Dead carbon in stalagmites: Carbonate bedrock paleodissolution vs. ageing of soil organic matter. Implications for ^{13}C variations in speleothems

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Abstract—Twenty-one ^{14}C accelerator mass spectrometric analyses were obtained for three Holocene stalagmites from the Uamh-an-Tartair cave (Sutherland, Scotland) in order to estimate the past dead carbon proportion (dcp). Results show that the dcp increases from 22 to 38% from 3780 years ago to the present. Because δ^{13}C variation is small within each sample, it is concluded that this dcp increase is the product of the ageing of soil organic matter related to peat bog development above the cave that produced older soil CO_2 and not from a more intense dissolution of the surrounding carbonates, which would have led to a δ^{13}C increase.

Comparison with samples from other sites in Europe shows no intersite correlation between dcp and δ^{13}C, but a relatively good intersite correlation is observed between dcp and average site temperature. Thus, temperature may be a major factor controlling the production of old soil organic matter CO_2 and, therefore, the dead carbon content of seepage water. In contrast to the Scotland stalagmites, two other Holocene samples from sites in southern France and Belgium exhibit a good correlation between δ^{13}C and dcp, which can be explained in terms of variations in the intensity of limestone dissolution. Consequently, δ^{13}C variations observed in stalagmites are not always due to changes in the vegetation type (C3/C4) as has been commonly assumed; ^{13}C/^{12}C variations in speleothem calcite may also be controlled by the soil organic matter age and, in some cases, by the intensity of the limestone dissolution. Conversely, a largely constant speleothem δ^{13}C signal, as observed for the Scotland stalagmites, does not necessarily imply that surface climate and vegetation conditions were stable since the dcp variations, in this case, are clearly related to the peat bog development during stalagmite growth. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

The dead carbon content (expressed here as dead carbon proportion or dcp) of speleothem-depositing seepage water depends on the specific and complex nature of the geochemical processes associated with recharge and carbonate dissolution/precipitation in karstic areas. Three stages can be discerned (Hendy, 1971), each having its own distinct set of processes. First, there is the initial equilibration of recharge water with a CO_2 reservoir, which determines the initial dcp and carbon isotope composition of the solution that will later dissolve carbonate rock. This CO_2 reservoir may be soil organic matter or the atmosphere if the site lacks a soil cover. Carbonate dissolution also may occur in the soil zone, and some carbonate deposition may occur here and in the vadose zone once a downward-percolating recharge water becomes saturated with calcite, but before it reaches a cave. Second, the subsequent dissolution of carbonate may occur under fully open system conditions (where CO_2 saturation and isotopic equilibrium is maintained between downward-percolating recharge water and the overlying CO_2 reservoir), under fully closed system conditions (where recharge water is initially equilibrated with a CO_2 reservoir but then isolated from it before carbonate dissolution commences), or under some intermediate state between

these two end-member situations. Finally, there is a set of unique processes associated with the deposition of secondary carbonate in the cave. Depending on the environmental conditions at the time of deposition, which are dynamic and can change significantly over the time scale of speleothem deposition at any single drip site, precipitation of calcium carbonate can occur under conditions of isotopic equilibrium or where an isotopic fractionation has occurred.

Given the complex nature of geochemical processes described, it can be inferred that the dcp should be affected directly by these processes and to different extents, depending of their relative importance (Fig. 1). The measurement of dcp has at least three areas of interest: (1) determination of the dead carbon correction for ^{14}C dating of speleothems and groundwaters, which is possible only if the dcp has not changed with time; (2) studying past environmental changes and, in particular, paleodissolution process changes; (3) better understanding of present day dissolution processes and the transfer dynamics of carbon in soil and in the unsaturated zone.

Recent studies have pointed out the importance accelerator mass spectrometry (AMS) measurements of ^{14}C of modern stalagmites. First, the atmospheric ^{14}C-bomb peak due to nuclear bomb tests is visible in stalagmites and can be used to quantify and model carbon transfer above the cave (Genty and Massault, 1999). It has been shown that the bomb peak found in stalagmites is dampened compared to the atmospheric peak

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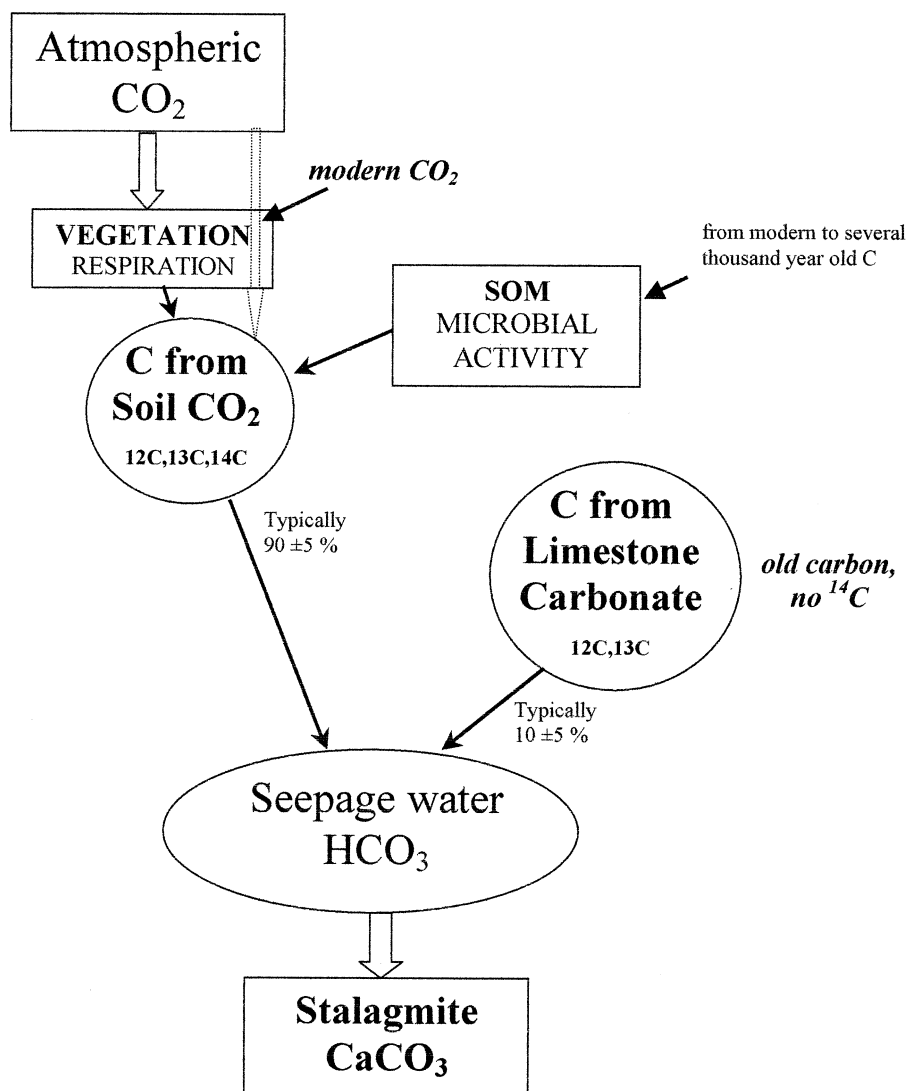
Fig. 1. Stalagmite carbon sources. The three possible sources of speleothem carbon are (1) atmospheric CO_2, (2) soil CO_2, and (3) the host carbonate rock (limestone or dolomite). From other sites that have been studied (Genty and Massault; 1999; Genty et al., 1999a), data suggest that carbon from soil CO_2 is the principal source for speleothem carbon (typically between 80 and 95%) but it can be much less at specific sites (60%, this study).

(by ~80%), and that the offset is site-variable (from 25–0 yr). These differences are due to the different rates of the soil organic matter (SOM) turnover. The construction of ^{14}C activity time series in modern stalagmites also allows one to determine the modern dcp value (called $dcp_{mod.}$) by measuring the activity at ~1950 A.D. in the stalagmite and in the atmosphere (Genty et al., 1998). For a few sites in Western Europe, $dcp_{mod.}$ values vary from 9 to 17.5 ± 1.5%, which demonstrates that most of the carbon found in stalagmites at these locations is derived from soil CO_2. However, no clear intersite relationship was found between $\delta^{13}C$ and dcp, so that observed $\delta^{13}C$-dcp variations have been explained by either variation in the open/closed system nature of the dissolution process or the possibility of prior calcite precipitation above the cave in the unsaturated zone (Genty et al., 1999a).

In the case of two Holocene stalagmites where thermal ionisation mass spectrometry (TIMS) $^{230}Th/^{234}U$ dates have

been obtained, ^{14}C activity measurements permitted the estimation of past dcp (dcp_{past}) based on dendrochronologic calibration curves. As documented by Genty et al. (1999a), it appeared that the dcp_{past} is essentially constant with time in a given sample: On one stalagmite from southwest France, which grew during the last 3000 yr, dcp_{past} is 9.4% ($\sigma = 1.6, n = 6$), and for another stalagmite from Belgium, which grew between 11 and 5 ka, dcp_{past} is 17.5% ($\sigma = 2.4, n = 10$). Consequently, for these samples at least, calibrated ^{14}C ages corrected with a constant dcp show excellent correlation with U/Th ages, thus validating the ^{14}C dating method. However, in this study we present new results for stalagmites from Scotland that differ from previously studied material in two ways: dcp_{past} values exhibit large variations and $dcp_{mod.}$ values are much higher than expected. Comparison of the speleothem datasets provides an enhanced understanding of the processes that control the dcp and $\delta^{13}C$ values of speleothems.
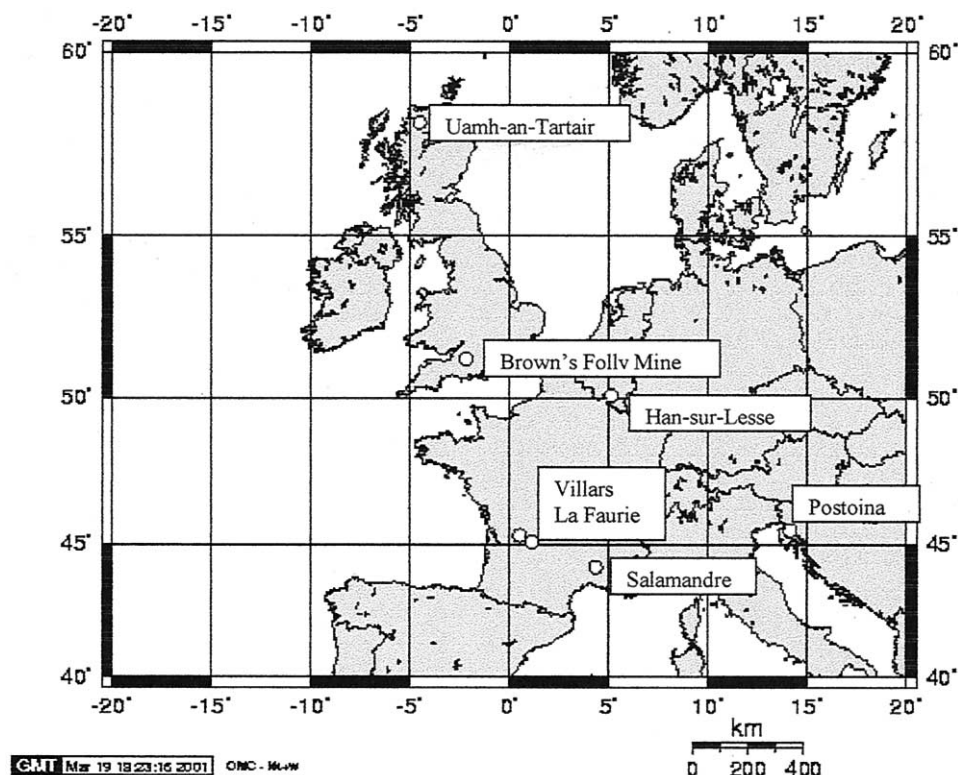
Fig. 2. Map of the western Europe indicating the sites included in this study. The main differences among these sites are the vegetation, which is denser in the northern part and sparse in the Mediterranean sites, and the average temperature, which ranges from 7.3°C at the Scotland site (Uamh-an-Tartair) to 14.5°C at the Mediterranean site (Salamandre).

2. SITE AND SAMPLE DESCRIPTION

The Uamh-an-Tartair cave (UAT: 58°15′N, 4°57′W, 220 m; see Fig. 2) is developed in Cambro-Ordovician dolomite (dolostone with accessory calcite) in northern Scotland. The average surface temperature is 7.3°C (similar to the cave temperature), and the mean annual rainfall is 1900 mm (Baker et al., 1999). The particular interest in this site is that it is covered by a 0.6 to 0.8 m peat layer, which started to develop ~3000 to 4000 yr ago (Baker et al., 1999). Hydrologic monitoring of the peat using two dipwells demonstrates that in summer the water level falls to the base of the peat, but for the rest of the year, the peat remains saturated with water levels within 10 cm of the surface, and that autumn recharge of the peat is very rapid. The three stalagmites analysed in this study were taken from a small chamber ("the grotto") a few meters apart from each other and 10 to 15 m below the surface. Each stalagmite (SU-96-7, SU2, and SU-96-1/2) contains luminescent laminae 20 to 200 μm thick that have been demonstrated to be annual by comparison with TIMS U/Th ages (Baker et al., 1993; Proctor et al., 2000; and unpubl. data). The stalagmites were sampled in a manner that would provide as even a chronology as possible over the last 4000 yr.

Results of this study are compared with those from six other European sites (five caves and one mine) where dcp and δ^{13}C data are available. Results have been published previously for all sites (Genty et al., 1999a) except the southernmost one, Salamandre, in southeastern France. From north to south, these include Browns Folly mine (England), Han-sur-Lesse (Belgium), Postojna (Slovenia), and Villars and La Faurie (southwestern France). The geologic and climatic settings of these sites are summarised in Table 1. All sites are relatively shallow. Average cave temperatures vary from 7.3°C (northernmost cave) to 14.5°C (southernmost cave). Rainfall varies from 787 to 1900 mm/yr; the most humid sites are in Scotland and Solvenia, where temperature is also the lowest (7.3 and 8°C, respectively). The warmest sites are not the driest ones, and even above the Salamandre cave, which is not far from the Mediterraean sea, rainfall is slightly higher than at the Belgian site.

3. METHODS

An absolute chronology for the UAT samples is derived from TIMS U-series dating and annual luminescent laminae counting. TIMS ^{230}Th/^{234}U analyses were carried out at the Open University (UK) using a Finnigan MAT262 mass spectrometer equipped with a reardind potential quadrupole and a secondary electron multiplier as described by Genty et al. (1999a,b). Laminae counting was performed on a Zeiss Axiotech microscope under UV (mercury source) light (Proctor et al., 2000). The Salamandre Cave stalagmite was dated by TIMS U-series techniques using a VG sector 54 mass spectrometer fitted with a Daly ion counter and an electronic filter (CEREGE Laboratory). Calcite powder samples for ^{14}C analysis were reacted with H_3PO_4 to obtain CO_2. The gas was graphitized on iron with hydrogen at 650°C for 100 min; residual gas was used for stable isotope measurements on a SIRA spectrometer. Carbon atoms were counted with an accelerated mass spectrometer (TANDETRON, CNRS-CEA, UMS T2004 Gif-sur-

Table 1. Environmental characteristics (geology, vegetation, and climate), plus dead carbon proportion (dcp) and carbon-isotope ($\delta^{13}C$) summary data for the seven cave locations discussed in this study.

| Site lat., long., alt.	Dead carbon proportion (%)	$\delta^{13}C$ range (‰)	Geology of karst aquifer	Limestone thickness above the cave (m)	Vegetation types and density of trees for the forest cover	Soil thickness above the cave (cm)	Mean annual rainfall (mm)	Mean annual temperature = cave temperature (°C)
Uamh an Tartair (Scotland) 58°15′N, 4°57′W, 220m	36.7 ± 1 33.6 ± 4.2 24.5 ± 2.9	−10.7 ± 0.1 −14.9 ± 0.1 −12.7 ± 0.1	Cambro-Ordovician dolostone	10 ± 5	Peat bog	60–80	>1900	7.3
Browns Folly Mine (England) 51°23′N, 2°22′W, 150m	17.5 ± 1.5	−10.0 ± 0.1	Jurassic limestone	10–15 ± 5	Mixed deciduous	5–30	800	10
Han-sur-Lesse (Belgium) 50°08′N, 5°10′E, 180m	12.2 ± 1.5 17.5 ± 1.5	−9.4 ± 0.1 −6.8 ± 0.1	Givetian limestone (Devonian)	50 ± 10	Hornbeams, limes, oaks, hazels	5–30	787 (6 yr)	8.9
Postojna (Slovenia) 45°46′N, 14°12′E, 529m	11.6 ± 1.5	−9.6 ± 0.1	Upper Cretaceous limestone	30 ± 10	Pine tree forest	5–10	1500	8
Villars (Dordogne, France) 45°30′N, 0°50′, 175m	9.4 ± 1.5	−9.9 ± 0.1	Bajocian limestone (Jurassic)	10 ± 5	Oaks (13 oaks/100m2; mean diam. = 17cm), hazels, junipers, mosses and grass	0–15	1048 (10 yr)	12.4
La Faurie (Dordogne, France) 45°08′N, 1.11′E, 225m	9 ± 1.5	−10.3 ± 0.1	Bajocian limestone (Jurassic)	15 ± 5	Grass, mosses, oaks (20 oaks/100m²; mean diam. = 10 cm)	0–20	861 (10 yr)	12.9
Salamandre (Gard, France) 44°15′N, 4°30′W, 230m	5.3 ± 3	−10.0 ± 0.1	Barremian limestone (Cretaceous)	35 ± 5	Bushes and Green Oaks	0–15	900	14.5
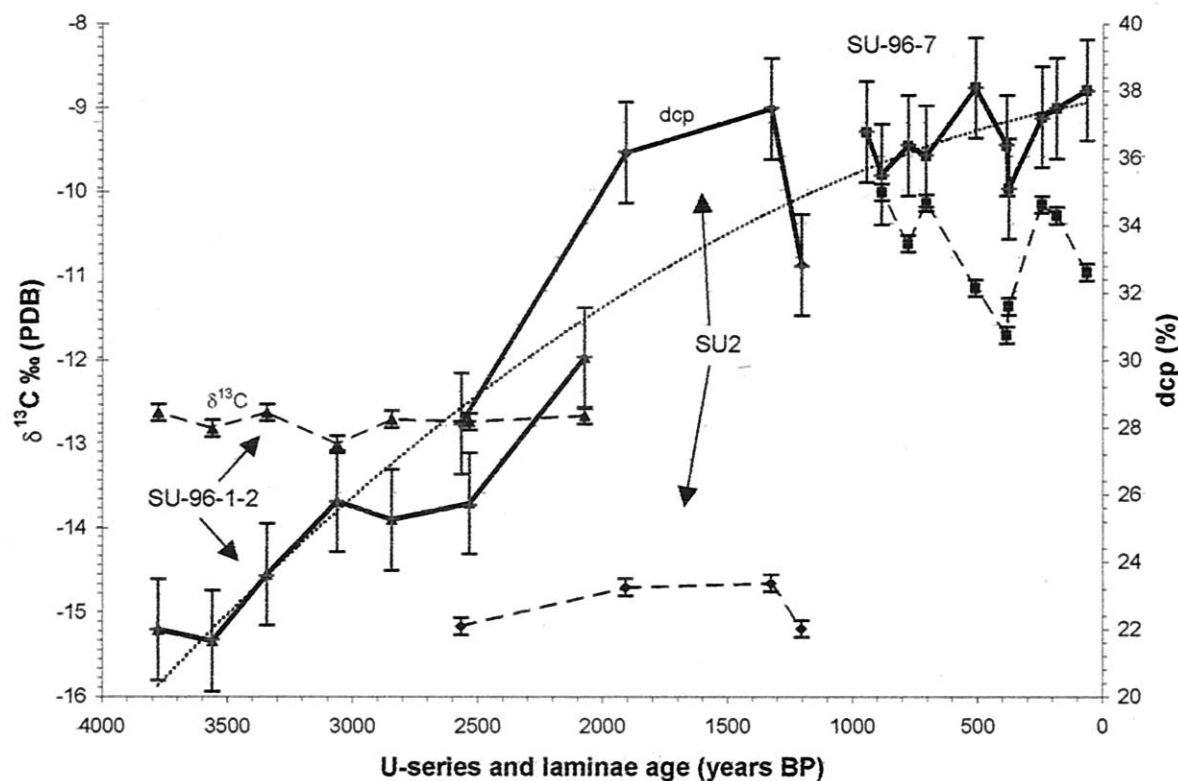
Fig. 3. Dead carbon proportion (dcp, solid lines) and stable isotope (δ^{13}C, dashed lines) variation in the three stalagmites from Uamh-an-Tartair cave in Sutherland, Scotland. Note the dcp increase (continuous line) since 3500 yr, from ~22 to 38% and the stability of the δ^{13}C (dashed line) for the SU-96-1-2 and SU2 stalagmites. Dashed curve is the polynomial fit of the dcp data.

Yvette, France). Analytical uncertainties, including laboratory errors, are ± 0.1‰ for δ^{13}C and between 0.4 and 0.6 pMC for ^{14}C activity.

Stalagmite dcp_{past} values were calculated by following the procedure of Genty and Massault (1999):

$$dcp_{past} = [1 - (a\ ^{14}C_{init.}/a\ ^{14}C_{atm.init.})] * 100\%; \quad (1)$$

where $a\ ^{14}C_{atm.\ Init.}$ is the atmosphere ^{14}C activity at the time of deposition and $a\ ^{14}C_{init.}$ is the initial ^{14}C activity of the calcite defined by:

$$a\ ^{14}C_{init.} = a\ ^{14}C_{mes.}/(exp(-\ln(2)/5730)*t); \quad (2)$$

with $t = {}^{230}$Th/^{234}U and/or laminae counting age in years and where $a^{14}C_{mes.}$ is the measured calcite activity. The $a^{14}C_{atm.\ Init.}$ value is found with the ^{230}Th/^{234}U or laminae counting age on the calibration curves (Bidecadal Δ^{14}C values of the Calib 3.0 data set) (Stuiver and Kra, 1986; Bronk, 1994). As explained in these studies, and assuming a mean error of 0.7% for ^{14}C activity values, the average dcp error is set at ± 1.5%.

4. RESULTS AND INTERPRETATION OF THE UAMH-AN-TARTAIR STALAGMITES

4.1. Results

As illustrated in Figure 3, the dcp_{past} measured on the three UAT stalagmites shows an increase of 16% (22–38%; see Table 2) from 3.8 Ka to present. This increase slows with time and reaches a relatively stable level at ~1 Ka. It can be fitted by the polynomial equation:

$$dcp_{past} = -9.10^{-7}*age^2 - 0.0014*age + 37.75; R^2 = 0.92$$

$$(3)$$

where SU-96-1/2 and SU2 samples are contemporaneous at ~2.5 Ka; there is a 1% difference in sample dcp_{past} values that just overlap within the uncertainty limits: 25.7% ± 1.5 for SU-96-1/2 and 28.1% ± 1.5 for SU2. Stalagmite SU-96-1/2 has a dcp_{past} trend which increases regularly from 22.0% at 3.8 Ka to 30.1% at 2.1 Ka (Δdcp = 8.1%). For sample SU2, the overall range of dcp_{past} variation is 9.4% (28.1–37.5) between 2.6 and 1.3 Ka. The dcp_{past} values of the most recent sample SU-96-7 are stable (mean = 36.7%; ± 1.0). Such dcp_{past} time variation is much greater than previously observed in two other Holocene samples from Western Europe, where the maximum dcp_{past} change measured was 3.8 and 6.3%, respectively (see above and Genty et al., 1999a). δ^{13}C values display a different time evolution. It is stable on the two samples where the greatest dcp_{past} variations were observed: -12.1 ± 0.1‰ for SU-96-1/2 and -14.9 ± 0.3‰ for SU2 (Figs. 1 and 3; Table 2). The SU-96-7 sample δ^{13}C shows more pronounced variations but its dcp is more stable than the two other stalagmites.

4.2. Interpretation

As described in the introduction, the δ^{13}C of the speleothem calcite is controlled by the complex geochemical and hydro-

Table 2. ^{14}C and U-series data for stalagmites from Uamh-an-Tartair cave (Sutherland, Scotland). nd = no data; int. = interpolated values assuming constant growth rates.

Sample	Lab. number	Quantities (mg)	mm from top (from base for SU2) ($\pm 1,0$)	Age from $^{230}Th/$ ^{234}U and lam. Count. (SU-96-7) (years BP)	Measured ^{14}C activity (pMC normalized)	Init. ^{14}C act. (pMC)	Init. ^{14}C atm. act. (pMC)	dcp (%) ($\pm 1,5$)	$\delta^{13}C$ (‰ PDB) ($\pm 0,1$)	$\delta^{18}O$ (‰ PDB) ($\pm 0,1$)
SU-96-2-4	PA 718	27,8	30	2073 ± 48	54,96 ± 0,45	70,6	101	30,1	−12,7	−4,4
SU-96-1-3	PA 753	21,5	42	2533 ± 60	55,75 ± 0,48	75,7	102	25,7	−12,7	−4,6
SU-96-1-A	PA 754	24,7	52	2844 (int)	54,06 ± 0,51	76,3	102,03	25,3	−12,7	−4,8
SU-96-1-B	PA 755	20,1	59	3062 (int)	52,61 ± 0,50	76,2	102,7	25,8	−13	−4,8
SU-96-1-2	PA 719	33,8	68	3342 ± 82	53,16 ± 0,43	79,6	104,3	23,6	−12,6	−4,5
SU-96-1-C	PA 756	22,8	75	3560 (int)	52,83 ± 0,54	81,3	103,73	21,7	−12,8	−4,6
SU-96-1-D	PA 757	24,3	82	3778 (int)	51,34 ± 0,48	81,1	103,94	22	−12,6	−4,7
SU2-14C-A	PA 743/H2311	51,1	0	2567 ± 120	53,5 ± 0,4	73	101,6	28,1	−15,2	−4,8
SU2-14C-C	PA 745/H2313	45	45	1909 ± 84	51,3 ± 0,5	64,7	101,3	36,2	−14,7	−5,1
SU2-14C-B	PA 744/H2312	42,7	90	1326 ± 64	53,9 ± 0,4	63,3	101,2	37,5	−14,7	−5
SU2-14C-D	PA 746/H2314	32,7	142	1204 ± 120	58,7 ± 0,5	67,9	101,1	32,8	−15,2	−5
SU-96-7 3,0	PA 615	34,1	3	65 ± 5	61,9 ± 0,5	62,3	100,6	38	−11	−4,6
SU-96-7 7,0	PA 660	32	7	185 ± 5	62,8 ± 0,8	64,2	102,63	37,5	−10,3	−4,3
SU-96-7 10,5	PA 683	30	10,5	244 ± 5	62,7 ± 0,5	64,5	102,7	37,2	−10,2	−3,7
SU-96-7 15,5	PA 684	30	15,5	377 ± 5	63,4 ± 0,5	66,3	102,1	35,1	−11,4	−4,8
SU-96-7 16	PA 613	20,1	16	385 ± 5	62 ± 0,5	64,9	102	36,4	−11,7	−3,7
SU-96-7 20	PA 688	30	20	509 ± 5	60,3 ± 0,6	64,1	103,5	38,1	−11,1	−4,8
SU-96-7 25	PA 687	30	25	707 ± 5	59,7 ± 0,6	65	101,7	36,1	−10,1	−5
SU-96-7 26	PA 614	30	26	780 ± 5	58,5 ± 0,6	64,3	101	36,4	−10,6	−4,3
SU-96-7 27,5	PA 661	30,8	27,5	885 ± 5	58,4 ± 0,5	64,9	100,7	35,5	−10	−4,2
SU-96-7 29,0	PA 715	13,1	29	946 ± 5	57,4 ± 0,5	64,3	101,7	36,8	nd	nd

logic processes that occur from the surface to the place in the subsurface where calcite is precipitated (Table 3). These processes are discussed in the context of the UAT data:

1. The type of vegetation (C3/C4 photosynthetic pathways) (Smith and Epstein, 1971; Deines, 1980; Vogel, 1983; Dorale et al., 1992): From the peat study, it is clear that the type of vegetation (peat bog) has not changed over the last 3.0 ka (Baker et al., 1999; Charman et al., 2001), and that all plants above the caves are of C3 type; consequently, a change in the type of vegetation cannot explain the interstalagmite $\delta^{13}C$ variations.

2. The possible process of soil gas mixing with the atmosphere due to a < 100% vegetation cover (Dulinski and Rozanski, 1990): A substantial $\delta^{13}C$ decrease (from +2‰ to −8‰ between 21 and 14 ka) observed in a New Zealand speleothem was recently interpreted by Hellstrom, et al. (1998) as reflecting a change in the soil pCO_2 due to the development of a vegetative cover above the cave. If such a process was the main cause of the $\delta^{13}C$ change observed in the UAT samples, a progressive trend toward lower $\delta^{13}C$ values would appear as the peat bog develops over the cave, which is not the case.

3. The quantity of carbon supplied by limestone or dolomite dissolution with a $\delta^{13}C$ at ~0‰ and which is controlled by the type of dissolution process (open/closed or coincident/sequential) (Hendy, 1971; Drake, 1983; Salomons and Mook, 1986): The type of dissolution (different ratio of open/closed system dissolution) is likely to explain the $\delta^{13}C$ variation of the studied samples. Hendy (1971) studied the consequences of such dissolution processes on the precipitated calcite $\delta^{13}C$: For a soil CO_2 $\delta^{13}C$ of −24‰ and an average temperature of 10°C, the $\delta^{13}C$ of precipitated calcite will be −13.5‰ under open system conditions and between −11.5 and −10.5‰ when closed system conditions prevail and for a soil pCO_2 of between 0.02 and 0.0003 atm. If we consider a lower SOM $\delta^{13}C$ (i.e., −28‰) as measured in peat soils (Baker et al., 1999; Charman et al., 2001), $\delta^{13}C$ of calcite will be lowered by 3 to 4‰, leading to a $\delta^{13}C$ of deposited calcite between −16 and −13‰, depending of the dissolution system process. These values are in agreement with the $\delta^{13}C$ of SU2 sample but are much lower than $\delta^{13}C$ of SU-96-1-2 and SU-96-7 (Fig. 3). C-isotope differences could be due to local differences in the flow path of seepage water feeding each sample. Differences in the peat layer overlying each sample can lead to a slightly different dissolution process, and the proportion of open/closed dissolution system will vary from one place to another. For example, small (< 1 m wide) dolines overlie the cave, and these lead to local variations in peat thickness and water flow paths. Additionally, the site was glaciated in the late Devensian, and patchy thin veneers of till are present at the base of some peat sections. Hence, local variations in $\delta^{13}C$ are to be expected, but the fact that for two stalagmites, the average $\delta^{13}C$ is higher than expected suggests that processes other than changes in open/closed dissolution system occur.

4. Karst water evolution along the flow path: Prior calcite precipitation by CO_2 degassing in voids or microfissures in the unsaturated zone above the cave and incongruent dissolution, which could occur in dolomitic terrain like our studied site (Fairchild et al., 2000), will increase the $\delta^{13}C$ of the precipitated calcite.

5. Kinetic fractionation due to the rate of $CaCO_3$ precipitation, which is linked to the drip rate, the rate of loss of CO_2, and/or evaporation (Hendy, 1971; Turner, 1982; Romanek et al., 1992; Dulinski and Rozanski, 1990): Laboratory

Table 3. Environmental factors controlling the carbon isotopic composition of speleothem calcite. The $\delta^{13}C$ presented in this tables are to show a trend rather than precise values because several of the following factors interact with each other. Because we deal with C3 type plants in our study, the $\delta^{13}C$ values for calcite are given with the hypothesis of a soil CO_2 $\delta^{13}C$ of $-25‰$.

	Soil CO_2 $\delta^{13}C$	Calcite $\delta^{13}C$	^{14}C activity
Type of vegetation			
C3 plant (typical in our study)	$-25‰$	Low i.e., $-14‰$	No influence
C4 plant (arid areas) (Smith and Epstein, 1971; Deines, 1980; Vogel, 1993; Dorale et al., 1992)	$-12‰$	High i.e., $-3‰$	No influence
Soil CO_2 concentration			
Low	Mixing between $-25‰$ (soil C3 CO_2)	High $> -14‰$	No significant change at the studied time scale (> 1 yr)
High (depends on vegetation density and mixing between soil and atmposhere; Dulinski and Rozanski, 1990)	and $-8‰$ (atmosphere)	Low i.e., $-14‰$ up to positive values	
Soil organic matter age (OM turnover rate; Genty and Massault, 1999; Genty et al., 2000)	No significant change	No significant change	Lower activity than atmosphere due to old organic C (to be added to dead C from rock dissolution)
Dissolution system			
Open	$-25‰$	-12 to $-14‰$	Approximately atmospheric ^{14}C
Closed (Hendy, 1971; Dulinski and Rozanski, 1990)	$-25‰$	-10.5 to $-11.5‰$	50 to 65% of atm. ^{14}C
Prior calcite precipitation (Baker et al., 1997; Fairchild et al., 2000; Gascoyne and Nelson, 1983)	No influence	High i.e., $> -14‰$	No significant change but decreases if incongruent dissolution occurs
$CaCO_3$ precipitation rate			
High	No influence	Low i.e. $-14‰$	No significant change
Low (Turner, 1982; Dulinski and Rozanski, 1990; Hellstrom, et al., 1998; Romanek et al., 1992)	No influence	High i.e., $> -14‰$ up to positive values	Might be influenced by cave CO_2 equilibration (slight increase)

experiments of $CaCO_3$ precipitation of supersaturated solutions have shown that $\delta^{13}C$ might be enriched by 0.5 to 4.0‰, depending of the rate of carbonate precipitation, that is, the lower precipitation rate, the higher the enrichment (Turner, 1982). More recent results have demonstrated that ^{13}C calcite enrichment was not as high, but experiments did not simulate the actual stalagmite formation (Romanek et al., 1992). The best approach is certainly the semidynamic model made by Dulinski and Rozanski (1990) to explain the $^{13}C/^{12}C$ ratio in speleothems: For an initial soil $\delta^{13}C$ of $-25‰$ (typical under C3 vegetation), a cave atmospheric pCO_2 of 0.05 atm, and a temperature between 5 and 15°C, they observed that 10 min after the beginning of calcite precipitation, the calcite $\delta^{13}C$ was between -8 and $-2‰$, much more than expected if all the dissolved carbonate had precipitated under isotopic equilibrium (i.e., $-13.5‰$ in an open system as explained above). Elevated and variable values of $\delta^{13}C$ in British speleothems have already been discussed and have highlighted most of these processes, suggesting caution in the interpretation of the $\delta^{13}C$ signal (Baker et al., 1997).

In conclusion, it seems difficult to ascertain which of the above processes are dominant at Uamh an Tartair. The fact that the dead carbon proportion does not follow the intersample $\delta^{13}C$ variations (Fig. 3) is important and suggests that the dcp change might not be due to a specific dissolution process like open/closed system evolution of recharge water.

4.2.1. dcp increase

In theory, an increase in dcp results from at least three causes: (1) an error in the absolute chronology (i.e., if too many growth laminae are counted, then the true age will be overestimated and the dcp will decrease when going back in time), (2) a more intense host rock dissolution (and/or incongruent dissolution) bringing more dead C from the host rock, and (3) a more important input of dead carbon coming from the soil CO_2.

The chronology of the stalagmites studied has been established with luminescent annual laminae counting. Comparison of laminae ages with TIMS U-series ages had validated these ages (Baker et al., 1993, 1999; Proctor et al., 2000; and unpubl. data). Moreover, a ^{14}C activity profile obtained on the top of the SU-96-7 stalagmite showed the peak due to bomb carbon and allowed the calculation of a growth rate (0.04–0.06 mm/yr), which is in good agreement with that determined independently from the laminae counting (Genty et al., 1999b). Consequently, we can be confident in the chronology of these samples.

At first glance, a dcp increase might indicate a more intense dissolution (which might be due to a more "closed" dissolution system) bringing more dead carbon from the host rock (limestone or dolostone). As seen above, the high stability of the $\delta^{13}C$ in two of the UAT stalagmites (SU-96-1/2 and SU2) demonstrates that the dissolution intensity was constant with time. This suggests that the proportion of C from the dolomite

Table 4. ^{14}C- and U-series data for stalagmites from the Salamandre cave (France). nd = no data.

Sample	Lab. number	cm from top ($\pm 0,1$)	^{230}Th/^{234}U age (yr BP)	Measured ^{14}C activity (pMC normalized)	Init. ^{14}C act. (pMC)	Init. ^{14}C atm. act. (pMC)	dcp (%) ($\pm 1,5$)	δ^{13}C (‰ PDB) ($\pm 0,1$)	δ^{18}O (‰ PDB) ($\pm 0,1$)
Sal-stm1-A	H2415/51S10-1	49	6658 ± 131	44,9 ± 0,4	100,4	108,6	7,6	−9,8	−5,1
Sal-stm1-B	H2412/51S15	40,7	6451 ± 38	44,9 ± 0,4	97,9	107,91	9,3	−9,3	−5
Sal-stm1-C	H2413/51S17	28	2265 ± 27	73,1 ± 0,5	96,1	98,62	2,5	nd	nd
Sal-stm1-D	H2400/50S16	12,6	1399 ± 22	80,4 ± 0,5	95,2	97,69	2,5	−10,4	−4,2
Sal-stm1-E	H2414/50S10	1	601 ± 13	88,1 ± 0,7	94,8	99,35	4,6	−10,4	−4,4

(dolostone δ^{13}C is ~0 ± 2‰ PDB) (Nicholas, 1996) is constant, and that rock dissolution did not change significantly, leading to the rejection of the second hypothesis.

Incongruent dissolution might also be a cause of an increased input of dead C in the seepage water. Because dissolution of dolomite is slower than calcite, the latter can be precipitated while dolomite is dissolved. This dissolution during the seepage of the water brings carbon from the host rock with a high δ^{13}C and dead carbon. But because the δ^{13}C variation does not correlate with dcp, we can assume that this process was not important at the UAT site.

The other main source of carbon in speleothems is the soil CO_2 that is either derived from the atmosphere or produced by plant root respiration and the degradation of soil organic matter (SOM). The total dcp can be calculated as:

$$dcp_{total} = dc_{Soil\ CO2} + dc_{rock}; \qquad (4)$$

where dcp_{total} is the total dead carbon proportion, $dc_{Soil\ CO2}$ is the dead carbon fraction from the soil CO_2, and dc_{rock} is the dead carbon fraction from the host rock.

If the dc_{rock} remains constant, then any change in dcp_{total} reflects a change in $dc_{Soil\ CO2}$. This suggests that increases in dcp observed in UAT stalagmites from 4 to 1 ka reflect an increase in $dc_{Soil\ CO2}$ and, therefore, an increase in the average age of soil organic matter. This phenomenon can be explained by the development of the peat layer above the cave, since ~3.7 Ka (interpolation of five ^{14}C ages at the deepest part of the peat core) (Baker et al., 1999). During the period of peat development, the newly formed vegetation is not completely decomposed by microbial activity; there is a positive balance between production and degradation of organic matter. Consequently, old OM accumulates year after year, producing a soil CO_2 that is increasingly depleted in ^{14}C. When equilibrium is attained between production and degradation, the dcp increase ceases, as observed in the UAT stalagmite material deposited since ~1 Ka. The time between the beginning of the dcp increase and the time when it stabilized is ~2500 yr. This is the time for the SOM to reach a new steady state, which can be compared to the SOM turnover rate. However, only a minimum estimate of the time of beginning of the dcp increase is obtained by this method, as we do not have access to older ages in our stalagmite samples.

The ageing of the SOM can be estimated, for example, for the SU-96-1/2 stalagmite whose dcp increased from 22%, 3780 yr ago to 30%, 2070 yr ago (Δdcp = 8%), while δ^{13}C remained constant at −12.1 ± 0.1‰. This shows that during the 1710 yr of stalagmite growth, the average age of the dissolved soil CO_2 increased by 950 yr. This result can be compared with average

soil turnover rates obtained previously, which may range from a few years for a fast turnover pool to more than 1000 yr for slow turnover pools (Milton and Kramer, 1995; Trumbore et al., 1989; Trumbore, 1993). Our results give an indirect but accurate idea of the SOM dynamics in such environments, which is of importance in understanding the global carbon cycle and its link to climate variations (Jenkinson et al., 1991).

5. COMPARISON WITH OTHER EUROPEAN SITES

Comparisons with other European sites have been made to better understand the most important environmental factors (temperature, climate, vegetation) controlling dcp and δ^{13}C. Dead carbon proportion, TIMS U/Th ages, ^{14}C results, and stable isotope data are presented for UAT samples and for Salamandre cave in Tables 2 and 4. Data for the other samples are available in previous publications (Genty et al., 1998; Genty and Massault, 1999; Genty et al., 1999a). For each site, the dcp was calculated either with the ^{14}C activity curve of the last 50 yr on modern stalagmites (dcp_{modern}) (Fau-stm14, Pos-stm4, Han-stm5, BFM-Boss) or with Holocene stalagmites where both ^{230}Th/^{234}U and AMS ^{14}C were available (dcp_{past}) (Han-stm1, Vil-stm1, SU-96-7, SU-96-1/2, SU2, Sal-stm1).

5.1. Intersite δ^{13}C and dcp Comparison

The data presented in Figure 4 and Table 5 show the following: (1) Despite some overlaps between spatially closed samples (Vil-stm1 and Fau-stm4; Dordogne, France), each stalagmite has a specific position on the plot characterised by a mean δ^{13}C and a mean dcp; (2) the UAT samples are distinct compared to other sites having very high dcp (between 21 and 38%) and among the lowest δ^{13}C (between −10 and −15‰), while other sites are characterised by a dcp of between 10 and 15% and a δ^{13}C between −11 and −9‰.

One might consider a broad positive covariation of δ^{13}C with dcp for all the sites except the UAT location (Fig. 4), showing the normal trend for karst areas with rendzina soils, with overall variations reflecting differences in the proportion of soil inorganic carbon able to be taken into solution and degree of open/closed system dissolution. The specific position of Sutherland samples can be explained by the difference in soil types (Table 5): Only the Sutherland site has a thick peat layer while the other sites have a regular thin brown rendzina soil. In the latter case, gas phase is more likely to occur during limestone dissolution than in the former case. Consequently, dissolution will occur under an open system (or coincident system) (Hendy, 1971; Drake, 1983), and a large part of the dead carbon dissolved from the limestone will be removed by the continu-
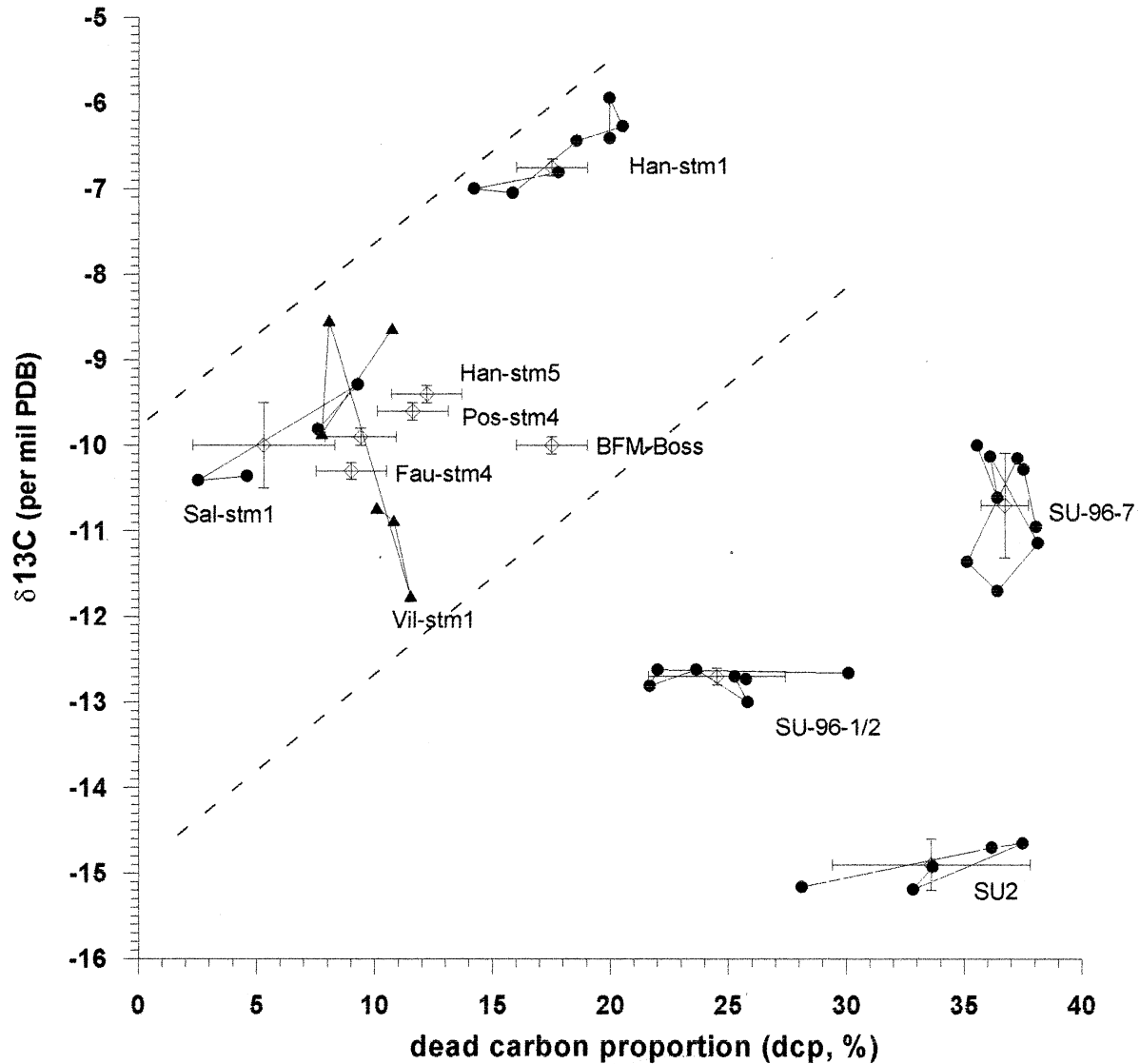
Fig. 4. Comparison of $\delta^{13}C$-dcp relationships for the stalagmites from Sutherland, Scotland with those observed for the other sites in Europe (Genty et al., 1999a, modified). Several environmental factors explain the tendency of the Sutherland stalagmites toward higher dcp and lower $\delta^{13}C$ values: (1) a more closed dissolution system, (2) a lower soil CO_2 $\delta^{13}C$, and (3) an ageing of the SOM. If we exclude the UAT stalagmites (SU samples), there is a broad positive covariation between $\delta^{13}C$ and dcp (between the dashed lines), which is more obvious for two individual stalagmites (Han-stm1 and Sal-stm1), demonstrating a pure limestone dissolution process. Diamonds denote mean values, circles (and triangles for Vil-stm1) indicate values for individual Holocene stalagmite subsamples.

ous and slow CO_2 exchange between water and gas. On the contrary, where we have a peat layer saturated with water, dissolution will occur in a closed (or sequential) system, and all the carbon from the limestone dissolution will remain in the seepage water, leading to a higher dcp. However, while this hypothesis about dcp is consistent with the former model developed by Hendy (1971) (where the dcp should be between 35 and 50% for a closed system), it does not work if we consider the $\delta^{13}C$ of dissolved species (and, consequently, on the stalagmite calcite because fractionation factors are negligible), which should be higher for closed systems. We observed the opposite: The open system sites are enriched by up to 4‰ PDB. Therefore, the open/closed system differences between

the sites cannot solely explain the intersite $\delta^{13}C$ changes. Two other hypotheses can be discussed:

1. The soil CO_2 $\delta^{13}C$ is lower in the Sutherland site because the SOM $\delta^{13}C$ is lower. Measured $\delta^{13}C$ lies between -30 and $-28‰$ PDB, while it is typically $\sim -25‰$ on the other sites (Baker et al., 1999). This would lead a calcite $\delta^{13}C$ of $-14 \pm 1‰$ for a pure closed system, similar to what we observe in one of the UAT samples (SU2), but different in the other two UAT samples, which have a higher $\delta^{13}C$ and which seem to refute this hypothesis (Figs. 3 and 4).

2. The closed system on the Sutherland site prevents mixing with atmospheric CO_2, and most of the dissolved CO_2 is of

Table 5. Comparison of dead carbon proportion (dcp), carbon isotope composition ($\delta^{13}C$), age, dissolved solute content [Ca2+], temperature, and annual precipitation at the cave locations examined in this and previous studies (1 = Genty and Massault, 1999; 2 = Genty et al., 1998; 3 = Genty et al., 1999a; 4 = this study).

Sample	Location	dcp (%)	$\delta^{13}C$ (‰ PDB, ±0,1)	Error	Number of analyses	Method	Stalagmite age	Cave T (°C, ±0,1)	[Ca^{2+}] (ppm, ±10)	Mean annual precipitation (mm)	Ref.
Fau-stm14	La Faurie (Dordogne, SW-France)	9 ± 1,5	−10,3	0,1	21	Bomb-^{14}C curve	modern	12,9	171	861	1
Han-stm5	Han-sur-Lesse (Belgium)	12,2 ± 1,5	−9,4	0,1	14	Bomb-^{14}C curve	modern	8,9		787	2
Pos-stm4	Postojna (Slovenia)	11,6 ± 1,5	−9,6	0,1	11	Bomb-^{14}C curve	modern	9,3	69	1500	2
BFM-Boss	Brown's Folly Mine (Great Britain)	17,5 ± 1,5	−10	0,1	5	Bomb-^{14}C curve	modern	10	95	800	3
Vil-stm1	Villars (SW-France)	9,4 ± 1,5	−9,9	0,1	11	U/Th-^{14}C age comparison	3.07 Ka to 0 Ka	12,4	138	1048	3
Han-stm1	Han-sur-Lesse (Belgium)	17,5 ± 1,5	−6,8	0,1	135	U/Th-^{14}C age comparison	11 Ka to 4.8 Ka	8,9		787	3
SU-96-7	UHT; Sutherland (Scotland)	36,7 ± 1,0	−10,7	0,1	10	U/Th-laminae-^{14}C age comparison	0.95 Ka to 0 Ka	7	37	1900	4
SU2	UHT; Sutherland (Scotland)	33,6 ± 4,2	−14,9	0,1	4	U/Th-laminae-^{14}C age comparison	2.6 Ka to 1.0 Ka	7		1900	4
SU-96-1	UHT; Sutherland (Scotland)	24,5 ± 2,9	−12,7	0,1	7	U/Th-laminae-^{14}C age comparison	3.8 Ka to 2.0 Ka	7		1900	4
Sal-stm1	Aven de la Salamandre (Gard,FR)	5,3 ± 3,0	−10	0,1	4	U/Th-^{14}C age comparison	6,6 Ka to 0.1 Ka	14,5		900	4

Table 6. Correlation coefficients between dead carbon proportion (dcp), $\delta^{13}C$ and mean annual rainfall (R), and cave temperature (Table 4). Note the significant negative correlation between the dcp and the temperature and the positive correlation between the temperature and the seepage water Ca^{2+} content. All correlations involve the 10 studied samples except those with Ca^{2+} where the number of available data is five.

Correlated factors	R^2	Correlation equation
dcp/$\delta^{13}C$	0,31	
dcp/T	0,85	$T = 3.99Ln(dcp) + 20.6$
dcp/R	0,61	$R = 36.76(dcp) + 586.5$
$\delta^{13}C$/T	0,13	
$\delta^{13}C$/R	0,53	$R = 170.8(\delta^{13}C) - 542.2$
Ca^{2+}/T	0,96	$Ca^{2+} = 21.8(T) - 123$
Ca^{2+}/dcp	0,68	$Ca^{2+} = 75.4Ln(dcp) + 303.5$
Ca^{2+}/$\delta^{13}C$	0	

biologic origin, while at the other sites, the very thin soil allows mixing between biologic and atmospheric CO_2, especially in winter when water excess increases, seepage water enters caves, and when soil respiration rate is low (Cerling, 1984).

Consequently, the intersite $\delta^{13}C$ variations cannot simply be due to the differences between open and closed system evolution of recharge water; comparison of isotope data with environmental factors will help to better understand the observed intersite variations.

5.2. Intersite Comparison Between dcp, $\delta^{13}C$, and Environmental Factors

Intrastalagmite dcp and $\delta^{13}C$ variations are smaller than interstalagmite variations for Han-sur-Lesse and Uamh-an-Tartair sites (Fig. 4). This demonstrates that for these samples: (1) Environmental changes during the Holocene were not sufficient to greatly modify the carbon transfer in speleothems and, consequently, the $\delta^{13}C$ and the dcp; (2) the carbon transfer is mainly controlled by local factors, e.g., geology, vegetation, and climate (Table 1), which are compared here with $\delta^{13}C$ and dcp (Table 6). Local factors, by variations in the microfissure network, in rainfall amount, in soil thickness, etc., control the vadose zone flow path, the degree of water-CO_2 equilibration, open/closed system evolution, and the degree of degassing during CO_2 precipitation. Linear regression coefficients among environmental factors (temperature, rainfall, calcium concentration) and dcp and $\delta^{13}C$ have been calculated for all the samples. Both modern and Holocene samples are included because all the site samples studied are necessary for the comparison with the widest possible range of climate.

5.2.1. Intersite $\delta^{13}C$ variations

No correlation was observed between the mean $\delta^{13}C$ and rainfall or temperature, nor with other qualitative geologic settings (Tables 5 and 6). As explained above, it is likely that intersite $\delta^{13}C$ differences are the consequence of several factors such as (1) the type of dissolution variations (open/closed system ratio); (2) the amount of mixing of soil and atmospheric CO_2 for sites where soil is very thin or locally not existent, like most of the studied sites except Uamh-an-Tartair; (3) kinetic effects during calcite precipitation; (4) geologic settings con-

trolling water flow paths along microfissures and leading to the possibility of different amounts of prior calcite precipitation in the unsaturated zone above the caves (Fairchild et al., 2000). For the latter case, the calcite $\delta^{13}C$ increases in response to progressive degassing. The ^{14}C activity (in the precipitated calcite) might increase as well due to successive fractionations during calcite precipitation, but it should not significantly influence the dcp, i.e., for a $\delta^{13}C$ enrichment of 5‰, the $a^{14}C$ increase will be ~1.1%, far less than intersite variations (Saliège and Fontes, 1984).

5.2.2. Intersite dcp variations

Except for the Sutherland samples where we have a thick peat bog, soils above the sites studied are very similar: brown rendzina < 30 cm thick. Geologic settings are also similar: limestone for all the sites except for Sutherland (mainly dolomite) and shallow caves or mine (< 50 m). It is difficult to see the role of the type of vegetation because of the limited number of sites studied. However, a latitudinal gradient in dcp is observed from north to south. The highest dcp is found under the peat bog in northern Scotland, the next highest dcp is found at the forested sites, i.e., oak, hornbeam, lime and hazel, pine (Browns Folly Mine, Han-sur-Lesse, Postojna and Villars), and the lower dcp values are observed under less dense vegetation (grass and sparse bushes at La Faurie and Salamandre). Vegetation is controlled by climate, which also explains the significant negative correlations found between dcp and average site temperature ($R^2 = 0.85$) and to a lesser extent, between dcp and rainfall ($R^2 = 0.61$) (Tables 5 and 6, Fig. 5). It is striking here to note that in a previous study on speleothems of Castelguard Cave in Canada, the proportion of dead carbon found in modern stalactites was very high (i.e., 65–70%) for a very low cave temperature (part of the cave is situated under a glacier ice cover, and the cave temperature is close to 0°C), and so is apparently in agreement with our results (Gascoyne and Nelson, 1983). However, the mechanism of formation of such speleothems is different from that at the European cave sites examined in this study; under the Columbia ice field, the primary source of CO_2 for carbonate dissolution is the atmosphere. Chemical evolution and carbonate dissolution take place under closed system conditions, and there is a strong kinetic control on speleothem precipitation for the present-day conditions, which leads to positive $\delta^{13}C$ values in modern speleothems. The high dead carbon content of the seepage water of this site might be due to oxidation of dead carbonaceous deposits in the bedrock and so may not be comparable. Table 6 also shows that temperature is very well correlated with the seepage water Ca^{2+} concentration ($R^2 = 0.96$, $n = 5$; Fig. 6), which clearly signifies that for the sites studied, at higher temperature the limestone dissolution is greater, as already observed and modelled at different karst springs (Drake, 1980, 1983). No correlation is observed between T and $\delta^{13}C$, confirming that intersite $\delta^{13}C$ variability is more complex but is not uniquely due to the dissolution.

The fact that at higher temperature sites we observe more limestone dissolution (higher Ca^{2+}) and a lower dcp is another indication that dcp is not controlled mainly by host rock dissolution. If dissolution controlled dcp, a positive covariation would be observed between Ca^{2+} and dcp. The soil organic
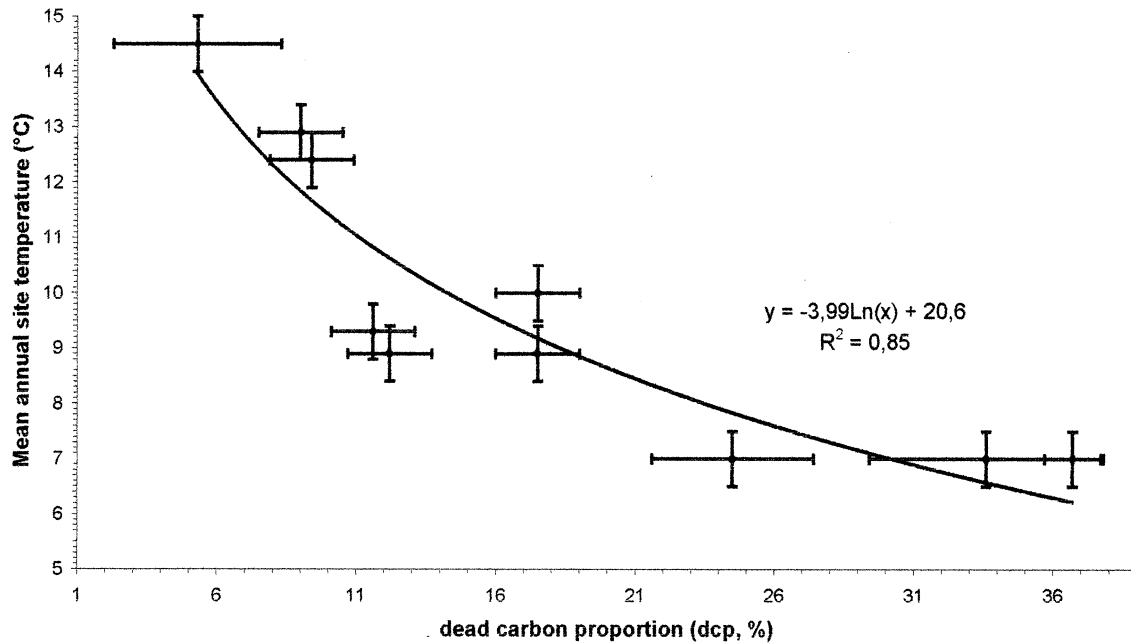
Fig. 5. Correlation between dcp and average site temperature: the lower the temperature, the higher the dcp. Such a correlation might be due to differences in the SOM turnover rate controlled by temperature, humidity, and vegetation density (see text).

matter turnover rate might play a major role, but the process involved is still not obvious. Two hypotheses can be suggested: (1) The ageing of soil CO_2 at a site is due to the denser vegetation producing coarser debris in the soil, which is more difficult to degrade and, thus, would produce an older CO_2 when decomposed; (2) the slow SOM decomposition could also be due to the lower temperature, leading to a decrease in the soil microbial activity favouring SOM accumulation in the
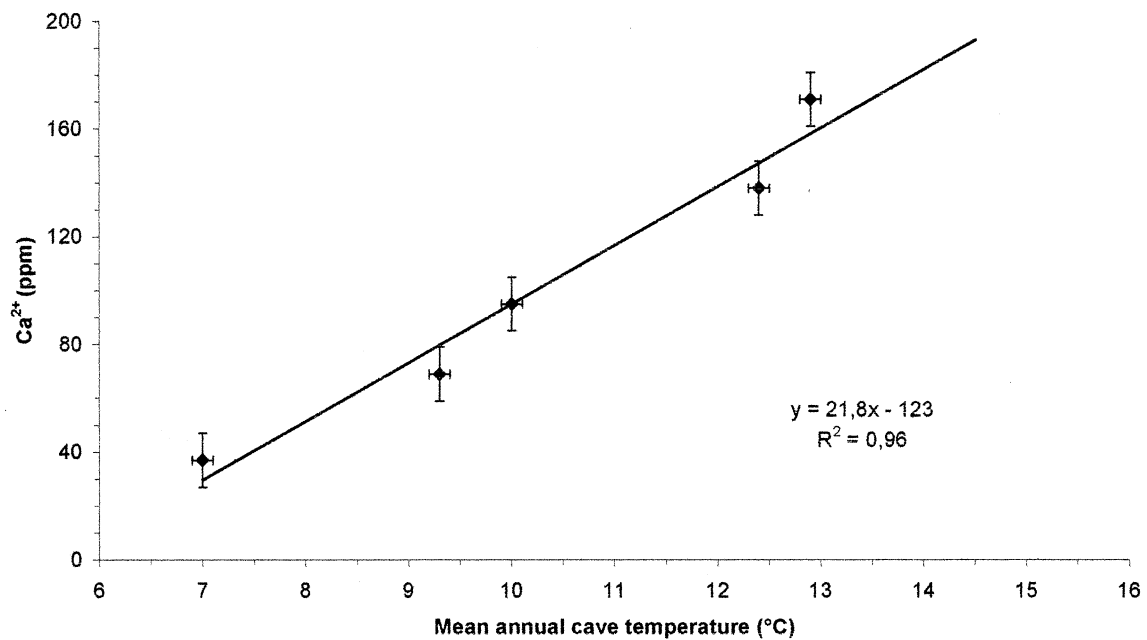
Fig. 6. Correlation between the average site temperature and the seepage water dissolved calcium content ($R^2 = 0.96$). Note that the gradient of this correlation is very steep (22 ppm/°C), which is higher than other published data from karst springs (Drake, 1980, 1983). This dependence of solute content on temperature may reflect the progressive transition from solution under more open system conditions in the south to more closed system conditions in the north.
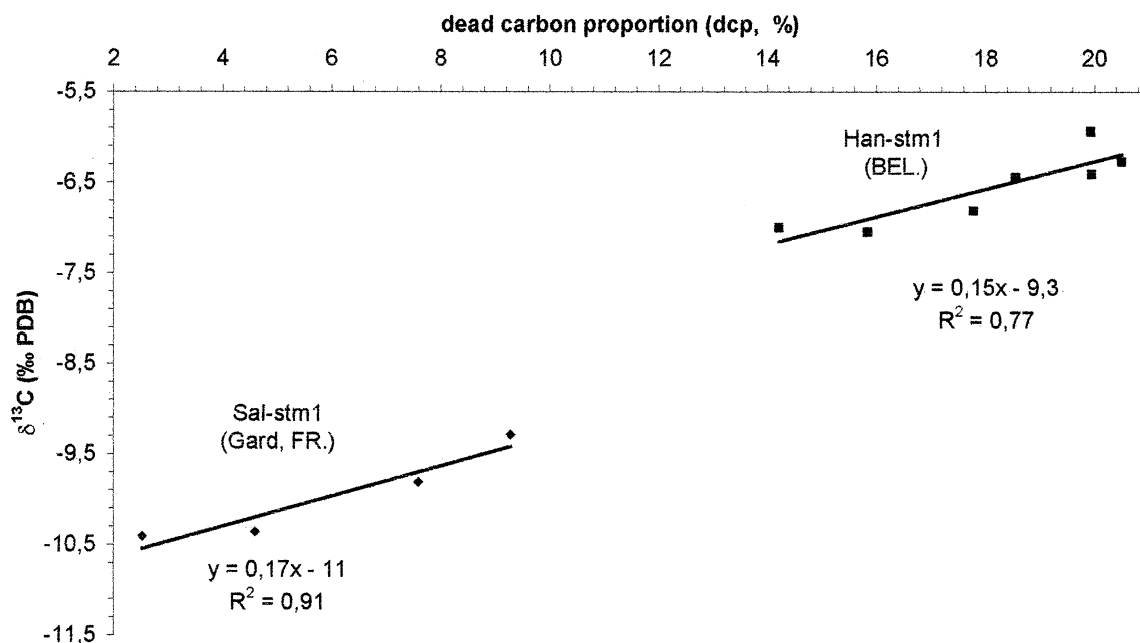
Fig. 7. Covariation between $\delta^{13}C$ and dcp data for Holocene stalagmites from France and Belgium. Note that both regression lines have the same slope (0.16 $\pm$ 0.01‰/%), which characterise a simple limestone dissolution (see text for calculations and discussion). Note also that the intersept of the equations gives the theoretic value of the DIC $\delta^{13}C$ before dissolution.

soil. Whatever the process, more dead carbon of organic origin is dissolved in the seepage water producing a lower dcp.

5.3. $\delta^{13}C$ and dcp Correlation on Two Stalagmites: A Dissolution Signature

The dcp-$\delta^{13}C$ relationships observed between sites are not necessarily reproduced within individual samples. We have seen on the Sutherland stalagmites that dcp and $\delta^{13}C$ variations are independent, demonstrating the role of the SOM in the dead carbon seepage water content, which is also confirmed by the intersite comparison. However, two stalagmites (Han-stm1 and Sal-stm1) display a significant correlation between $\delta^{13}C$ and dcp (R^2 = 0.77 and 0.91, Fig. 7). The average slope of the linear correlation is similar for both samples (0.16 $\pm$ 0.01) and indicates that there is an enrichment of 0.16‰ in the speleothem $\delta^{13}C$ when the dcp is increased by 1%. A similar value is obtained if the calcite $\delta^{13}C$ variation for a limestone dissolution change of 1% is calculated. The different isotope fractionation stages are shown as follows (see Genty and Massault, 1999 for detailed equations):

- Soil CO_2 dissolution (Mook et al., 1974): If we consider a mean soil CO_2 $\delta^{13}C$ of -25‰, typical value soil values (Deines et al., 1974; Fleyfel and Bakalowicz, 1980; Dever et al. 1982), and an average temperature of 10°C, values close to those of the sites studied, then the $\delta^{13}C$ of the dissolved inorganic carbon after the soil CO_2 dissolution = -15.3‰.
- Limestone dissolution (typically $\delta^{13}C_{limestone}$ = 0‰): If it is assumed that dissolution brings 10% of carbon (dcp = 10%), then after limestone dissolution, the $\delta^{13}C$ of the dissolved inor-

ganic species is -13.9‰, which is very similar to the $\delta^{13}C$ of the precipitated calcite under closed conditions (Mook, 1980).

Therefore, for a 10% dcp, the $\delta^{13}C$ change is -1.6‰ (-15.3‰ $- -13.9$‰), which leads to a gradient of 0.16‰/%. This is similar to the gradient observed for the Han-stm1 and Sal-stm1 stalagmites. This suggests that the correlation observed between the dcp and the $\delta^{13}C$ on these two stalagmites is the direct consequence of the limestone dissolution. It is interesting to note that the offset of each linear equation gives a mean value of the DIC $\delta^{13}C$ before limestone dissolution (dcp = 0): It is -9.3‰ for Han-stm1 and -11.0‰ for Sal-stm1. Temporal $\delta^{13}C$ variations observed on these samples is likely due to dissolution intensity changes (Fig. 8) and not to vegetation type change (C3/C4 plant) as is commonly suggested. Such an idea has been suggested recently for the sudden $\delta^{13}C$ variations observed on stalagmites from the Soreq Cave (Bar-Matthews et al., 2000), and a dcp determination for the Holocene part of these samples could confirm this hypothesis. The fact that there is no significant $\delta^{13}C$ vs. dcp correlation for the other studied stalagmites suggests that temporal $\delta^{13}C$ variation is controlled by other processes (see section 4.1).

6. CONCLUSIONS

The study of the dead carbon proportion and of ^{13}C content of the Uamh-an-Tartair stalagmites and its comparison with other European sites suggest the following results:

- At UAT since 3.5Ka, dcp almost doubled, from 22 to 38%, while the $\delta^{13}C$ remained stable for two individual stalagmites, demonstrating that at least for these samples, the dcp
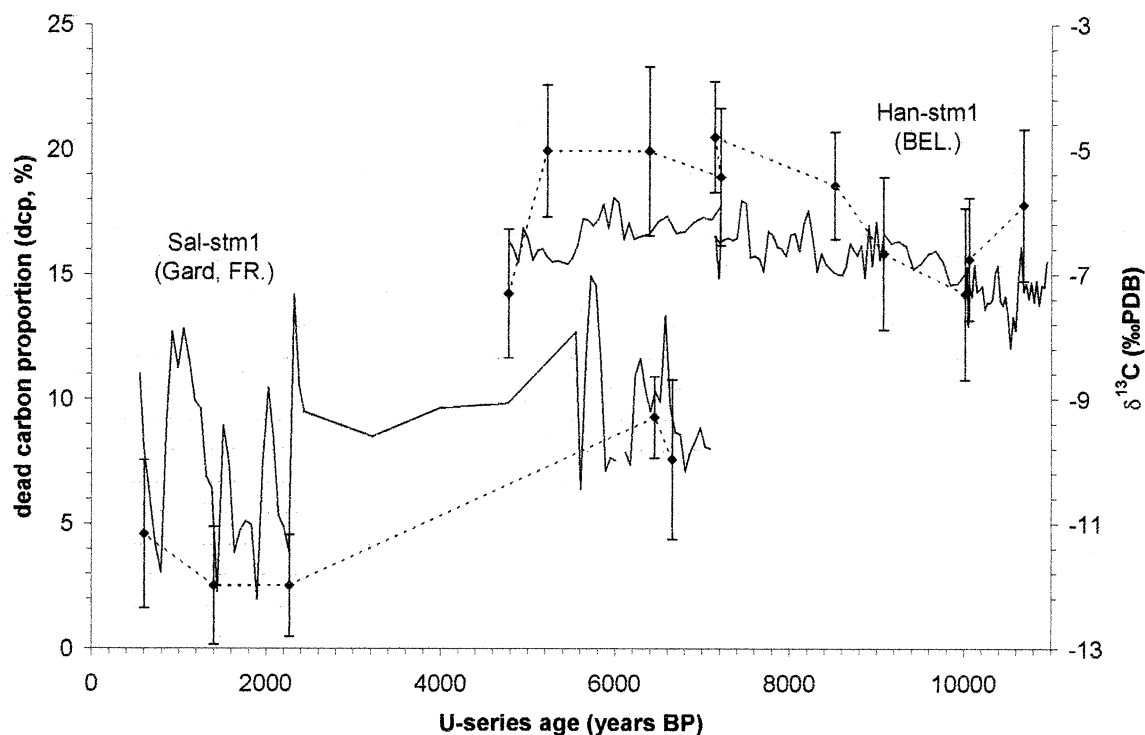
Fig. 8. $\delta^{13}C$ vs. time variations for Holocene stalagmites from France and Belgium. Note that $\delta^{13}C$ variations correlate with dcp changes, which suggests that carbon isotope variations are due to variations in the intensity of limestone dissolution. The $\delta^{13}C$ profiles have been made on the other stalagmite half-section rather than those used for dcp measurements, which explains small differences that might be observed in the $\delta^{13}C$ compared with those obtained with the CO_2 used for ^{14}C analysis.

increase is likely due to the ageing of the peat bog layer above the cave.

- Intersite samples from European countries where temperature amplitude is $\sim 7°C$ (7.3–14.5°C) show significant correlations between mean site dcp and mean site temperature ($R^2 = 0.85$). Dcp decreases when temperature increases; because the latter is also well correlated with seepage water Ca^{2+} ($R^2 = 0.96$), it is likely that intersite dcp variations are not due to limestone dissolution but to SOM turnover rate. This is slower at low temperature (due to either the low temperature and/or the denser vegetation of northern sites compared to that of the Mediterranean), where organic matter accumulates in soils producing older soil CO_2 when decomposed by microbial activity and, consequently, a higher dcp.

- Intersite $\delta^{13}C$ variations are not correlated with any climatic data or with other qualitative geologic settings. It is likely that they are the consequence of several factors such as variations in the type of dissolution (open/closed system ratio), the extent of mixing of soil and atmospheric CO_2, localized geologic settings (which determine water flow paths along microfissures and lead to the possibility of more or less prior calcite precipitation in the unsaturated zone above the cave), and kinetic effects during calcite precipitation.

- Among the 10 stalagmites studied, two display a significant correlation between their $\delta^{13}C$ values and their past dcp, with an average gradient of 0.16‰/%. This is consistent with the

fact that for these samples, the $\delta^{13}C$ variations are uniquely due to the intensity of limestone dissolution.

It is demonstrated here that the dcp in karst area is controlled not only by the limestone dissolution process, but also by the age of the SOM, which can be the dominant factor. It is therefore necessary to distinguish, in the global term dcp, the dcp that comes from the SOM (dcp_{SOM}) and the dcp that comes from the limestone dissolution ($dcp_{limestone}$). The study of these terms can be helpful to better understand the dissolution processes in karstic areas and the origin of the carbon in a speleothem. It appears that the $\delta^{13}C$ changes are difficult to interpret without any other proxy like the dcp: It can be changes in the relative proportion of C3 vs. C4 plants (i.e., $\delta^{13}C$ varies but dcp stays stable), but it can also be a simple limestone dissolution intensity variation (i.e., $\delta^{13}C$ and dcp both change), or a change in the soil CO_2 $\delta^{13}C$ composition due to variations in the mixing with atmospheric CO_2. In contrast, a stable $\delta^{13}C$ signal does not prove that no environmental change occurred, and that as we observe in the UAT samples, a variation in the mean age of soil organic matter due to the development of the vegetation cover is possible (i.e., $\delta^{13}C$ stays stable and dcp varies). These results have important consequences for the interpretation of groundwater ages.

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