed hydrogen reduction of the CO_2. The resultant
172 graphite was transferred to aluminum targets for determination of ^{14}C activities
173 ($a^{14}C$) using a Mini radioCarbon Dating System (MICADAS) accelerator mass
174 spectrometer (AMS) (Synal et al., 2007) at the Laboratory for Ion Beam Physics
175 (LIP) at ETH Zurich. In addition, detailed sampling and ^{14}C analysis was
176 undertaken to detect the atmospheric ^{14}C bomb spike imprint. For this, the top
177 1mm of NIED08-05 was milled at an extremely high resolution (100μm per
178 sample) over four different tracks. Approximately 0.8 mg of carbonate were
179 dissolved in 85% H_3PO_4, and the CO_2 produced was measured directly on the
180 MICADAS using a Gas Ion Source (GIS) system (Ruff et al., 2007), again at LIP. A
181 series of laboratory standards (Oxalic acid II, IAEA C1 and C2, and a modern
182 coral standard) were used to ensure high precision: Oxalic acid II was measured
183 to a precision of better than 2‰ for graphite and 10‰ for GIS analyses. In
184 addition, ^{14}C-dead stalagmite material (stalagmite material from NE India, MAW-
185 1: ~170 kyr, based on U-Th dates) was used as a procedural blank during all
186 measurement runs.
187
188 3.2 Stable isotope and trace element analysis
189 260 samples for stable isotope analysis were milled continuously along the
190 growth axis, using a Proxxon micromill at Durham University. The samples were
191 transferred to glass Exetainer vials and flushed with He to remove outside air
192 before acid digestion using 103% H_3PO_4. The measurement was conducted on a
193 Thermo-Finnigan MAT253 Isotope Ratio Mass Spectrometer at Durham
194 University, and uncertainties were assessed from standards NBS-18, NBS-19,
195 LSVEC and an in-house standard. External analytical uncertainties for both $\delta^{13}C$
196 and $\delta^{18}O$ are 0.1‰ and presented relative to the Vienna Pee Dee Belemnite (V-
197 PDB).
198
199 A high-resolution profile of major trace elements over the top ca. 105 mm of
200 NIED08-05 was produced using a prototype RESOlution M-50 excimer (193 nm)
201 laser-ablation system with a two-volume laser-ablation cell coupled to an Agilent
202 7500ce/cs quadrupole ICPMS at Royal Holloway University, London. Müller et al.

203 (2009) describe in detail the analytical configuration and initial performance

204 metrics. The profile was measured using a 140 by 10μm rectangular laser slit, a

205 15Hz repetition rate of a 90mJ laser spot, and a 10μm s^{-1} scan speed. Samples

206 were bracketed by analyses of NIST 612, NIST 610 and MACS3 standards for

207 quantification. Data reduction was performed using the Iolite software package

208 using NIST 610/612 standards for external standardization (Paton et al., 2011).

209 Calcium-43 was measured throughout the sample runs as an internal standard.

210

211 4. Results

212 4.1. ^{14}C measurements: chronology and bomb spike identification

213 Twenty-five high-precision graphite ^{14}C ages, ranging from 1,139±27 years at 5

214 mm from the top to 8,909±38 years at the base (122 mm from the top), were all

215 in stratigraphic order within measurement uncertainty, apart from a small

216 reversal at 102 mm depth (Fig. 2a, Table 1). The ^{14}C data suggest the NIED08-05

217 growth spans much of the Holocene, in agreement with the initial assumption

218 based on the very imprecise U-Th ages. Very regularly increasing ^{14}C ages with

219 depth suggest generally constant stalagmite growth. However, an abrupt 1,700-

220 year shift occurs between 47 and 52 mm from top coinciding with a thin white

221 microcrystalline layer, strongly suggesting the presence of a growth hiatus (Fig.

222 2a). Similar microcrystalline layers elsewhere in the stalagmite suggest that

223 other hiatuses exist, but because the ^{14}C ages do not indicate growth interruption

224 at these times these possible (probably very brief) hiatuses were not considered

225 in the final chronology. The very high resolution GIS measurements along the top

226 1 mm of NIED08-05 show considerably increased ^{14}C activity in the uppermost

227 0.4 mm in three out of four replicate tracks, confirming the presence of the bomb

228 spike (Fig. 2b, Suppl. Table 1). The different manifestations of the atmospheric

229 ^{14}C bomb spike in the four traverses is attributable to strong signal attenuation

230 in the karst (max. a^{14}C = 0.96 fraction modern (fM) compared with 1.98 fM in the

231 atmosphere in 1963; Hua et al., 2013), to sampling bias due to the transect

232 position relative to stalagmite curvature, and to the remarkably high-resolution

233 nature of these ^{14}C analyses. All samples were larger than the threshold where

234 significant blank contributions occur that could influence the reliability of the

235 results (see section **Error! Reference source not found.**).   To our knowledge,

236   these are the first high-resolution ^{14}C measurements performed on replicate
237   tracks in a stalagmite.

238   Replicate blank measurements on milled aliquots of the ^{14}C-dead stalagmite
239   MAW-1 ensure that no contamination from modern atmospheric ^{14}C during
240   carbonate drilling, as encountered by previous studies (Hoffmann et al., 2010;
241   Southon et al., 2012), occurred.

242

243   4.2. Stable isotope and trace element analysis

244   Overall, in NIED08-05 δ^{13}C remains very stationary with only a minor longer-
245   term trend (mean = -7.48‰, σ = 1.17, Suppl. Fig. 1). Conversely, Mg
246   concentrations are quite variable throughout the stalagmite (mean Mg/Ca ratio x
247   1000 = 2.56, σ = 0.85). Several large excursions exist within the Mg dataset, with
248   gradual increases in Mg/Ca followed by more abrupt decreases (e.g. at 10 mm,
249   44 mm and 51.5 mm from top) possibly reflecting karst hydrology processes
250   and/or growth hiatuses (Suppl. Fig. 1).

251

252   5. Chronology development

253   The technique described herein does not utilise ^{14}C ages as discrete dates, but
254   instead focusses on the topology of the long-term a^{14}C-depth relationship.
255   Regularly decreasing a^{14}C with depth from the sample top strongly suggests that
256   only small stalagmite growth rate and DCF changes occurred, and that
257   exponentially decreasing a^{14}C is only due to radioactive decay. In this case, the
258   best-fit line describing the ^{14}C data should reflect the stalagmite's long-term
259   average growth rate, and a simple chronology can be built by anchoring the
260   growth rate to a point of known age (such as collection date, or the bomb spike).
261   Similar approaches are used in other fields of geochronology, for example in
262   ^{210}Pb dating of sediments over the last 100 years (Appleby & Oldfield, 1978;
263   Baskaran et al., 2014) or in ^{230}Th excess dating of deep sea sediments (Francois
264   et al., 1990). However, whereas those methods generally assume that
265   radionuclide incorporation rate is essentially constant over time, this is not the
266   case with ^{14}C due to past variations in atmospheric a^{14}C (e.g., Reimer et al.,
267   2013).

268

269   The model presented here identifies stalagmites with 'stationary' growth rates
270   over long time intervals (i.e., samples with growth rates that vary around a long-
271   term mean value). Stationarity in DCF implies that no secular changes in both the
272   soil organic matter age and the host rock dissolution systems (open vs. closed)
273   occurred. Secular changes in DCF define long-term trends resulting from large
274   fluctuations in climate (e.g. deglaciations (Rudzka et al., 2011)) or changes in the
275   cave's carbon cycle (e.g. build-up of soils (Genty et al., 2001; Scholz et al., 2012)).
276   These trends in DCF are detectable using through other geochemical proxies,
277   such as δ^{13}C and Mg/Ca, as demonstrated by many previous studies (e.g. Scholz
278   et al., 2012, Genty et al., 2001, Rudzka et al., 2011). Such long-term changes in
279   DCF would preclude a stalagmite to be suitable for the method presented here.
280   Small DCF variations around a long-term mean value, however, are permissible.
281

282   Assuming that the stationarity condition is met, the model builds an age-depth
283   relationship accounting for both variable DCF and atmospheric ^{14}C. There are
284   two principal steps to the process: *i*) the chronology is anchored to an
285   independent point of known age and *ii*) an iterative, MATLAB-based process
286   adjusts modelled stalagmite growth rate by considering past atmospheric a^{14}C
287   variability. If DCF remains stationary on long timescales, short-term (seasonal or
288   longer term) DCF fluctuations around a mean value do not affect the calculations.
289   This is not dissimilar to U-Th dating, which only produces ages for a few select
290   depths and infers the ages of other depths (and consequently growth rates)
291   using best-fit equations.
292

293   5.1. Model setup
294   The model is based on the radioactive decay equation, expressed by:
295

296     $$A/A_0 = e^{-\lambda t} \qquad\qquad\qquad (2)$$

297   where A is the ^{14}C activity measured in the stalagmite, A_0 is the initial stalagmite
298   ^{14}C activity, and λ is the ^{14}C decay constant (1/8267 yr^{-1}). Carbonate deposition
299   age (t) is unknown and is expressed as:
300

301     $t = {d}/{R}$ (3)

302   where d is the depth from the stalagmite top and R is the growth rate.

303   Converting equation 2 to its linear form with respect to t yields:

304

305     $\ln\left({A}/{A_0}\right) = -\lambda t$ (1)

306   and if

307

308     $\ln\left({A}/{A_0}\right) = -\lambda * {d}/{R}$ (2)

309   the slope is proportional to $1/R$.

310

311   Variable atmospheric ^{14}C and karst carbon transfer dynamics (i.e., DCF)

312   complicate quantifying A_0. A point of known age anchors the entire chronology

313   taking into account DCF, and thus atmospheric $a^{14}C$ entirely drives A_0.

314

315   5.2. Anchor point selection and identifying the best-fit decay curve

316   The model requires a point of known age to account for DCF, and therefore the

317   'anchor point' needs to be defined before starting the modelling procedure. For

318   stalagmites that were growing when collected, the collection date is suitable.

319   Other possibilities are the beginning of the bomb spike rise (i.e., the first

320   indication of bomb ^{14}C in the atmosphere, 1955 AD), or a robust U-Th

321   measurement, if available. In the first step, the model computes a best fit through

322   all $a^{14}C$ measurements in the dataset, defining an initial growth rate (Fig. 3a). A_0

323   is kept at 1 for this step (i.e., constant atmospheric ^{14}C). The anchor point

324   permits calculation of each sample's calendar age via the growth rate. Because A_0

325   = 1, this initial age-depth relationship requires further refinement. In the second

326   iteration, atmospheric ^{14}C values from the IntCal13 calibration curve (Reimer et

327   al., 2013), corresponding to the calculated sample ages, are assigned as new A_0

328   values and a new, slightly different growth rate is calculated. Atmospheric ^{14}C

329   values from the IntCal13 are smoothed prior to the fitting procedure using a

330   moving average (window size 5) to mimic the effect of soil organic matter and

331   vegetation on the soil CO_2 (Fohlmeister et al., 2011). The stalagmite ages are then

332   re-adjusted accordingly, with a static anchor point (i.e., unchanged from iteration

333   1). The procedure is repeated until convergence is reached and growth rate

334   changes become insignificant (<0.0001mm yr^{-1}). This condition is typically

335   reached after four to six iterations of the fitting procedure (Fig. 3).

336

337   5.3. Hiatus integration in the model

338   Constraining and delimiting the duration and exact timing of hiatuses is critical

339   for developing accurate chronologies. The probable lack of an anchor point

340   below hiatuses complicates applying the model described here, as is the case in

341   NIED08-05 for the growth interval older than the depositional hiatus ('pre-

342   hiatus'). A modified version of the method can develop the pre-hiatus

343   chronology, although only qualitatively.

344

345   For stalagmites with a depositional hiatus, the model initially constrains the

346   post-hiatus interval as in section 5.2., permitting the calculation of mean DCF for

347   that interval. Assuming stationary DCF over the entire stalagmite, this mean DCF

348   and its standard deviation are applied to all ^{14}C ages from the pre-hiatus interval.

349   The DCF corrected ^{14}C ages are then calibrated to calendar years using a

350   procedure similar to commonly available calibration tools, but built into the

351   MATLAB modelling procedure. Correcting and calibrating all pre-hiatus ages

352   prevents over- or under-estimation of the stalagmite age due to a single offset

353   age (from a possible extreme DCF value), and is therefore more robust than

354   treating only one individual (i.e., the first) pre-hiatus age. The calibration of the

355   DCF corrected ^{14}C ages provides a probability density distribution in time for

356   each ^{14}C age. The best growth rate (Fig. 3b, red line) through the probability

357   densities of all ages is determined by using the following procedure: *i)* the

358   youngest pre-hiatus age acts as a preliminary anchor point, and the constant

359   growth rate line is positioned through that point (Fig. 3b, red line); *ii)* The

360   growth rate line is then shifted gradually through time, intersecting each point of

361   the calibrated age probability distribution at a certain point (Fig. 3b); *iii)* The

362   probabilities of the intersection points are added and quantify the constant

363   growth rate line's fit to the entire data (Fig. 3c). *iv)* Shifting the line of constant

364   growth through the calibrated ^{14}C ages establishes a new probability function for

365 the placement of this line. The best placement is determined using the weighted

366 mean of the probability distribution, which again ensures that the model is not

367 biased by single offset ages (Fig. 3c).

368

369 5.4. Uncertainties and error estimation

370 The model considers different sources of error, including: A) Estimated growth

371 rate error, related to the goodness of the fit through the measured ^{14}C data; B)

372 Measurement error regarding the depth from stalagmite top (i.e. uncertainty

373 introduced from the sampling); C) Error on the calculated mean DCF, defined by

374 its standard deviation, and D) Uncertainty from the calibration, given by the

375 probability density distribution of the calibrated ^{14}C ages.

376

377 For the simple case of an age model without any hiatus, the resulting uncertainty

378 depends only on errors of type A and B. The chronological uncertainty is

379 calculated using common error propagation, and increases with distance from

380 the anchor point, due to uncertainty in the growth rate estimate (uncertainty in

381 the slope determined during the fitting procedure). In this case, the model's

382 chronological error is small, and depends on how well the anchor point is

383 constrained. If a hiatus is present, the chronological uncertainty for the lower

384 part is assessed differently, and the uncertainty is governed largely by type C and

385 D errors, whereas other errors are trivial and not considered. Because the age

386 model's pre-hiatus interval is not based on a single anchor point, but rather all

387 ^{14}C ages act as anchor points, the uncertainty is defined by the new probability

388 function for the placement of the constant growth rate line (Fig. 3c). This results

389 in much larger errors than for the case with no hiatus.

390

391 6. Model testing and application

392 6.1. Stalagmite HS4 (Heshang Cave)

393 The model was tested using a previously published stalagmite ^{14}C dataset from

394 Heshang Cave (China) (Noronha et al., 2014). Stalagmite HS4 is 250 cm tall and

395 was dated using U-Th techniques, which suggest continuous growth with an

396 almost constant growth rate over the past ~8,000 years (Hu et al., 2008). DCF is

397 stationary but varied between 7 and 14% (Noronha et al., 2014); therefore the

398 sample is ideal for testing the reliability of the ^{14}C chronology development
399 technique presented here.
400
401 The exponential decay function was transformed to a linear relationship to
402 simplify data visualization and handling. Removing the linear trend from the
403 natural logarithm of the a[14]C ('ln (a[14]C)') data reveals that the top three ^{14}C ages
404 in HS4 are anomalous (defined as ages more than 1σ away from the dataset's
405 mean (Suppl. Fig. 2)), possibly due to a shift in growth rate or DCF. If a growth
406 rate shift occurred, and an anchor point were chosen in the anomalous interval,
407 an offset in the age-depth model may result. To avoid chronological bias, the
408 anchor was therefore set to the first ^{14}C data point beyond the anomalous top
409 interval (the fourth ^{14}C point from the top overall) (Suppl. Fig. 2), rather than at
410 the first data point from the top of the ^{14}C dataset. Growth rate convergence was
411 reached after four iterations, and comparison between modelled and actual
412 growth rate (derived from U-Th dating) show excellent agreement (modelled [14]C
413 growth rate = 0.0262 ±0.00047 cm yr^{-1}; U-Th growth rate = 0.0259 cm yr^{-1}). The
414 model's chronological error is between ±1 and ±155 years (Fig. 4). In
415 comparison, if the first data point from the top of the ^{14}C dataset is used as
416 anchor point, the modelled ages are overestimated throughout most of the
417 chronology. Consequently DCF is underestimated on average by 3% (max.
418 underestimation = 6%), although the chronological precision is unchanged (Fig.
419 4). A shortcoming of the model is therefore its dependency on the choice of
420 anchor point; even with prolonged, nearly constant growth rate, the anchor point
421 determines chronological accuracy. A detailed analysis of the raw ^{14}C data profile
422 can help evaluating the suitability of any chosen anchor point, and assessment of
423 whether that point is representative of average DCF throughout the stalagmite.
424
425 6.2. NIED08-05 (Niedźwiedzia Cave)
426 The procedure was applied to develop a chronology for stalagmite NIED08-05
427 from Niedźwiedzia Cave, which lacks a robust U-Th chronology. Dating with U-
428 Th was attempted and roughly confirms growth during most of the Holocene
429 (present – 9000 yr BP). However, very large errors and numerous stratigraphic

430   inversions, related to low ^{230}Th and unknown initial ^{230}Th/^{232}Th ratios, prevent

431   the construction of a reliable U-Th chronology for this stalagmite.

432

433   A continuous a^{14}C decrease with increasing depth suggests that DCF and growth

434   rate were stationary. Very stable δ^{13}C values (i.e., only a minor long-term trend)

435   support this interpretation (Suppl. Fig. 1). However, the a^{14}C values suggest that

436   a hiatus exists and that growth rate is slightly different before and after the

437   hiatus. The pre- and post-hiatus intervals were therefore considered separately,

438   and two different growth models were constructed.

439

440   The younger (post-hiatus) interval was anchored to 2008 AD (the year of

441   collection). The choice of the anchor point is justified by active dripping of the

442   feeding stalactite and by the presence of the bomb spike in the top 0.4 mm of the

443   stalagmite, both strongly suggesting recent growth. Additionally, the top ln

444   (a^{14}C) value lies within the dataset's 1σ boundary, suggesting no growth rate

445   anomalies (as was the case for HS4, Suppl. Fig. 2). The model reached

446   convergence after four iterations, yielding a calculated mean growth rate of

447   0.0132 ± 0.0012 mm yr^{-1} and a growth interval from 3,833 ± 330 yr BP until

448   2008 AD (Fig. 5). The mean modelled DCF for the post-hiatus interval is 10%

449   (±4%), similar to the DCF calculated from the bomb spike (~14%).

450

451   No independent anchor points exist below the hiatus and the chronology for pre-

452   hiatus growth was developed using the methodology outlined in section 5.3.

453   After three iterations, the model reached convergence, resulting in a mean

454   growth rate of 0.0227 ± 0.00054 mm yr^{-1} over this lower interval. The modelled

455   ages suggest that stalagmite NIED08-05 began growing at 7,961 ± 1,354 yr BP

456   and continued until 4,876 ± 1,354 yr BP, at which point growth stopped for

457   ~1,000 years (Fig. 5). However, because of the large dating uncertainty in this

458   interval, these ages should be considered as only qualitative.

459

460   Because ^{14}C sample powders were obtained at a resolution (every 5 mm) that

461   prevents pinpointing the location of the hiatus, the high resolution LA-ICPMS Mg

462   concentration profile was used to locate its exact depth. At 51.5 mm depth, a

463   gradual increase to very high Mg values within the two ^{14}C samples bracketing

464   the hiatus and coinciding with its probable petrographic expression occurs. This

465   is followed by a very abrupt return to lower values (Suppl. Fig. 1), strongly

466   suggesting that the hiatus is located at 51.5 mm depth. This feature probably

467   reflects decreased rainfall and elevated Mg concentrations derived from high

468   prior calcite precipitation (PCP) or bedrock dissolution (Sherwin & Baldini,

469   2011; Stoll et al., 2012), followed by abrupt growth cessation. Once drip water

470   flow resumed and/or the drip water was again supersaturated with respect to

471   calcite, stalagmite growth re-initiated and calcite Mg concentrations abruptly

472   returned to lower values. Therefore, the exact location of the hiatus was placed

473   at the transition between the highest Mg/Ca point and the return to the baseline.

474   We are aware of the fact that other prominent excursions in Mg/Ca, as well as

475   petrographic layers, exist throughout the record, which could indicate the

476   presence of more growth hiatuses. However, the fact that these excursions are

477   not accompanied by substantial shifts in ^{14}C suggests that these potential

478   hiatuses (if present) were very short lived, and do not have a significant impact

479   on the final chronology.

480

481   ## 7. Evaluation of the age model

482   The procedure presented here provides accurate ^{14}C-based chronologies for

483   some stalagmites where U-Th dating is not possible. Stalagmites amenable to this

484   dating method are characterised by: *i)* stationary DCF without long-term secular

485   variability, ii) stationary growth rate, iii) measurable ^{14}C decay, iv) the presence

486   of an 'anchor point' (an independent age estimate) determined by other means,

487   *iii)* growth during the last ~50ka (the current ^{14}C detection limit). The model

488   provides a mean growth rate for a stalagmite by finding the best fit through all

489   available ^{14}C ages, so small-scale growth rate variability is not resolvable. Two

490   problems arise from this: first, stalagmites that experienced substantial growth

491   rate shifts will have larger chronological uncertainty, potentially impeding the

492   convergence of the iterative process, especially in the case of young stalagmites

493   (i.e., where little ^{14}C-decay has occurred). However, a sufficiently high-resolution

494   ^{14}C dataset could detect and model a growth rate change if the shift was large

495   enough and occurred over a long time period. To test this, we produced a

496 synthetic dataset of a 192 mm long stalagmite where a substantial growth rate
497 change occurs at 77.5 mm depth (0.0613 to 0.0133 mm yr^{-1}) and DCF varies
498 between 12 and 16%. The ln (a^{14}C)-depth relationship highlights the growth rate
499 change in the synthetic dataset (Fig. 6), illustrating that pronounced growth rate
500 changes are detectable using raw ^{14}C data, and that, conversely, the model can
501 confirm stationary growth rates (e.g., as in NIED08-05). Future refinements to
502 the model could be made to fit the sections individually.

503

504 Additionally, and probably more importantly, the anchor point used in the model
505 ultimately affects chronological accuracy. If the anchor point lies in an interval
506 where the growth rate deviates considerably from its mean value, the resulting
507 chronology will over- or under-estimate actual ages. Anchor selection and
508 evaluation of the ^{14}C data is therefore crucial. As shown for stalagmite HS4,
509 apparently small deviations of ln (a^{14}C) data can result in substantial offset of the
510 final chronology, if not considered. Careful evaluation of potential anchor points
511 with respect to their representativity of the entire dataset prior to the modelling
512 procedure is therefore essential (Suppl. Fig. 2), and can help identify the best
513 possible option in cases where multiple anchor points are available.

514

515 The ^{14}C data also highlight longer growth hiatuses, which complicate
516 chronological development for older (pre-hiatus) intervals and introduce very
517 large uncertainties. In the case of NIED08-05, mean pre-hiatus uncertainty is ±
518 1,354 years, essentially providing no chronological control except for a
519 qualitative indication of the general growth interval (i.e., the early Holocene).
520 Therefore, although the technique produces accurate chronologies for stalagmite
521 growth periods with independent anchor points, intervals below hiatuses are
522 currently problematic, and cannot be resolved quantitatively without an
523 additional independent anchor point (e.g. one accurate U-Th age). Other
524 geochemical information (e.g., Mg or δ^{13}C) might provide useful constraints on
525 DCF independent of an anchor point, greatly reducing dating uncertainties below
526 hiatuses.

527

528 As high precision ^{14}C analysis requires much smaller sample sizes than U-Th
529 (especially for young samples), a combination of high-resolution ^{14}C
530 measurements and low-resolution U-Th measurements could provide a powerful
531 tool to develop precise chronologies that have the advantage of high
532 spatiotemporal resolution. This would allow determination of multiple anchor
533 points for the procedure, providing more robust chronologies. Although U-Th
534 remains the method of choice for high-precision dating of stalagmites, such a
535 combined method could provide a powerful additional tool for dating Holocene
536 stalagmites.

537

538 8. Refining the model: the potential for independent DCF estimation
539 Several studies illustrate that vegetation, soil, and hydrological conditions
540 modulate DCF (Genty et al., 2001; Griffiths et al., 2012; Noronha et al., 2014;
541 Oster et al., 2010; Rudzka et al., 2011; Rudzka-Phillips et al., 2013). Griffiths et al.
542 (2012) found strong similarities between DCF and both Mg/Ca and δ^{13}C values in
543 an Indonesian stalagmite from Liang Luar cave. Mg/Ca and δ^{13}C reflect karst
544 hydrological conditions and general hydroclimate (Johnson et al. 2006; Partin et
545 al. 2013; Stoll et al. 2012; Ridley et al. 2015), with drier conditions favouring
546 higher δ^{13}C and Mg/Ca values because of lower soil bioproductivity, increased
547 bedrock dissolution, enhanced degassing, and PCP (Johnson et al. 2006; Griffiths
548 et al. 2012; Tremaine & Froelich 2013). For Liang Luar cave and several other
549 sites, low recharge during dry periods promotes open system conditions (i.e.,
550 where water is in contact with an unlimited reservoir of soil CO_2) within the
551 karst, allowing drip water dissolved inorganic carbon (DIC) to re-equilibrate
552 with soil CO_2 and consequently lowering DCF. Conversely, closed system
553 conditions associated with wetter periods promote higher DCF due to
554 'waterlogging' of the karst leading to reduced exchange between drip water and
555 soil air (Fohlmeister et al., 2010; Griffiths et al., 2012).

556

557 Published Mg/Ca and δ^{13}C data from individual stalagmites often co-vary,
558 implying hydrological control on both parameters (Fig. 7). Independent DCF
559 estimation is theoretically possible on such stalagmites, due to the link between
560 Mg/Ca, δ^{13}C, and DCF. Data from stalagmite HS4 (Heshang cave, China) (Hu et al.,

561 2008; Liu et al., 2013; Noronha et al., 2014) were used to investigate this

562 possibility. Because the original $\delta^{13}C$, Mg/Ca, and DCF were all sampled

563 individually and at different depths, the datasets were resampled and smoothed

564 to bring all parameters on the same timescale and reduce sampling bias. $\delta^{13}C$ and

565 Mg/Ca are significantly correlated ($r^2=0.68$), and smoothing markedly improves

566 the correlation ($r^2=0.91$, $p<0.001$). DCF and $\delta^{13}C$ are weakly correlated ($r^2=0.13$

567 for the original data; $r^2=0.29$, $p<0.001$, for smoothed data), and similarly DCF and

568 Mg/Ca ($r^2=0.21$, for the original data; $r^2=0.37$, $p<0.001$, for smoothed data).

569 Higher (lower) DCF values correspond to lower (higher) Mg/Ca and $\delta^{13}C$ values

570 (Fig. 8). However, other factors such as contributions from the soil/vegetation

571 system must drive a significant portion of the signal, impacting both $\delta^{13}C$ and

572 DCF (Fohlmeister et al., 2011; Oster et al., 2010).

573

574 Considering only karst processes, the distance of a coupled Mg/Ca-$\delta^{13}C$

575 measurement from the point of initial DIC (before the start of limestone

576 dissolution) should reflect DCF (Fig. 8). When applied to the HS4 dataset, this

577 approach estimates DCF moderately well, although the amplitude of variation in

578 the modelled results is much lower than measured, due to the smoothing of the

579 $\delta^{13}C$ and Mg/Ca datasets (Suppl. Fig. 3). However, DCF varies considerably

580 depending on cave and climatic settings (Genty et al. 1999), so that DCF from a

581 single stalagmite (e.g., HS4) cannot be used to calibrate samples from other

582 locations. Available published data suggest that very different and sample-

583 specific relationships between DCF and $\delta^{13}C$ exist, and no clear pattern related to

584 climate or cave settings is apparent (Suppl. Fig. 4). However, many of the

585 available datasets are limited in size, and the relationships presented are not

586 statistically significant.

587

588 These results illustrate that constraining DCF via Mg/Ca, and $\delta^{13}C$ data is

589 potentially attainable, but the underlying processes and the interdependencies

590 between parameters remains elusive. The lack of available data at sufficiently

591 high resolution and in many cases sampling bias, such as not measuring all

592 proxies on the same aliquot of powder, contribute to the uncertainty. Although

the paucity of robust datasets precludes reaching any firm conclusions with respect to these observations, our work and previous studies on DCF and soil-cave carbon transfer (e.g. Genty et al., 2001; Rudzka et al., 2011; Rudzka-Phillips et al., 2013) suggest that climate does influence DCF. Tropical sites where temperature is high throughout the year but rainfall is very seasonal (e.g., Liang Luar cave) might produce different DCF responses than temperate sites where both rainfall and temperature may vary seasonally (e.g., Niedźwiedzia cave). It is likely that specific climate conditions at a cave site result in a continuum of systems between tropical and temperate end members, resulting in different DCF-δ^{13}C relationships.

9. Corral the chronology for DCF variations

Our model estimates DCF, which can help adjust the final chronology for subtle offsets from the constant growth trend. The residual DCF (i.e., the deviation of each calculated DCF data point from the mean DCF) is used to calculate the correction in years for each data point (using the modeled ages). These corrections are applied to the modelled chronology, resulting in an "DCF corrected" chronology that is compatible with existing chronology development software (e.g., COPRA (Breitenbach et al., 2012), StalAge (Scholz and Hoffmann, 2011)). Dating uncertainty is comprised by the modelling uncertainty plus the DCF estimation error. Applying this correction to the modelled HS4 chronology reproduces long-term trends apparent in the U-Th based chronology (Fig. 9a and b). The correction does introduce some age reversals, particularly in the older and highly resolved intervals of HS4; the chronology was therefore downsampled to remove inversions prior to COPRA treatment.

The model can reliably estimate DCF (Fig. 4c), suggesting that a common process controls both growth rate and DCF, possibly recharge conditions. Growth rate and DCF in stalagmite HS4 appear weakly anti-correlated ($r^2 = 0.14$), and it is possible that elevated rainfall at the Heshang cave site encourages closed-system conditions and increased DCF, while simultaneously reducing the DIC of the percolation water and stalagmite growth rate. We emphasise that although the model appears to yield reasonable DCF estimates, the reasons why DCF is linked

to growth rate are unclear. Furthermore, although the DCF correction appears to work for HS4, its applicability to non-monsoonal sites where temperature may play a larger role in DCF determination is unknown. We present a provisional DCF-corrected chronology for NIED08-05, but emphasise that whether the relationship observed in HS4 is transferrable to NIED08-05 is not known. Despite these uncertainties, the DCF corrected NIED08-05 chronology shows only very minor differences to the uncorrected chronology, consistent with the stationary $\delta^{13}C$ and the stable, slow growth rate of the sample.

10. Summary and conclusions

This study describes a novel approach to develop chronologies for stalagmites using ^{14}C. The model introduced estimates the average growth rate of a stalagmite from ^{14}C ages, taking into account past variations in atmospheric ^{14}C, and anchors the chronology to a point of known age. The model does not require DCF estimation, which is advantageous considered that DCF remains an enigmatic parameter with respect to its influencing factors. Application of the model on a U-Th dated stalagmite, a synthetic dataset, and a stalagmite without a U-Th chronology, demonstrates that this method produces reliable chronologies provided the sample's long-term growth rate was regular and DCF was stationary. The choice of the anchor point is crucial and ultimately defines chronological accuracy. This currently leads to two main issues:

- Deviations from the long-term growth rate close to the anchor point will lead to chronological bias, as illustrated in the case of stalagmite HS4. However, measured ^{14}C ages, particularly when highly resolved, can reveal potentially anomalous growth rate shifts, and justify anchor point selection.

- Depositional hiatuses result in very large chronological uncertainty in the pre-hiatus interval of stalagmite growth, if no independent anchor point exists. The magnitude of the error (>1000 yr) results in virtually no chronological control for those intervals, and provides only qualitative information.

659

660 Future work may overcome these limitations, possibly by coupling the approach

661 described here with other lines of geochemical information (e.g., Mg/Ca and δ^{13}C

662 data) that may provide independent constrains on DCF. Although still being less

663 precise than dating using the U-Th method, this current model as presented

664 provides chronologies for stalagmites meeting certain criteria, and represents a

665 useful alternative in cases where more established techniques are not applicable,

666 or in combination with U-Th dating.

667

676

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865

866   Figure captions:

867 **Figure 1:** Map of Niedźwiedzia Cave and location of the cave in SW Poland (insert). The
868 stalagmite NIED08-05 sampling location is indicated in red.

869

870 **Figure 2:** Results of the ^{14}C analysis on stalagmite NIED08-05. A: [14]C ages vs. depth from graphite
871 analysis are shown in black; error bars denote 1σ errors. A scan of the stalagmite is shown on the
872 far right, including indication of the sampling locations for ^{14}C and the location of the hiatus. B:
873 results of high-resolution GIS measurements for ^{14}C across the top 1mm of stalagmite NIED08-
874 05. Four different tracks were milled and analysed (shown in different colors and symbols), the
875 average of all tracks is shown in black. Three of four profiles show a significant increase in a[14]C in
876 the top 0.5 mm, indicating the presence of bomb carbon and confirming recent growth of
877 NIED08-05.

878 **Figure 3:** Flowchart illustrating the modelling steps in MATLAB for the construction of
879 chronologies using [14]C. Small figures show some key steps in the modelling procedure. A)
880 Conceptual figure illustrating the exponential decay pattern in measured ^{14}C data, a prerequisite
881 for the successful construction of an age model. B) Calibration of pre-hiatus ages (when no
882 independent anchor point is available). The growth rate line (red line) is positioned at the
883 youngest of all calibrated ages and then shifted through time until the best fit (i.e. point with
884 highest probability for all ages) is found. 95% confidence intervals from calibration and DCF
885 estimation are shown in light pink. C) While shifting the line through the probabilities, a new
886 probability density distribution is established with respect to the youngest position, which
887 reaches convergence after a few iterations of the model. The weighted mean (red line) of the
888 probability density distribution is determined and used to find the best placement of the growth
889 rate.

890 **Figure 4:** Modelling results for stalagmite HS4 from Heshang Cave, China. A: published age-depth
891 relationship derived from the U-Th age model (black line), with 95% confidence bounds in grey
892 (Hu et al., 2008; Noronha et al., 2014). Blue symbols show the measured, uncorrected and
893 uncalibrated ^{14}C ages (Noronha et al., 2014). The red line indicates the age model derived from
894 ^{14}C using the anchor point at 43 cm from top, with 95% confidence interval (this study). The
895 dashed blue line is the modelled growth rate that would result if the anchor point was placed at
896 the 24.6 cm from top (beginning of the ^{14}C dataset), where the actual growth rate deviates from
897 the long-term mean (and ^{14}C ages are anomalous). This anchor point would result in a less
898 accurate chronology, due to the bias from the ^{14}C ages. B: Expanded view of the top of the HS4
899 age model. The anchor point (fourth ^{14}C age, 43 cm from top) is indicated. C: DCF vs. depth plot.
900 The black line indicates DCF derived from U-Th ages, the red line shows the DCF derived from
901 our model anchored at 43 cm from top, and the blue dashed line is the modelled DCF using the
902 anchor point at 24.6 cm from top.

903

Figure 5: Chronology developed for stalagmite NIED08-05 from Niedźwiedzia Cave, Poland. Blue symbols show the measured ^{14}C ages (25 from graphite AMS analysis and one additional from GIS analysis averaging all measurements taken at 0.3 mm from top), and the anchor point used (2008 = year of collection). The red line indicates the best fitting growth rate derived from the presented model, with 95% confidence intervals. The depositional hiatus at 51.5 mm depth is marked by the grey dashed line. Very large age uncertainties in the pre-hiatus interval (due to the lack of an independent anchor point), result in this being only a qualitative chronology. It is also apparent that the uncertainty estimates for the pre-hiatus chronology are conservative, since most measured ^{14}C ages are younger than the maximum error. This problem could be solved by applying a stalagmite-specific threshold for the uncertainty, so that the resulting modelled chronology is younger than the measured ^{14}C ages (not shown).

Figure 6: ln (a[14]C)-depth relationships for stalagmite HS4 (blue diamonds), NIED08-05 (red squares) and a synthetic dataset showing a large and prolonged change in growth rate (grey crosses). The change in growth rate is clearly visible as a change in the slope of the synthetic dataset. This shows that major changes in growth rate can be detected in stalagmites with the procedure described in this study, and corroborates our assumption that NIED08-05 experienced relatively constant growth rates and is a suitable sample for the method described in this study.

Figure 7: Compilation of Mg/Ca vs. $\delta^{13}C$ relationship for published stalagmite datasets from different cave systems. Abbreviations indicate the cave system: NIED- stalagmite NIED08-05, Niedźwiedzia cave, Poland, (this study); CC – Stalagmite CC-Bil, Crag cave, Ireland (McDermott et al., 1999); PNC – stalagmite PN95, Pere Noel cave, France (Verheyden et al., 2000); BF – Brown's Folly mine, England (Baldini et al., 2005); BR – flowstone RL-4, Buca della Renella, Italy (Drysdale et al., 2006); HC – stalagmite HS4, Heshang cave, China (Hu et al., 2008; Liu et al., 2013); LLC – stalagmite LR06-B1, Liang Luar cave, Indonesia (Griffiths et al., 2010). The regression lines showing the best fit are shown for each stalagmite, highlighting different Mg/Ca vs. $\delta^{13}C$ relationships depending on dripwater degassing rate, as described by Johnson et al. (2006).

Figure 8: Relationships between $\delta^{13}C$, Mg/Ca and DCF in stalagmite HS4 from Heshang cave, China (Hu et al., 2008; Liu et al., 2013; Noronha et al., 2014). DCF decreases with increasing $\delta^{13}C$ and Mg/Ca, and could theoretically be quantified this way.

Figure 9: A) Offset corrected chronology for stalagmite HS4. Measured ^{14}C ages (blue) are compared to the U-Th chronology (black) and to the final corrected ^{14}C-derived chronology (red, uncertainty in pink). B) Detail of the HS4 chronology. C) Offset corrected chronology for stalagmite NIED08-05. Measured ^{14}C ages (blue) and final corrected ^{14}C-derived chronology (red, uncertainty in pink) are shown.

Suppl. Figure 1: A) $\delta^{13}C$ record for stalagmite NIED08-05. The dashed grey line indicates mean $\delta^{13}C$, the black line is the linear trendline of the dataset. Variation in $\delta^{13}C$ is relatively small (average: -7.48‰, σ: 1.17), and there is only a negligible long-term trend in the dataset, corroborating the assumption that variations in DCF were small as well. B) High resolution laser ablation Mg/Ca record for NIED08-05. Black dots indicate the position of ^{14}C ages. The dashed grey line shows the location of the hiatus at the local maximum Mg/Ca value. The gradual increase in Mg/Ca, followed by a sharp decrease back to baseline values is interpreted as increasingly dry conditions and enhanced PCP, followed by a growth stop until water started flowing again (with lower Mg/Ca). Therefore, the exact depth of the hiatus in NIED08-05 is placed at 51.5 mm from top.

Suppl. Figure 2: Detrended ln ($a^{14}C$) data for stalagmites NIED08-05 and HS4 highlighting the importance of $a^{14}C$ values representative of the entire dataset at the anchor point. The top panel shows ln ($a^{14}C$) values for NIED08-05, including the mean and standard deviation. It is apparent that the top $a^{14}C$ value lies within the stalagmites 1σ boundary, justifying the choice of the anchor point at the top of the sample. In the lower panel, ln ($a^{14}C$) values, their mean and standard deviation for stalagmite HS4 are shown. The top three ln ($a^{14}C$) values are anomalous (outside of 1σ boundaries) and will therefore result in a chronological bias if used. The fourth ln ($a^{14}C$) value, however, is within the 1σ boundaries and can be used. This procedure should always be applied as a quality control for the chronology, and could greatly help in choosing the best anchor point if multiple possible anchors exist.

Suppl. Figure 3: Example of DCF modelling using Mg/Ca vs. $\delta^{13}C$ from stalagmite HS4, Heshang cave (Hu et al., 2008; Liu et al., 2013; Noronha et al., 2014), and re-applying the relationship on the same stalagmite. DCF calculated from U-Th chronology (blue line) and DCF estimated from the Mg/Ca vs. $\delta^{13}C$ relationship (red line) are shown. It is apparent that DCF variations can be modelled to a certain extent using this approach; however, the estimated DCF is strongly muted with respect to the actual DCF, due to the smoothing processes prior to the modelling. At present, this approach cannot be widely applied to stalagmites with unknown DCF, as the Mg/Ca vs. $\delta^{13}C$ – DCF relationship is cave-specific and difficult to quantify for the general case.

Suppl. Figure 4: Compilation of DCF vs. $\delta^{13}C$ relationships for published datasets from different caves. Positive correlation (red symbols): HC - stalagmite HS4, Heshang cave, China (Hu et al., 2008; Noronha et al., 2014); LGC - stalagmite GAR-01, La Garma cave, Spain (Rudzka et al., 2011); VC - stalagmite Vil-stm1, Villars cave, France (Genty et al. 1999); SOC - stalagmite So-1, Sofular cave, Turkey (Rudzka et al., 2011); Negative correlation (blue symbols): HSLC - stalagmites Han-stm1 and Han-stm5, Han-sur-Lesse cave, Belgium (Genty et al., 1999, 1998); UTC - stalagmites SU-2, SU-96-1, SU-96-7, Uamh-an-Tartair cave, Scotland (Genty et al., 2001); SC - stalagmite Sal-stm1, Salamandre cave, France (Genty et al., 2001); no correlation (green symbols): MC -

981   stalagmite MC3, Moaning cave, California (Oster et al., 2010); LLC - stalagmite LR06-B1, Liang

982   Luar cave, Indonesia (Griffiths et al., 2012); EPC - stalagmite Candela, El Pindal cave, Spain

983   (Rudzka et al., 2011); HUC - stalagmite H-82, Hulu cave, China (Southon et al., 2012). High p-

984   values for most of the correlations indicate their low significance, and therefore most of these

985   relationships should be carefully evaluated. Datasets with more paired DCF-δ^{13}C measurements

986   could help improve our understanding of the governing factors for both proxies at specific sites

987   and regionally/globally.

988

989   **Table 1:** Results from the high precision graphite AMS ^{14}C analysis for stalagmite NIED08-05.

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991   **Suppl. Table 1:** Results from the high-resolution tracks of the top 1 mm of stalagmite NIED08-05.

992   Analyses were conducted using a Gas Ion Source (GIS).

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