Radiocarbon Evidence for Decomposition of Aged Organic Matter in the Vadose Zone as the Main Source of Speleothem Carbon

Alexandra L Noronha ^{a,1,*}, Kathleen R Johnson^a, John R Southon^a,
Chaoyang Hu^b, Jiaoyang Ruan^{b,2}, Staryl McCabe-Glynn^a

^a*Department of Earth System Science, University of California, Irvine, 92697, USA*

^b*State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, 430074, PR China*

Abstract

Several recent studies have used records of the radiocarbon (^{14}C) bomb peak in speleothems to inversely model the soil $\alpha^{14}\text{CO}_2$ and the age distribution of soil organic material (SOM) above caves, in part to investigate the potential of speleothems as sensitive records of past SOM dynamics. The results of these modeling studies have suggested that soil CO_2 at karst sites is derived primarily from the decomposition of SOM with turnover times on the order of decades to centuries. This result is in stark contrast with observations of soil $\alpha^{14}\text{CO}_2$ at non-karst sites, which indicate that soil CO_2 is derived primarily from root respiration and decomposition of SOM with much shorter turnover times. This discrepancy suggests that SOM in karst settings may have a very different age distribution than sites that have been studied previously and/or that soil CO_2 is not the main source of speleothem carbon. To

*Corresponding author: anoronha@uci.edu

¹Now at, Jackson School of Geosciences, University of Texas at Austin, 78712, USA

²Now at, Laboratoire des Sciences du Climat et de l'Environnement (LSCE), CNRS/CEA/UVSQ, L'Orme des Merisiers, 91191 Gif-sur-Yvette Cedex, France

help resolve this discrepancy, we present an improved inverse model which we use to estimate the age of CO₂ above several caves. We also present results from a detailed case study of soil carbon dynamics at Heshang Cave, China. This work demonstrates that SOM in karst sites may be much older than SOM in non-karst soils that have been studied previously, but that CO₂ produced in the shallow soil zone is unlikely to be the main source of speleothem carbon. A review of the literature suggests that the most likely explanation for the aforementioned discrepancy is that decomposition of down-washed SOM in the vadose zone is the dominant source of speleothem carbon.

Keywords:

speleothems, carbon cycle, radiocarbon, soil carbon, carbon isotopes

1. Introduction

Speleothem calcite carbon isotope records contain valuable paleoenvironmental information, but are largely under-exploited as interpretation of these records has proved challenging due to the potential for large variations in the carbon isotope ratio of the source material, as well as the numerous processes during dissolution and precipitation of calcite which alter carbon isotope ratios. While much work has been done to understand the physical and chemical controls on speleothem carbon isotope ratios (e.g. Hendy, 1971; Genty et al., 2001; Mickler et al., 2004; Spötl et al., 2005; Fairchild et al., 2006; Dreybrodt, 2008; Frisia et al., 2011), the basic conceptual model of the sources of speleothem carbon which suggests that it is derived from two main sources - soil CO₂ and carbonate bedrock - has remained largely unchanged. Given the large difference between carbon isotope ratios of soil CO₂ ($\delta^{13}\text{C}$

≈ -10 to -27‰ , $a^{14}\text{C} \geq 100$ pMC) and carbonate bedrock ($\delta^{13}\text{C} \approx 0\text{‰}$, $a^{14}\text{C} = 0$ pMC), where carbonate dissolution occurs along the soil to bedrock profile is the one of the most important factors in determining dripwater dissolved inorganic carbon (DIC) isotope ratios. If carbonate dissolution occurs in the soil zone where water is simultaneously in contact with both soil CO_2 and carbonates in the soil, continuous equilibration between soil water DIC and soil CO_2 occurs during carbonate dissolution. In this scenario, which is referred to as open-system dissolution, DIC isotope ratios are determined by the soil CO_2 isotope ratios. In the alternative scenario, closed-system dissolution, carbonate dissolution does not begin until waters that have equilibrated with soil CO_2 enter the pore space and fractures of the carbonate bedrock where carbonate dissolution occurs isolated from CO_2 . Closed-system dissolution leads to a DIC isotope ratio determined by an approximately 50/50 mixture of soil CO_2 and carbonate bedrock, as reaction stoichiometry dictates that dissolution of one mole of CaCO_3 is necessary to neutralize one mole of dissolved CO_2 (Hendy, 1971). In natural systems carbonate dissolution usually falls somewhere between the two end member scenarios.

Measurements of $a^{14}\text{C}$ are reported corrected for isotope fractionation (Stuiver and Polach, 1977), allowing for interpretation of speleothem $a^{14}\text{C}$ as a reflection of only the carbonate dissolution regime and the soil $a^{14}\text{CO}_2$. Soil CO_2 is a mixture of atmospheric CO_2 , CO_2 produced by root respiration, and CO_2 produced by decomposition of aged soil organic matter (SOM). Therefore speleothem calcite $a^{14}\text{C}$ is affected by the decomposition of aged SOM and is influenced by changes in SOM dynamics. Under the assumption the carbonate dissolution regime at a site can be taken to be

relatively invariable over the twentieth century, several recent studies have interpreted speleothem-based $a^{14}\text{C}$ records of the twentieth century atmospheric $a^{14}\text{C}$ bomb peak as records of soil $a^{14}\text{CO}_2$ (e.g. Genty and Massault, 1999; Fohlmeister et al., 2010; Fohlmeister et al., 2011a; Griffiths et al., 2012; and Rudzka-Phillips et al., 2013). These studies have employed a simple soil carbon model to inversely model the age distribution of SOM at karst sites using speleothem $a^{14}\text{C}$ bomb peak records, in part to investigate the potential of speleothems as sensitive recorders of past soil carbon dynamics.

The results of these studies have suggested that karst soil CO_2 has pre-bomb mean ages ranging from 42-488 years. These predictions are at odds with observations of soil CO_2 ages in non-karst sites, which are typically on the order of years, with CO_2 derived from root respiration and decomposition of organic matter with a turnover time of <1 yr comprising 50-60% of soil CO_2 in boreal and temperate sites and $>80\%$ in tropical sites (Trumbore, 2000). To date there is only one published measurement of soil $a^{14}\text{CO}_2$ in karst terrain, from Cave of the Bells, Arizona, which was indistinguishable from contemporaneous atmospheric $a^{14}\text{CO}_2$ (Breecker et al., 2012). This discrepancy between observed soil CO_2 ages and the predicted mean age of soil CO_2 in karst settings based on the shape of the bomb peak in speleothems suggests that:

1. soil carbon dynamics in karst settings may be very different than those in sites that have been studied previously and/or
2. soil CO_2 is not the main source of speleothem carbon.

Both of these hypotheses have major implications for interpretation of speleothem $\delta^{13}\text{C}$ and $a^{14}\text{C}$ records, as well as for understanding the role of karst soils in

64 the global carbon cycle.

65 This study seeks to resolve the cause of the discrepancy between obser-
66 vations of soil CO₂ and speleothem bomb peak records through observations
67 of soil $\delta^{13}\text{C}$ and $\alpha^{14}\text{C}$ in Heshang Cave, China. This work presents a new
68 bomb peak record from speleothem HS4 from Heshang Cave, China and a
69 geochemical box model that builds on previous attempts to infer the age of
70 the source of speleothem carbon. This model is used to evaluate the age
71 spectrum of SOM required to produce the speleothem bomb peak at HS4
72 and 13 other speleothem bomb peak records in the literature (Table 1).

73 2. Site and sample description

74 Heshang Cave is located in the Hubei Province of China (30.44 °N, 110.42 °E,
75 294 m asl), ~100 km west of the city of Yichang in the middle reaches of
76 the Yangtze Valley. The cave is 250 m long, roughly horizontal, and overlain
77 with ~400 m of Cambrian dolomite. The hillside has a very thin soil cover
78 of 5-30 cm of well-developed soil derived from dolomite bedrock, wind-blown
79 silicate dust, and organic matter from the dense local vegetation. The cave
80 has a large entrance with a height of about 20 m and is well ventilated. An-
81 nual average temperature in the study area is ~18 °C, with daily averages
82 ranging from 5 °C to 28 °C. Unlike many caves, cave temperature at Heshang
83 Cave exhibits a seasonal cycle, ranging from 16 °C to 22 °C, lagging the local
84 temperature cycle by 2-3 months (Johnson et al., 2006).

85 HS4 is a 2.5 m long annually banded stalagmite that was actively form-
86 ing when it was collected from Heshang Cave in 2001. The HS4 site is
87 located ~150 m from the entrance of the cave, and was still actively dripping

when this study was undertaken. Records of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and $a^{14}\text{C}$ covering the Holocene measured on HS4 have been previously reported by Hu et al. (2008b), Liu et al. (2013), and Noronha et al. (2014). The age model for the final 150 years of stalagmite growth is well-defined by annual layer counting (Hu et al., 2008b). Average transit time of water from the infiltration zone to the drip site at HS4 has been shown to be <1 yr based on the seasonal cycle of drip water $\delta^{18}\text{O}$ (Johnson et al., 2006).

3. Methods

3.1. *Speleothem calcite*

The stalagmite, HS4, was previously cut in half parallel to the growth axis and the surface was polished to reveal laminations consisting of sub-mm scale light and dark couplets, which has been shown to be annual (Hu et al., 2008b). HS4 calcite is milky, opaque, and porous, with a fabric dominantly characterized as open columnar using the terminology of Frisia and Borsato (2010). Speleothem calcite for the twentieth century record of $a^{14}\text{C}$ was drilled parallel to growth lamina as powder using a New Wave Research micromill. The age model for the twentieth century is based on annual layer counting described in Hu et al. (2008a).

Speleothem calcite samples were pretreated with a 10% HCl leach, and subsequently hydrolyzed in 85% H_3PO_4 . After conversion to CO_2 , calcite samples were converted to graphite via iron catalyzed hydrogen reduction following standard protocols as described in Santos et al. (2007).

110 3.2. Soil organic matter

111 Because access to the recharge zone is difficult, all soil sampling was
112 conducted at a site near the entrance of the cave. One expedition to the
113 recharge zone in August 2004 described the soil at the recharge zone as
114 30 cm deep with reasonably dense vegetation (Hu et al., 2008a), which is
115 consistent with the site at which sampling was conducted. Soil was collected
116 from a site near the cave entrance during the field trip in March 2010 in 5
117 cm depth intervals until the bedrock was reached. Prior to measurement,
118 visible roots were picked out and soil samples were dried in an oven at 65 °C
119 for 12-24 hrs.

120 SOM was analyzed for $\delta^{14}\text{C}$ and $\delta^{13}\text{C}$ in both bulk and size fractionated
121 form. Size fractions used are defined as coarse sand ($>425\ \mu\text{m}$), medium
122 sand ($425\text{-}250\ \mu\text{m}$), fine sand ($250\text{-}63\ \mu\text{m}$), and silt and clay ($<63\ \mu\text{m}$). All
123 SOM samples were ground to powder because of the presence of dolomite,
124 which is more resistant to acid hydrolysis than calcite. Soil samples were
125 acidified with 1N HCl overnight to remove carbonate. Following acidification,
126 SOM samples were converted to CO_2 via combustion in evacuated sealed
127 quartz tubes at 900 °C for 3.5 hrs, cryogenically purified, and graphitized via
128 hydrogen reduction.

129 3.3. Soil CO_2

130 Soil CO_2 from depth was sampled using stainless steel gas wells, which
131 were installed in the soil at a variety of depths. CO_2 was sampled 12-24 hrs
132 after installation of wells, and wells removed at the end of each field trip.
133 Wells were flushed with soil gas following installation. $p\text{CO}_2$ was measured
134 with a portable infra-red gas analyzer (LI-820 CO_2 Analyzer, LICOR Inc.,

135 Lincoln, NE, USA). When $p\text{CO}_2$ was above 2,000 ppm sample was collected
136 in 0.5 L evacuated stainless steel canisters to achieve the in desired sample
137 size of ~ 1 mg carbon. When sampling with stainless steel canisters, flow was
138 restricted by stainless steel capillary ($0.010 \text{ cm} \times 0.063 \text{ cm} \times 30 \text{ cm}$, Fisher).
139 When $p\text{CO}_2$ was below 2,000 ppm, samples were collected by pumping for
140 ~ 15 minutes through steel traps containing activated molecular sieves ($13 \times$
141 powder-free 133 8/12 beads, Grace) using a diaphragm pump (Hargraves
142 Fluidics BTC Series miniature). The very large sample volumes necessary,
143 especially when pumping was required, render the samples representative of
144 a depth integrated average instead of representative of the depth at which
145 they were collected. Samples were filtered through Drierite desiccant (W.A.
146 Hammond Drierite Co. Ltd., Xenia, OH, USA), and flow rate was measured
147 as 1 L/min. One sample of atmospheric CO_2 was collected in a steel trap at
148 the cave site during the field trip in March 2010. To prevent $\delta^{14}\text{C}$ memory
149 effects traps were pre-conditioned by baking at 630°C for 45 mins under
150 vacuum.

151 Soil CO_2 samples collected in evacuated flasks were extracted on line, and
152 CO_2 collected in steel traps was released for isotopic analysis by baking the
153 traps at 475°C . All CO_2 samples were cryogenically purified and converted
154 to graphite via the sealed tube zinc reduction method (Xu et al., 2007).

155 3.4. Tree ring record of atmospheric $\delta^{14}\text{C}$

156 A pine tree of unknown species from a location across the river from
157 Heshang Cave was felled in July 2011 to create a record of local atmospheric
158 $\delta^{14}\text{C}$. A tree that was located ~ 50 m away from a low traffic road was selected
159 to avoid bias from point sources of fossil fuels. The 25 rings were assumed

160 to be annual, and were counted to create a calendar age model for a record
161 of local atmospheric $a^{14}\text{C}$. The tree appeared to be colonized by blue-stain
162 fungus, but a study by English et al. (2011) showed that blue-stain fungus
163 colonization did not detectably alter whole wood or α -cellulose $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$,
164 suggesting that translocation effects are minimal. The tree was sampled at an
165 annual resolution, and pretreated to α -cellulose using the methods described
166 in Southon and Magana (2010). Briefly, ~ 30 mg of shaved wood was treated
167 with a standard acid-base-acid treatment, followed by a bleaching treatment
168 to isolate hollocellulose, and a strong base treatment to isolate α -cellulose.
169 All samples were treated in individual 13 mm glass test tubes.

170 Tree cellulose was converted to CO_2 via combustion in evacuated sealed
171 quartz tubes at 900°C for 3.5 hrs, cryogenically purified, and graphitized by
172 iron catalyzed hydrogen reduction.

173 3.5. Isotope analysis

174 After conversion to graphite, all $a^{14}\text{C}$ measurements were made at Uni-
175 versity of California Irvine on a NEC Compact (1.5 SDH) AMS system, using
176 six aliquots of Oxalic Acid I as the normalizing standard. Each mg-sized car-
177 bon sample was measured multiple times (typically 8 to 15 runs) over a 24
178 hr period.

179 $\delta^{13}\text{C}$ were measured by isotope ratio mass spectrometry at University of
180 California, Irvine. Measurements on samples collected as gas were made on
181 splits of CO_2 injected into He-filled vials to a target concentration of 3,500
182 ppm CO_2 using a Thermo Finnigan DeltaPlus equipped with a GasBench II
183 autosampler. $\delta^{13}\text{C}$ measurements on SOM were made by placing acidified,
184 ground soil in tin capsules that are combusted to CO_2 and analyzed by

185 isotope ratio mass spectrometry on a Thermo Finnigan DeltaPlus equipped
 186 with a Fisons NA1500NC elemental analyzer. Replicate measurement errors
 187 on known standards were approximately $\pm 0.1\%$.

188 3.6. Soil Carbon Model

Previous attempts to evaluate the age distribution of soil carbon above caves using speleothem bomb peak records (e.g. Genty and Massault, 1999; Fohlmeister et al., 2010; Fohlmeister et al., 2011a; Griffiths et al., 2012; and Rudzka-Phillips et al., 2013) estimated the radiocarbon activity of soil CO₂ ($a^{14}C_g$) using the equations originally proposed by Genty and Massault (1999):

$$a^{14}C_g = C_1 (a^{14}C_{atm-y_1}) + C_2 (a^{14}C_{atm-y_2}) + C_3 (a^{14}C_{atm-y_3})$$

where C_1 , C_2 , and C_3 are the relative proportion of three SOM pools such that:

$$C_1 + C_2 + C_3 = 1$$

and the $a^{14}C_{atm-y_j}$ is the $a^{14}C$ of the pool approximated by a moving average, with a window, y , equal to the turnover time of the SOM pool:

$$a^{14}C_{atm-y} = \frac{\sum_{i=1}^y a^{14}C_{atm_i}}{y}$$

189 Approximating SOM $a^{14}C$ via moving average results in modeling SOM pools
 190 as heterogenous, and decomposition of SOM as a zero-order process. That
 191 is, a moving average assumes the inputs to the SOM pool from each year
 192 contribute a constant and equal mass to the soil CO₂ at every time step
 193 until the inputs are exhausted after y time steps. This deviates from typical

194 geochemical box modeling approaches, where SOM within a given pool is
195 homogenized, and the homogenized pool decomposes as a first-order process
196 (Six and Jastrow, 2002). Additionally, these models did not include a pool
197 with a turnover time of one year, essentially allowing for the possibility of soils
198 where no root respiration or mixing with atmospheric CO₂ was occurring.

199 Accordingly this study builds on these previous works by modeling SOM
200 using a more typical geochemical box modeling approach with a total of 4
201 boxes - 3 homogenous SOM pools which decompose as a first-order process,
202 and a pool with a turnover time (τ) equal to one year which represents
203 root respiration, decomposition of organic matter of annual age, and any
204 contribution from atmospheric CO₂. This model is based on the steady-
205 state time dependent model presented by Trumbore (1993) and described
206 in detail by Gaudinski et al. (2000). The model is implemented using the
207 Matlab Global Optimization solver tool, **MultiStart**, to generate 1,000 sets
208 of random start points for the parameters P_j and τ_j , where $j=1:4$ and P_j
209 represents the relative proportions of four SOM pools, and τ_j is the associated
210 turnover time for each SOM pool. The parameters P_j are constrained to
211 satisfy the requirements, $\sum P_j = 1$ and $0 < P_j < 1$. The first pool is fixed
212 as an annual pool (i.e. $\tau_1 = 1$), and the rest of the pools are constrained
213 to represent pools with turnover times on the order of years to decades,
214 centuries, and millennia (i.e. $1 < \tau_2 < 100$; $100 < \tau_3 < 1,000$; $1,000 < \tau_4 <$
215 $10,000$). The model is initialized by starting calculations 100 years before
216 the year of deposition of the first speleothem $a^{14}\text{C}$ measurement, and setting
217 the initial $a^{14}\text{C}$ of each SOM pool equal to the average of the decay corrected
218 $a^{14}\text{C}$ of the atmosphere over the last τ years.

These parameters (P_j) are taken to represent the relative proportions and turnover times of SOM pools, and the relative proportion of the soil CO_2 fluxes are derived from them, instead of estimating the relative proportions of SOM contributions to the soil CO_2 directly. This distinction is highlighted because, in part due to the use of the moving average approach to estimating $a^{14}\text{C}$ of SOM pools, the language in previous studies was ambiguous and at times erroneously implied that the contribution of a SOM pool to the total amount of SOM is equal to the contribution of CO_2 of that pool to the soil CO_2 e.g. in a soil that is a 50/50 mixture of SOM pools with $\tau = 5$ yr and $\tau = 100$ yr, both pools are assumed to produce the same mass of CO_2 . In reality, at steady state, making the assumption that the only loss pathway for a SOM is decomposition, the size of a flux of CO_2 from a SOM pool is a function of its turnover time τ :

$$F = \frac{M}{\tau}$$

219 where F is the flux from a pool, and M is the mass of the pool. Therefore
 220 the steady state loss of the pool with $\tau = 5$ yr will be $1/5$ of its mass, and
 221 the steady state loss of the pool with $\tau = 100$ yr will be $1/100$ of its mass,
 222 meaning that the flux from the pool with a τ of 5 years will make up 95%
 223 of the soil CO_2 . In this manuscript, the relative parameters representing the
 224 proportions of the CO_2 fluxes are referred to as F_j .

After calculating the steady state fluxes from the SOM pools and their relative contributions to the CO_2 , the $a^{14}\text{C}$ of the SOM pool at each time step is calculated via:

$$a^{14}C_{jy_i} = a^{14}C_{jy_{i-1}} \left(1 - \frac{1}{\tau_j}\right) (e^{-\lambda}) + a^{14}C_{atm_{y_i}} \left(\frac{1}{\tau_j}\right)$$

225 where i is the current model step year and j refers to the SOM pool 1-4,
 226 and λ is radiocarbon decay constant using a 5,370 yr half life. The inputs
 227 to all pools have the $a^{14}\text{C}$ of the atmosphere at the given model step year
 228 $(a^{14}\text{C}_{atm_{y_i}})$.

Fluxes are then multiplied by the $a^{14}\text{C}$ of the pools at the model step and summed together to find the $a^{14}\text{CO}_2$ at the model step:

$$a^{14}\text{CO}_{2(y_i)} = \sum_{j=1}^4 F_j (a^{14}\text{C}_{j_{y_i}})$$

229 Once the entire twentieth century soil $a^{14}\text{CO}_2$ record is calculated from the
 230 start points generated, the offset between the pre-bomb interval ($y < 1955$)
 231 of the calculated curve to the measured speleothem bomb peak curve to
 232 estimate the contribution from ^{14}C -free sources is found, and this difference is
 233 subtracted from the entire curve. After this step, the residuals are computed
 234 and using the Matlab optimization function, **fmincon**, the parameters that
 235 yield the best fit with the measured speleothem bomb peak is iteratively
 236 calculated from each set of start points.

237 Atmospheric $a^{14}\text{C}$ used in the model for the post-bomb era is based on
 238 the Hua et al. (2013) reconstructions of regional atmospheric $a^{14}\text{C}$ at annual
 239 resolution, and values for the pre-bomb era are based on linear interpola-
 240 tion of the IntCal13 Northern and Southern Hemisphere curves to annual
 241 resolution (Reimer et al., 2013). In addition to modeling the soil gas age
 242 at the infiltration site for HS4, the model is applied to 13 speleothem bomb
 243 peak records (shown in Table 1) from the literature that have published age
 244 models which are based on independent methods, i.e. adjustments to age
 245 models and speleothems with age models based $a^{14}\text{C}$ bomb peak evidence

246 are excluded.

247 In contrast to some previous models, fractionation effects are not consid-
248 ered in these calculations. Because these models do not consider tempera-
249 ture, fractionation affects all time steps by the same constant term. Therefore
250 ignoring fractionation does not affect the shape of the bomb peak curve gen-
251 erated by the model, only the contribution of aged carbon from dead sources.
252 Additionally, it is worth noting that there has been significant confusion in
253 the speleothem literature recently about the correct formulae to correct for
254 fractionation. Several speleothem geochemical modeling studies have used a
255 value of 2.3 for fractionation changes in $^{14}\text{C}/^{12}\text{C}$ vs. $^{13}\text{C}/^{12}\text{C}$ based on an at-
256 tempt to determine the fractionation of ^{14}C relative to ^{13}C in photosynthesis
257 (Saliege and Fontes, 1984). The experiment was probably compromised by
258 contributions of fossil fuel and the value of 2.3 has no support from quantum
259 theory (Southon, 2011).

260 4. Results

261 4.1. Measurements

262 The results of the tree ring record of local atmospheric $a^{14}\text{C}$ and the single
263 measurement of atmospheric $a^{14}\text{CO}_2$ are shown in Figure 1 and suggest that
264 atmospheric $a^{14}\text{C}$ at the study site is similar to, though slightly lower than,
265 the regional atmospheric $a^{14}\text{C}$ as approximated by the Northern Hemisphere
266 zone 3 reconstruction from Hua et al. (2013). There appears to be an in-
267 creasing divergence with time between the tree ring record and the Northern
268 Hemisphere zone 3 reconstruction, which is probably a regional offset due
269 to the rapid increase in emission of ^{14}C -free fossil fuel derived CO_2 in China

Table 1: Speleothem bomb peak records referred to in this text. Modified from Table 1 in Rudzka-Phillips et al., 2013

Speleothem	reference
Asfa-3	Baker et al., 2007
CC-Bil	Rudzka-Phillips et al., 2013
ER-77	Fohlmeister et al., 2011a
Fau-stm14	Genty and Massault, 1999
GAR-02	Rudzka-Phillips et al., 2013
Gib04a	Mattey et al., 2008
Han-stm5	Genty et al., 1998
HS4	this publication
LR06-B1	Griffiths et al., 2012
Merc-1	Baker et al., 2007
Obi84	Smith et al., 2009
Pos-stm4	Genty et al., 1998
So-11	Rudzka-Phillips et al., 2013
T7	Sundqvist et al., 2013

270 during the beginning of the 21st century. Given the good agreement between
271 the tree ring record and the Northern Hemisphere zone 3 reconstruction be-
272 fore 2000 AD, the Northern Hemisphere zone 3 reconstruction is considered
273 to be an appropriate approximation of atmospheric $\delta^{14}\text{CO}_2$ at Heshang Cave
274 for the use in the soil carbon model.

275 HS4 speleothem calcite $\delta^{14}\text{C}$ begins to increase in response to the at-
276 mospheric $\delta^{14}\text{C}$ bomb peak by 1959 from the pre-bomb average value of

277 88.30±0.18 pMC and increases gradually to a maximum of 96.90±0.24 pMC
278 in 1999 (Figure 1). The total increase in speleothem $a^{14}\text{C}$ in response to the
279 atmospheric $a^{14}\text{C}$ bomb peak increase in Northern Hemisphere zone 3 of ~70
280 pMC is 8.6 pMC.

281 Soil $a^{14}\text{CO}_2$ is generally lower than atmospheric $a^{14}\text{CO}_2$, ranging from
282 96.20±0.16 to 105.34±0.38 pMC (Figure 2). Soil $p\text{CO}_2$ is typically <5,000
283 ppm and generally increases with depth as shown in Figure 3. Soil $p\text{CO}_2$ was
284 lowest in March, with 2,435 ppm being highest value observed occurring at
285 30 cm depth, and the maximum observed value of 15,005 ppm observed in
286 July at 30 cm depth.

287 Bulk SOM $a^{14}\text{C}$ is shown in Table 2, and generally decreases with depth
288 with an average value of 44±12 pMC in the 0-5 cm depth interval, 27±5
289 pMC in the 5-10 cm interval, and 29±16 pMC in the 10-15 cm interval. Soil
290 from 10-15 cm depth was analyzed for $a^{14}\text{C}$ by size fractions. Sand fractions
291 typically each accounted for ~1/3 of the SOM by mass while silt and clay
292 accounted for only ~1%. Coarser size fractions have lower $a^{14}\text{C}$ than finer
293 size fractions. Coarse sand has an average $a^{14}\text{C}$ = 25±3 pMC, medium sand
294 = 38±15 pMC, fine sand = 54±16 pMC, and silt and clay = 73±20 pMC.

295 4.2. Geochemical box model

296 Results of the soil carbon geochemical box modeling of speleothem bomb
297 peak records are shown in Table 3. Shown in the table are the parameters
298 P_j , F_j , τ_j for the best model fit, as well as the average percentage of soil
299 CO_2 derived from the annual pool (F_1) in all successful model runs. The
300 minimum of the predicted soil CO_2 age calculated from SOM parameters of
301 all successful model runs is also shown. Plots of model results are given the

302 Supplementary Material.

303 Modeled F_1 range from $<1\%$ to 28% , with most speleothem records show-
304 ing a contribution from root respiration and decomposition of organic matter
305 of annual age accounting for $<10\%$ of the carbon. Gib04a and CC-Bil show
306 the largest contribution of carbon with $\tau=1$ (28% and 23% respectively).
307 Model results show ER-77, Pos-stm4, and T7 speleothem carbon is derived
308 predominately from a pool of decadal age, and Han-stm5 is a mixture of
309 decadal and centennially aged pools. All other records showed a dominance
310 of the flux of CO_2 derived from organic carbon with a $\tau > 100$ yr. The mini-
311 mum age of soil CO_2 predicted by the all successful model runs is consistently
312 on the order of decades or centuries, which contrasts starkly with observa-
313 tions of soil gas in temperate and tropical sites (Trumbore, 2000) as well as
314 the single published measurement of soil CO_2 in karst soil (Breecker et al.,
315 2012).

316 5. Discussion

317 5.1. Heshang Cave soil carbon

318 Measurements of $\delta^{14}\text{C}$ in Heshang Cave SOM and soil CO_2 are both
319 very different than published observations of $\delta^{14}\text{C}$ in shallow tropical soils.
320 The size fractionated SOM $\delta^{14}\text{C}$ measurements show a trend opposite to the
321 trend expected when separating out SOM by size fractions - typically coarse
322 material is composed of younger material and finer fractions account for the
323 occluded older carbon. All of the SOM $\delta^{14}\text{C}$ measurements are much lower
324 than is typically found in measurements of $\delta^{14}\text{C}$ in similar shallow intervals
325 of tropical and karst soils (e.g. 96.6 ± 0.6 pMC in a Chinese mollisol (Becker-

326 Heidmann et al., 1988); 109.49 ± 0.43 to 95.58 ± 0.49 pMC in a South China
327 forest soil (Ding et al., 2010); 96.8 ± 0.6 pMC Australian karst soil (Hobley
328 et al., 2014)).

329 The very stark contrast between bulk SOM $\delta^{14}\text{C}$ values observed at Hes-
330 hang Cave (<58 pMC) and SOM $\delta^{14}\text{C}$ values observed in other similar soils
331 (>95 pMC) raises concerns that the pretreatment methods may have af-
332 fected the measurements. Soil samples from Heshang Cave were carbonate
333 rich, with an average value of $\sim 45\%$ carbonate by mass. It is possible that
334 dolomite was not completely removed during pretreatment, therefore biasing
335 SOM $\delta^{14}\text{C}$ lower. However, the $\delta^{13}\text{C}$ values of the bulk SOM samples ranged
336 from -23.7 to -25.9‰ , which is typical of SOM suggesting that dolomite
337 was successfully removed by pretreatment with 1N HCl overnight. Further-
338 more, assuming SOM samples did contain some residual dolomite with a
339 $\delta^{13}\text{C}$ of 0‰ , and using a $\delta^{13}\text{C}$ of -27‰ to represent SOM derived of pure
340 C3 biomass (Cerling, 1984) a simple mass balance calculation can be per-
341 formed. This mass balance suggests dolomite would account for a maximum
342 of 12% of the sample carbon, which would shift the range of $\delta^{14}\text{C}$ for the
343 bulk measurements from 17 - 58 pMC to at most 19 - 66 pMC. This latter
344 range still represents very old carbon (3,400 to 13,300 ^{14}C years).

345 In contrast to incomplete removal of carbonates, it is possible that the
346 pretreatment with 1N HCl overnight may have digested some of the young
347 organic carbon in the SOM. This pretreatment method is one that is a com-
348 monly employed, and similar to the methods employed in the measurements
349 on other soils cited here. Analysis of SOM samples before and after pre-
350 treatment with 2N HCl for 1 hr presented in Krull et al. (2006) show no

351 statistically significant difference in SOM $\delta^{13}\text{C}$ or total organic carbon con-
 352 centration. We therefore believe that these exceptionally low $a^{14}\text{C}$ values
 353 reported here are representative of the $a^{14}\text{C}$ of bulk SOM at Heshang Cave.
 354 $a^{14}\text{C}$ measurements of SOM at Heshang Cave shows that SOM at Hes-
 355 hang Cave is composed primarily of carbon of multi-millennial age, and the
 356 absence of bulk or size fractionated SOM measurements with post-bomb $a^{14}\text{C}$
 357 values suggests that the annual inputs of organic carbon to the soil are very
 358 low. If annual carbon inputs to soil are low, most carbon fixed in a given
 359 year must be respired in that same year, which would yield very large fluxes
 360 of CO_2 with $a^{14}\text{C}$ close to atmospheric, and soil $a^{14}\text{CO}_2$ would be roughly
 361 equal to atmospheric $a^{14}\text{CO}_2$. Indeed, observations of $a^{14}\text{CO}_2$ in tropical
 362 soils generally suggest that they are dominated by root respiration and de-
 363 composition of decadal age SOM, which has post-bomb $a^{14}\text{C}$, yielding a soil
 364 $a^{14}\text{CO}_2$ that is higher than that of atmospheric $a^{14}\text{CO}_2$ (e.g. Ding et al., 2010
 365 and Trumbore, 2000). However, soil $a^{14}\text{CO}_2$ measured at Heshang Cave is
 366 generally much lower than clean atmospheric $a^{14}\text{CO}_2$ (Figure 2).

367 There are several potential sources of depleted $a^{14}\text{CO}_2$ observed in Hes-
 368 hang Cave soil, both because of sampling methods and properties of the karst
 369 system. The installation of wells used to sample soil CO_2 at depth causes
 370 disturbance of the soil profile and the ecosystem, which could potentially bias
 371 soil $a^{14}\text{C}$, though this contribution would most likely increase decomposition
 372 of labile carbon with contemporaneous and post-bomb $a^{14}\text{C}$ and therefore
 373 increase the measured $a^{14}\text{CO}_2$. However, given the especially low $a^{14}\text{C}$ of
 374 SOM and the apparent absence of decadal aged carbon, even in an undis-
 375 turbed profile, a small flux of decomposition of multi-millennial aged SOM

376 found at Heshang Cave could achieve the observed offset of soil $\delta^{14}\text{C}$ from
377 atmospheric $\delta^{14}\text{C}$.

378 Given the very high carbonate concentration of the soil, it is also possible
379 that some of the soil CO_2 is derived from $\delta^{14}\text{C}$ -free carbonates through active
380 carbonate dissolution and precipitation processes occurring in the soil. The
381 open-system model of carbonate dissolution assumes continuous equilibra-
382 tion of soil water DIC with soil CO_2 , causing the incorporation of $\delta^{14}\text{C}$ -free
383 carbon derived from dissolution of the carbonate bedrock into to soil DIC
384 pool, including the soil CO_2 . Very large fluxes of non-biogenic CO_2 have
385 been observed karst terrains (Sanchez-Cañete et al., 2011), suggesting that
386 it is possible for carbonate dissolution and precipitation processes to have an
387 appreciable affect on the carbon isotope ratios of soil CO_2 in karst terrains.

388 Modeling results suggest that the CO_2 from which speleothem carbon
389 in HS4 is derived predominately from decomposition of a single pool with
390 a $\tau = 136$ yr. This result predicts that soil $\delta^{14}\text{C}$ would be 105.7 pMC
391 in 2010, which is essentially indistinguishable from contemporaneous at-
392 mospheric $\delta^{14}\text{C}$, but inconsistent with measured soil $\delta^{14}\text{C}$ (Figure 2).
393 Given the dense local vegetation and absence of post-bomb $\delta^{14}\text{C}$ in the SOM,
394 we believe that soil CO_2 at Heshang Cave is most likely derived predomi-
395 nately from carbon fixed during the current year and offset from contem-
396 poraneous atmospheric $\delta^{14}\text{C}$ by incorporation of $\delta^{14}\text{C}$ -free bedrock de-
397 rived carbon in the soil DIC pool due open-system carbonate dissolution
398 and carbonate precipitation. However, the measurements made in this study
399 are insufficient to confirm this hypothesis, and suggest that soil carbon dy-
400 namics are very complicated at this site, and perhaps across karst sites in

401 general. The unusual soil $a^{14}\text{C}$ measurements presented in this manuscript
402 highlight the need for further investigations of soil carbon dynamics in karst
403 sites to determine if they are consistently storing large quantities of very old
404 SOM and how SOM decomposition at these sites responds to global climate
405 change. Furthermore the disagreement between the modeled soil Heshang
406 Cave $a^{14}\text{CO}_2$ based on the HS4 speleothem $a^{14}\text{C}$ bomb peak profile and ob-
407 served Heshang Cave $a^{14}\text{CO}_2$ suggest that the conceptional model of the
408 sources of speleothem carbon is in need of revision.

409 5.2. *The sources of speleothem carbon*

410 Modeling results suggest that CO_2 derived from root respiration and de-
411 composition of organic matter with $\tau < 1$ year does not represent a significant
412 portion of speleothem carbon, which is similar to the results of similar stud-
413 ies. Genty and Massault (1997) referred to the soil $a^{14}\text{CO}_2$ measurements of
414 Dörr and Münnich (1986) which suggested that under forested soil in Ger-
415 many decomposition of SOM with $\tau = 100$ years composes 25% of soil CO_2
416 flux in the summer and 75% of the flux in the winter. Under the assump-
417 tion that the majority of infiltration in temperate settings occurs during the
418 winter months, when photosynthesis is at a minimum, previous studies have
419 argued that model parameters that suggest that speleothem carbon is derived
420 from soil CO_2 that is primarily derived from decomposition of old SOM are
421 in good agreement with observations of winter soil $a^{14}\text{CO}_2$.

422 However, even if this assumption is accurate for sites where the grow-
423 ing season is out of phase with the rainy season, it is certainly not the case
424 in tropical and sub-tropical sites with monsoon climates where the grow-
425 ing season and rainy season are in phase. Moreover, the assumption that

426 speleothem carbon is predominantly derived from winter soil CO_2 is difficult
427 to reconcile even in temperate sites because of the particularly low soil $p\text{CO}_2$
428 in temperate sites during the winter. Dörr and Münnich (1986) measured
429 winter $p\text{CO}_2$ in the forested soil of $<3,000$ ppm, and Tegen and Dorr (1996)
430 typically observed concentrations of $<2,000$ ppm in German forest during
431 cold seasons. Measurements of soil $p\text{CO}_2$ at Grotto di Ernesto also showed
432 values of $\sim 2,000$ ppm in winter.

433 Modeling drip water carbonate chemistry using these observed low soil
434 $p\text{CO}_2$ values has proved difficult to reconcile with observed drip water Ca^{2+}
435 concentrations. For example, Fohlmeister et al. (2011b) used a carbonate
436 dissolution model to calculate Grotto di Ernesto ER-G1 drip water carbon
437 isotope ratios and Ca^{2+} concentrations using the annual average soil $p\text{CO}_2$
438 observed above Grotto di Ernesto of 4,000 ppm. When the model was able
439 to accurately reproduce drip water $\delta^{14}\text{C}$, it underestimated the Ca^{2+} con-
440 centration by a factor of ~ 2 . Fohlmeister et al. (2011b) suggested that the
441 discrepancy could be due to the longer time necessary to establish equilib-
442 rium between soil water and soil gas for carbon isotopes than Ca^{2+} , however,
443 another possibility is that the initial $p\text{CO}_2$ used in the model was too low.
444 In fact, to attain typically observed drip water Ca^{2+} concentrations of ~ 2
445 mmol/L via completely open-system dissolution requires an initial $p\text{CO}_2$ of
446 10,000 ppm, while completely closed-system dissolution requires an initial
447 $p\text{CO}_2$ of 50,000 ppm (Hansen et al., 2013).

448 When Fohlmeister et al. (2011b) forced their model to fit observed drip
449 water Ca^{2+} values, calculated drip water $\delta^{14}\text{C}$ was higher than observed drip
450 water $\delta^{14}\text{C}$ by 6.5 pMC. The initial value used for the soil $\delta^{14}\text{CO}_2$ was based

on the soil carbon parameters modeled from a bomb peak record from ER-77 using the moving average approach to estimate soil $a^{14}\text{CO}_2$ (Fohlmeister et al., 2011a). The best fit to ER-77 using the model described in this manuscript suggests that the a lower initial $a^{14}\text{CO}_2$ may be appropriate for the carbon source for ER-77, which could potentially improve the performance of the Fohlmeister et al. (2011b) model in estimating drip water geochemistry.

Given the low $p\text{CO}_2$ observed in shallow karst soils, and the disagreement between observations of soil $a^{14}\text{CO}_2$ and the $a^{14}\text{CO}_2$ necessary to reproduce the speleothem bomb peak records as predicted by all modeling approaches attempted, we suggest that in many karst systems CO_2 in the soil zone is not the dominant source of speleothem carbon. The near absence of root respiration signal in speleothem carbon suggests the possibility of a source of CO_2 that is removed from the soil zone, where decomposition of aged SOM occurs in isolation.

Very high vadose zone $p\text{CO}_2$ has long been known to occur in both carbonate and carbonate-free settings, (e.g. Bacon and Keller, 1998; Murphy et al., 1992; Keller, 1991; Keller and Bacon, 1998; Wood and Petraitis, 1984; Wood et al., 1993; Hendry et al., 1993; Hendry and Wassenaar, 2005; and Lawrence et al., 2000), and isotopic evidence suggest that microbial respiration of organic material is the dominant source of subterranean CO_2 . Most relevant to karst settings, Benavente et al. (2010) measured soil and vadose zone $p\text{CO}_2$ and $\delta^{13}\text{C}$ in a Mediterranean karst. Benavente et al. (2010) measured $p\text{CO}_2$ of $<2,000$ ppm with a $\delta^{13}\text{C}$ of -11.2 to -20.6‰ in the soil, and $p\text{CO}_2$ of $>20,000$ ppm in wells at depths of >10 m, with a $\delta^{13}\text{C}$ ranging

476 from -19.7 to -22.1‰ , suggesting the CO_2 was derived from an organic
 477 matter source. Peyraube et al. (2013) estimated vadose zone $p\text{CO}_2$ based on
 478 carbon isotopic evidence in cave drip water and CO_2 , and suggests vadose
 479 zone $p\text{CO}_2$ values of 4.4% (44,000 ppm) in winter and 10% in summer with
 480 $\delta^{13}\text{C}$ values of -22.31‰ and -24.20‰ , which is in good agreement with the
 481 observations presented by Benavente et al. (2010). Additionally a study of
 482 the sources of cave CO_2 by Breecker et al. (2012) also hypothesized that the
 483 majority of cave CO_2 is advected from a deep biogenic source, and numerous
 484 studies have suggested that generation of subterranean CO_2 is an important,
 485 and possibly necessary, driver of carbonate dissolution and karst development
 486 (e.g. Wood, 1985; Atkinson, 1977; Gabrovšek et al., 2000; and Gulley et al.,
 487 2014)

488 *5.3. Implications for interpretation of speleothem carbon isotope records*

489 The apparent stability of the offset between speleothem $a^{14}\text{C}$ and con-
 490 temporaneous atmospheric $a^{14}\text{CO}_2$, commonly referred to as the dead carbon
 491 proportion (DCP), in some speleothems observed across major climate tran-
 492 sitions has been both the most promising and puzzling result of attempts to
 493 produce speleothem-based records of atmospheric $a^{14}\text{C}$. Most exceptionally
 494 in the Hulu Cave speleothem, H82, DCP showed no response throughout the
 495 Younger Dryas despite the changes in summer monsoon intensity inferred
 496 from speleothem $\delta^{18}\text{O}$, and vegetation changes inferred by pollen evidence
 497 (Southon et al., 2012). The hypothesis that some speleothems are formed
 498 predominately from CO_2 in the vadose zone derived from microbial decompo-
 499 sition of aged organic matter could potentially begin to explain the apparent
 500 stability of DCP in speleothems through major climate transitions. Changes

501 in temperature and moisture conditions at the surface would be expected to
502 induce relatively less variability in the conditions of the deep vadose zone.
503 If speleothem carbon is derived predominately from decomposition of SOM
504 in the insulated subsurface, this process would act to filter out both abrupt
505 changes in global atmospheric $\delta^{14}\text{C}$, like the twentieth century atmospheric
506 $\delta^{14}\text{C}$ bomb peak, and short-term changes in surface soil dynamics.

507 Changes in hydrology appear to be the most important driver of speleothem
508 DCP (Griffiths et al., 2012 and Noronha et al., 2014), with a working hypoth-
509 esis that higher precipitation increases soil moisture, therefore limiting CO_2
510 diffusion and open-system dissolution, and leading to a higher proportion of
511 carbon derived from the $\delta^{14}\text{C}$ -free bedrock. In a system where most drip
512 water DIC is acquired during open-system dissolution occurring at depth in
513 the vadose zone, open-system dissolution, which relies on the assumption
514 of a functionally infinite supply of CO_2 could only occur when voids in the
515 bedrock are filled with more gas than water. During periods of higher infil-
516 tration this condition would be met less often, and closed-system dissolution
517 would dominate, leading to higher speleothem DCP during periods of higher
518 recharge.

519 This smoothing of surface changes in speleothem $\delta^{14}\text{C}$, driven by domi-
520 nance of carbon derived from decomposition of aged SOM in the deep vadose
521 zone over root respiration in the shallow soil zone, suggests that SOM derived
522 changes in speleothem $\delta^{13}\text{C}$ records must be similarly muted. Complicated
523 organic carbon cycling in karst terrains suggests that shifts between vegeta-
524 tion using C3 and C4 photosynthetic pathways will be muted and lagged in
525 both organic and inorganic carbon isotope records. In addition to the im-

portance of interpreting speleothem carbon isotope records in light of these temporal lags and the attenuation of surface signals, there exists a growing body of research developing paleoenvironmental proxies using organic matter preserved in speleothem calcite and organic-mineral associations (e.g. Xie et al., 2003; Blyth et al., 2008; Huang et al., 2008; Perrette et al., 2008; Li et al., 2011; Hartland et al., 2012; and Blyth et al., 2013) which should be interpreted in light of the complicated carbon cycling and unique transport mechanisms occurring in karst systems.

6. Conclusion

We have developed an improved model of the sources of speleothem carbon which allows prediction the SOM age distribution required to produce the shape of the speleothem twentieth century $\delta^{14}\text{C}$ bomb peak. The results of this modeling work confirm the results of previous studies, which suggest that a large flux of CO_2 derived from organic material with turnover times on the order of centuries is necessary to produce the observed speleothem $\delta^{14}\text{C}$ bomb peak. This result suggests that soil CO_2 is not the main source of speleothem carbon, and therefore we argue that CO_2 produced by microbial decomposition of SOM in the deep vadose zone is likely to be the main source of speleothem carbon.

Our observations of soil carbon at Heshang Cave, China and a review of the literature indicates that karst systems are unique ecosystems where organic matter undergoes complicated alterations and transformations, which currently have received relatively little attention. Continued study of carbon cycling in karst settings is crucially important to improve our understanding

550 of the role of karst soils in the global carbon-climate feedback cycle and to
551 improve interpretation of speleothem-based paleoenvironmental records.

552 **7. Acknowledgements**

553 This research was supported by NSF AGS-0903101 to KRJ, NSF EAPSI-
554 1107922 to ALN, and NSFC 41072262 to HCY. We thank Xioamei Xu, Clau-
555 dia Czimeczik, and Guaciera dos Santos for laboratory assistance and helpful
556 conversations, the guest editors of this special issue, Jens Fohlmeister, and
557 one anonymous reviewer for their comments which significantly improved this
558 manuscript. The model Matlab code is available at <https://github.com/anoronha>.

559 Atkinson, T. C., 1977. Carbon dioxide in the atmosphere of the unsaturated
560 zone: an important control of groundwater hardness in limestones. *Journal*
561 *of Hydrology* 35, 111–123.

562 Bacon, D. H., Keller, C. K., 1998. Carbon dioxide respiration in the deep
563 vadose zone: Implications for groundwater age dating. *Water Resources*
564 *Research* 34 (11), 3069–3077.

565 Baker, A., Asrat, A., Fairchild, I. J., Leng, M. J., Wynn, P. M., Bryant,
566 C. L., Genty, D., Umer, M., 2007. Analysis of the climate signal contained
567 within $\delta^{18}\text{O}$ and growth rate parameters in two Ethiopian stalagmites.
568 *Geochimica et Cosmochimica Acta* 71 (12), 2975–2988.

569 Becker-Heidmann, P., Liang-wu, L., Scharpenseel, H.-W., 1988. Radiocarbon
570 Dating of Organic Matter Fractions of a Chinese Mollisol. *Zeitschrift für*
571 *Pflanzenernährung und Bodenkunde* 151 (1), 37–39.

- 572 Benavente, J., Vadillo, I., Carrasco, F., Soler, a., Liñán, C., Moral, F., 2010.
573 Air Carbon Dioxide Contents in the Vadose Zone of a Mediterranean Karst.
574 Vadose Zone Journal 9 (1), 126.
- 575 Blyth, A. J., Baker, A., Collins, M. J., Penkman, K. E., Gilmour, M. a.,
576 Moss, J. S., Genty, D., Drysdale, R. N., 2008. Molecular organic matter
577 in speleothems and its potential as an environmental proxy. Quaternary
578 Science Reviews 27 (9-10), 905–921.
- 579 Blyth, A. J., Smith, C. I., Drysdale, R. N., 2013. A new perspective on
580 the $\delta^{13}\text{C}$ signal preserved in speleothems using LC-IRMS analysis of bulk
581 organic matter and compound specific stable isotope analysis. Quaternary
582 Science Reviews 75, 143–149.
- 583 Breecker, D. O., Payne, A. E., Quade, J., Banner, J. L., Ball, C. E., Meyer,
584 K. W., Cowan, B. D., 2012. The sources and sinks of CO_2 in caves under
585 mixed woodland and grassland vegetation. Geochimica et Cosmochimica
586 Acta 96, 230–246.
- 587 Cerling, T. E., 1984. The stable isotopic composition of modern soil carbonate
588 and its relationship to climate. Earth and Planetary Science Letters 71 (2),
589 229–240.
- 590 Ding, P., Shen, C. D., Wang, N., Yi, W. X., Ding, X. F., Fu, D. P., Liu, K. X.,
591 Zhou, L. P., 2010. Turnover Rate Of Soil Organic Matter And Origin
592 Of Soil $^{14}\text{CO}_2$ In Deep Soil From A Subtropical Forest In Dinghushan
593 Biosphere Reserve, South China. Radiocarbon 52 (2), 1422–1434.

- 594 Dörr, H., Münnich, K. O., 1986. Annual variations of the ^{14}C Content of Soil
595 CO_2 . Radiocarbon 28 (2A), 338–345.
- 596 Dreybrodt, W., 2008. Evolution of the isotopic composition of carbon and
597 oxygen in a calcite precipitating $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$ solution and the related
598 isotopic composition of calcite in stalagmites. Geochimica et Cosmochimica
599 Acta 72 (19), 4712–4724.
- 600 English, N. B., McDowell, N. G., Allen, C. D., Mora, C., 2011. The effects
601 of α -cellulose extraction and blue-stain fungus on retrospective studies of
602 carbon and oxygen isotope variation in live and dead trees. Rapid Com-
603 munications in Mass Spectrometry 25 (20), 3083–3090.
- 604 Fairchild, I. J., Smith, C. L., Baker, A., Fuller, L., Spötl, C., Matthey, D. P.,
605 McDermott, F., 2006. Modification and preservation of environmental sig-
606 nals in speleothems. Earth-Science Reviews 75 (1-4), 105–153.
- 607 Fohlmeister, J., Kromer, B., Mangini, A., 2011a. The Influence Of Soil Or-
608 ganic Matter Age Spectrum On The Reconstruction Of Atmospheric ^{14}C
609 Levels Via Stalagmites. Radiocarbon 53 (1), 99–115.
- 610 Fohlmeister, J., Scholz, D., Kromer, B., Mangini, A., 2011b. Modelling car-
611 bon isotopes of carbonates in cave drip water. Geochimica et Cosmochim-
612 ica Acta 75 (18), 5219–5228.
- 613 Fohlmeister, J., Schröder-Ritzrau, A., Spötl, C., 2010. The Influences Of
614 Hydrology On The Radiogenic And Stable Carbon Isotope Composition
615 Of Cave Drip Water, Grotta Di Ernesto (Italy). Radiocarbon 52 (4), 1529–
616 1544.

617 Frisia, S., Borsato, A., 2010. Chapter 6: Karst. In: Alonso-Zarza, A. M.,
618 Tanner, L. H. (Eds.), Carbonates in Continental Settings: Facies, Envi-
619 ronments, and Processes. Vol. 61. Elsevier, pp. 61, 269–318.

620 Frisia, S., Fairchild, I. J., Fohlmeister, J., Miorandi, R., Spötl, C., Borsato,
621 A., 2011. Carbon mass-balance modelling and carbon isotope exchange
622 processes in dynamic caves. *Geochimica et Cosmochimica Acta* 75 (2),
623 380–400.

624 Gabrovšek, F., Menne, B., Dreybrodt, W., 2000. A model of early evolution
625 of karst conduits affected by subterranean CO₂ sources. *Environmental*
626 *Geology* 39 (6), 531–543.

627 Gaudinski, J. B., Trumbore, S. E., Davidson, E. A., Zheng, S., Eric, A.,
628 2000. Soil carbon cycling in a temperate forest: radiocarbon-based esti-
629 mates of residence times, sequestration rates and partitioning of fluxes.
630 *Biogeochemistry* 51, 33–69.

631 Genty, D., Baker, A., Massault, M., Proctor, C., Gilmour, M., Pons-Branchu,
632 E., Hamelin, B., 2001. Dead carbon in stalagmites: carbonate bedrock pa-
633 leodissolution vs. ageing of soil organic matter. Implications for ¹³C vari-
634 ations in speleothems. *Geochimica et Cosmochimica Acta* 65 (20), 3443–
635 3457.

636 Genty, D., Massault, M., 1997. Bomb ¹⁴C Recorded in laminated
637 Speleothems: Calculations of Dead Carbon Proportion. *Radiocarbon*
638 39 (1), 33–48.

- 639 Genty, D., Massault, M., 1999. Carbon transfer dynamics from bomb- ^{14}C and
640 $\delta^{13}\text{C}$ time series of a laminated stalagmite from SW France - modelling and
641 comparison with other stalagmite records. *Geochimica et Cosmochimica*
642 *Acta* 63 (10), 1537–1548.
- 643 Genty, D., Vokal, B., Obelić, B., 1998. Bomb ^{14}C time history recorded in
644 two modern stalagmites - importance for soil organic matter dynamics
645 and bomb ^{14}C distribution over continents. *Earth and Planetary Science*
646 *Letters* 160, 795–809.
- 647 Griffiths, M., Fohlmeister, J., Drysdale, R., Hua, Q., Johnson, K. R., Hell-
648 strom, J., Gagan, M., Zhao, J.-X., 2012. Hydrological control of the dead
649 carbon fraction in a Holocene tropical speleothem. *Quaternary Geochronol-*
650 *ogy* 14, 81–93.
- 651 Gulley, J., Martin, J., Moore, P., 2014. Vadose CO_2 gas drives dissolution
652 at water tables in eogenetic karst aquifers more than mixing dissolution.
653 *Earth Surface Processes and Landforms* 39 (13), 1833–1846.
- 654 Hansen, M., Dreybrodt, W., Scholz, D., 2013. Chemical evolution of dissolved
655 inorganic carbon species flowing in thin water films and its implications
656 for (rapid) degassing of CO_2 during speleothem growth. *Geochimica et*
657 *Cosmochimica Acta* 107, 242–251.
- 658 Hartland, A., Fairchild, I. J., Lead, J. R., Borsato, A., Baker, A., Frisia,
659 S., Baalousha, M., 2012. From soil to cave: Transport of trace metals
660 by natural organic matter in karst dripwaters. *Chemical Geology* 304-305,
661 68–82.

- 662 Hendry, M. J., Lawrence, J. R., Zanyk, B. N., Kirkland, R., 1993. Microbial
663 Production of CO₂ in Unsaturated Geologic Media in a Geologic Media in
664 a Mesoscale Model. *Water Resources Research* 29 (4), 973–984.
- 665 Hendry, M. J., Wassenaar, L. I., 2005. Origin and migration of dissolved
666 organic carbon fractions in a clay-rich aquitard: ¹⁴C and $\delta^{13}\text{C}$ evidence.
667 *Water Resources Research* 41 (2).
- 668 Hendy, C., 1971. The isotopic geochemistry of speleothems - I. The calcula-
669 tion of the effects of different modes of formation on the isotopic compo-
670 sition of speleothems and their applicability as palaeoclimatic indicators.
671 *Geochimica et Cosmochimica Acta* 35 (8), 801–824.
- 672 Hobley, E., Willgoose, G. R., Frisia, S., Jacobsen, G., 2014. Stability and
673 storage of soil organic carbon in a heavy-textured Karst soil from south-
674 eastern Australia. *Soil Research* 52, 476–482.
- 675 Hu, C., Henderson, G., Huang, J., Chen, Z., Johnson, K. R., 2008a. Report
676 of a three-year monitoring programme at Heshang Cave, Central China.
677 *International Journal of Speleology* 37 (3), 143–151.
- 678 Hu, C., Henderson, G. M., Huang, J., Xie, S., Sun, Y., Johnson, K. R.,
679 2008b. Quantification of Holocene Asian monsoon rainfall from spatially
680 separated cave records. *Earth and Planetary Science Letters* 266 (3-4),
681 221–232.
- 682 Hua, Q., Barbetti, M., Rakowski, A., 2013. Atmospheric radiocarbon for the
683 period 1950–2010. *Radiocarbon* 55 (4), 2059–2072.

- 684 Huang, X., Cui, J., Pu, Y., Huang, J., Blyth, A. J., 2008. Identifying “free”
685 and “bound” lipid fractions in stalagmite samples: An example from Hes-
686 hang Cave, Southern China. *Applied Geochemistry* 23 (9), 2589–2595.
- 687 Johnson, K. R., Hu, C., Belshaw, N., Henderson, G., 2006. Seasonal trace-
688 element and stable-isotope variations in a Chinese speleothem: The poten-
689 tial for high-resolution paleomonsoon reconstruction. *Earth and Planetary*
690 *Science Letters* 244 (1-2), 394–407.
- 691 Keller, C. K., 1991. Hydrogeochemistry of a Clayey Till - Sources of CO₂.
692 *Water Resources Research* 27 (10), 2555–2564.
- 693 Keller, C. K., Bacon, D. H., 1998. Soil respiration and georespiration distin-
694 guished by transport analyses of vadose CO₂, ¹³CO₂, and ¹⁴CO₂. *Global*
695 *Biogeochemical Cycles* 12 (2), 361–372.
- 696 Krull, E., Bestland, E., Gates, W., Ding, P., Shen, C., Wang, N., Yi, W.,
697 2006. Soil organic matter decomposition and turnover in a tropical Ultisol:
698 evidence from $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and geochemistry. *Radiocarbon* 44 (1), 1422–
699 1434.
- 700 Lawrence, J., Hendry, M., Wassenaar, L. I., Germida, J., Wolfaardt, G.,
701 Fortin, N., Greer, C., 2000. Distribution and Biogeochemical Importance
702 of Bacterial Populations in a Thick Clay-Rich Aquitard System. *Microbial*
703 *Ecology* 40 (4), 273–291.
- 704 Levin, I., Kromer, B., Hammer, S., 2013. Atmospheric $\Delta^{14}\text{CO}_2$ trend in
705 Western European background air from 2000 to 2012. *Tellus B* (65), 1–7.

- 706 Li, X., Wang, C., Huang, J., Hu, C., Xie, S., 2011. Seasonal variation of fatty
707 acids from drip water in Heshang Cave, central China. *Applied Geochem-*
708 *istry* 26 (3), 341–347.
- 709 Liu, Y.-H., Henderson, G. M., Hu, C.-Y., Mason, a. J., Charnley, N., John-
710 son, K. R., Xie, S.-C., 2013. Links between the East Asian monsoon and
711 North Atlantic climate during the 8,200 year event. *Nature Geoscience*
712 6 (2), 117–120.
- 713 Matthey, D. P., Lowry, D., Duffet, J., Fisher, R., Hodge, E., Frisia, S., 2008. A
714 53year seasonally resolved oxygen and carbon isotope record from a modern
715 Gibraltar speleothem: Reconstructed drip water and relationship to local
716 precipitation. *Earth and Planetary Science Letters* 269 (1-2), 80–95.
- 717 Mickler, P. J., Banner, J. L., Stern, L., Asmerom, Y., Edwards, R. L., Ito, E.,
718 2004. Stable isotope variations in modern tropical speleothems: Evaluating
719 equilibrium vs. kinetic isotope effects. *Geochimica et Cosmochimica Acta*
720 68 (21), 4381–4393.
- 721 Murphy, E. M., Schramke, J. A., Fredrickson, J. K., Bledsoe, H. W., Francis,
722 A. J., Sklarew, D., Linehan, J. C., 1992. The influence of microbial ac-
723 tivity and sedimentary organic carbon on the isotope geochemistry of the
724 Middendorf aquifer. *Water Resources Research* 28 (3), 723–740.
- 725 Noronha, A. L., Johnson, K. R., Hu, C., Ruan, J., Southon, J. R., Ferguson,
726 J. E., 2014. Assessing influences on speleothem dead carbon variability over
727 the Holocene: Implications for speleothem-based radiocarbon calibration.
728 *Earth and Planetary Science Letters* 394, 20–29.

- 729 Perrette, Y., Poulenard, J., Saber, A.-I., Fanget, B., Guittonneau, S., Ghaleb,
730 B., Garaudee, S., 2008. Polycyclic Aromatic Hydrocarbons in stalagmites:
731 Occurrence and use for analyzing past environments. *Chemical Geology*
732 251 (1-4), 67–76.
- 733 Peyraube, N., Lastennet, R., Denis, a., Malaurent, P., 2013. Estimation of
734 epikarst air $p\text{CO}_2$ using measurements of water $\delta^{13}\text{C}_{TDIC}$, cave air $p\text{CO}_2$
735 and $\delta^{13}\text{C}\text{O}_2$. *Geochimica et Cosmochimica Acta* 118, 1–17.
- 736 Reimer, P. J., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Ramsey,
737 C. B., Buck, C. E., Cheng, H., Edwards, R. L., Friedrich, M., Grootes,
738 P. M., Guilderson, T. P., Haffidason, H., Hajdas, I., Hatte, C., Heaton,
739 T. J., Hoffmann, D. L., Hogg, A. G., Hughen, K. A., Kaiser, K. F., Kromer,
740 B., Manning, S. W., Niu, M., Reimer, R. W., Richards, D. A., Scott, E. M.,
741 Southon, J. R., Staff, R., Turney, C. S. M., van der Plicht, J., 2013. Int-
742 Cal13 and Marine13 Radiocarbon Age Calibration Curves 0-50,000 years
743 cal BP. *Radiocarbon* 55 (4), 1869–1887.
- 744 Rudzka-Phillips, D., McDermott, F., Jackson, a., Fleitmann, D., 2013. In-
745 verse modelling of the ^{14}C bomb pulse in stalagmites to constrain the dy-
746 namics of soil carbon cycling at selected European cave sites. *Geochimica*
747 *et Cosmochimica Acta* 112, 32–51.
- 748 Saliege, J., Fontes, J., 1984. Essai de détermination expérimentale du frac-
749 tionnement des isotopes ^{13}C et ^{14}C du carbone au cours de processus na-
750 turels. *The International Journal of Applied Radiation and Isotopes* 35 (1),
751 55–62.

- Sanchez-Cañete, E. P., Serrano-Ortiz, P., Kowalski, A. S., Oyonarte, C.,
Domingo, F., 2011. Subterranean CO₂ ventilation and its role in the net
ecosystem carbon balance of a karstic shrubland. *Geophysical Research
Letters* 38 (9).
- Santos, G., Moore, R. B., Southon, J. R., Griffin, S., Hinger, E., Zhang, D.,
2007. AMS ¹⁴C Sample preparation at the KCCAMS/UCI Facility: Status
Report and Performance of Small Samples. *Radiocarbon* 49 (2), 255–269.
- Six, J., Jastrow, J. D., 2002. Organic Matter Turnover. In: *Encyclopedia of
Soil Science*. pp. 936–942.
- Smith, C. L., Fairchild, I. J., Spötl, C., Frisia, S., Borsato, A., Moreton,
S. G., Wynn, P. M., 2009. Chronology building using objective identifica-
tion of annual signals in trace element profiles of stalagmites. *Quaternary
Geochronology* 4 (1), 11–21.
- Southon, J. R., 2011. Are the Fractionation Corrections Correct: Are the iso-
topic shifts for ¹⁴C/¹²C ratios in physical processes and chemical reactions
really twice those for ¹³C/¹²C? *Radiocarbon* 53 (4), 691–704.
- Southon, J. R., Magana, A. L., 2010. A Comparison Of Cellulose Extraction
And ABA Pretreatment Methods For AMS ¹⁴C Dating Of Ancient Wood.
Radiocarbon 52 (3), 1371–1379.
- Southon, J. R., Noronha, A. L., Cheng, H., Edwards, R. L., Wang, Y.,
2012. A high-resolution record of atmospheric ¹⁴C based on Hulu Cave
speleothem H82. *Quaternary Science Reviews* 33, 32–41.

774 Spötl, C., Fairchild, I. J., Tooth, A. F., 2005. Cave air control on dripwater
775 geochemistry, Obir Caves (Austria): Implications for speleothem deposi-
776 tion in dynamically ventilated caves. *Geochimica et Cosmochimica Acta*
777 69 (10), 2451–2468.

778 Stuiver, M., Polach, H. A., 1977. Reporting of C-14 data. *Radiocarbon* 19 (3),
779 355–363.

780 Sundqvist, H. S., Holmgren, K., Fohlmeister, J., Zhang, Q., Matthews, M. B.,
781 Spötl, C., Körnich, H., 2013. Evidence of a large cooling between 1690 and
782 1740 AD in southern Africa. *Scientific Reports* 3, 1767.

783 Tegen, I., Dorr, H., 1996. ^{14}C measurements of soil organic matter, soil CO_2
784 and dissolved organic carbon (1987-1992). *Radiocarbon* 38 (2), 247–251.

785 Trumbore, S. E., 1993. Comparison of carbon dynamics in tropical and tem-
786 perate soils using radiocarbon measurements. *Global Biogeochemical Cy-*
787 *cles* 7 (2), 275–290.

788 Trumbore, S. E., 2000. Age of soil organic matter and soil respiration: Radio-
789 carbon constraints on belowground C dynamics. *Ecological Applications*
790 10 (2), 399–411.

791 Wood, B. D., Keller, C. K., Johnston, D. L., 1993. In Situ Measurement
792 of Microbial Activity and Controls on Microbial CO_2 Production in the
793 Unsaturated Zone. *Water Resources Research* 29 (3).

794 Wood, W. W., 1985. Origin of caves and other solution openings in the
795 unsaturated (vadose) zone of carbonate rocks: A model. *Geology* 13, 822–
796 824.

- 797 Wood, W. W., Petraitis, M. J., 1984. Origin and Distribution of Carbon
798 Dioxide in the Unsaturated Zone of the Southern High Plains of Texas.
799 Water Resources Research 20 (9), 1193–1208.
- 800 Xie, S., Yi, Y., Huang, J., Hu, C., Cai, Y., Collins, M., Baker, A., 2003.
801 Lipid distribution in a subtropical southern China stalagmite as a record
802 of soil ecosystem response to paleoclimate change. Quaternary Research
803 60, 340–347.
- 804 Xu, X., Trumbore, S. E., Zheng, S., Southon, J. R., McDuffee, K. E., Luttgen,
805 M., Liu, J. C., 2007. Modifying a sealed tube zinc reduction method for
806 preparation of AMS graphite targets: Reducing background and attain-
807 ing high precision. Nuclear Instruments and Methods in Physics Research
808 Section B: Beam Interactions with Materials and Atoms 259 (1), 320–329.

Figure 1: Speleothem HS4 twentieth century $a^{14}\text{C}$ (green) plotted with Northern Hemisphere zone 3 Hua et al. (2013) regional atmospheric $a^{14}\text{C}$ record (black), and results of local atmospheric $a^{14}\text{CO}_2$ at Heshang Cave based on tree ring reconstruction (red), and a single atmospheric $a^{14}\text{CO}_2$ measurement (blue). Best model fit shown in dashed line (black).

Figure 2: Observed atmospheric $a^{14}\text{CO}_2$ in Schauinsland, Germany (Levin et al., 2013) with observed and inversely modeled Heshang Cave soil $a^{14}\text{CO}_2$.

Figure 3: Heshang Cave soil $p\text{CO}_2$ by depth

Figure 5: Supplemental Figure: Speleothem bomb peak records (black points) referred to in this manuscript plotted with their regional atmospheric $a^{14}\text{C}$ curves (Hua et al., 2013) (black line), and the results of all successful model runs of the geochemical box model described in the text (grey lines). The best model fit is highlighted (red lines).