

Elevated and variable values of ^{13}C in speleothems in a British cave system

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Abstract

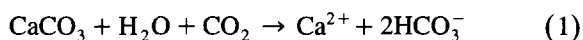
$\delta^{13}\text{C}$ isotope variations in speleothems have been investigated for samples from the British Isles, where plants which use the Hatch–Slack or C_4 photosynthetic pathway are not present. The range of $\delta^{13}\text{C}$ expected in speleothem carbonate formed in isotopic equilibrium with soil CO_2 derived from the overlying C_3 vegetation should thus fall in the range -12 to -6‰ . Forty-one actively growing speleothem samples from low-discharge sites were analysed from Stump Cross Caverns, Yorkshire, England. Ten percent have $\delta^{13}\text{C}$ greater than -6‰ . In addition, a large range of $\delta^{13}\text{C}$ was observed ($-8.06 \pm 1.38\text{‰}$, a 1σ variability of 17%), with adjacent samples having $\delta^{13}\text{C}$ differing by a maximum of 4.74‰. Similar findings were obtained from a review of analyses of late Quaternary speleothem samples from the British Isles, with 75% of flowstone samples and 57% of high-flow stalagmite samples exhibiting elevated $\delta^{13}\text{C}$. Three possible processes are proposed as possible causes of elevated $\delta^{13}\text{C}$ in speleothems. Firstly, fractionation may occur between the stalactite and stalagmite due to evaporation or degassing. Secondly, degassing of the groundwaters may have occurred within the aquifer before reaching the cave void, allowing release of some CO_2 from the water whilst remaining saturated in calcium. Finally, the elevated $\delta^{13}\text{C}$ may be due to short water residence times in the soil, such that equilibrium between soil water and soil CO_2 is not reached. Evidence presented here demonstrates that any one of these mechanisms may be important in the karst areas of the British Isles. Caution is needed before interpreting the $\delta^{13}\text{C}$ signal within speleothems in terms of palaeovegetation.

Keywords: ^{13}C ; Speleothems; Palaeovegetation; Isotopes; Quaternary

1. Introduction

Studies of $\delta^{13}\text{C}$ in pedogenic carbonates have demonstrated a clear relationship between carbonate $\delta^{13}\text{C}$ and climate and vegetation (Quade et al., 1989).

This may arise because of differences in $\delta^{13}\text{C}$ of respired CO_2 for C_3 photosynthetic pathway plants and C_4 plants (-26 to -20‰ for C_3 plants and -16 to -10‰ for C_4 plants; Cerling, 1984). Soil CO_2 dissolves in water to give carbonic acid which generates bedrock dissolution:



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Typically complete equilibration occurs between soil CO₂ and the dissolved bicarbonate of the soil solution, and thus almost no imprint of the parent limestone can be detected in the carbonate subsequently deposited from solution (Quade et al., 1989). Geochemical models indicate carbonate δ¹³C of –14 to –6‰ for C₃ pathway plants, and –6 to +2‰ for C₄ plants (Dreybrodt, 1980). Furthermore, these differences remain distinguishable even after kinetic fractionation effects. C₄ plants are typically adapted to conditions of extreme aridity and warmth (although some temperate agricultural species do have a C₄ pathway). Thus δ¹³C in fossil soil carbonate may give a palaeovegetation or limited palaeoclimate record. However, for semi-arid environments, there are additional complexities, with plant density (Amundson et al., 1988) and soil respiration rates (Quade et al., 1989) also reported to control pedogenic carbonate δ¹³C.

Speleothems have also been used to derive records of palaeoenvironmental change from δ¹³C variations. Those samples formed under conditions of high humidity (~100%) and gradual degassing of CO₂ are commonly found to be in oxygen and carbon isotopic equilibrium with the drip water from which they grow (Hendy, 1971; Schwarcz, 1986); such samples generally are found in deep cave interiors with little air circulation and with drip sources. Recent studies have investigated changes in speleothem δ¹³C over time to indicate changes in the overlying plant community (Brook et al., 1990; Dorale et al., 1992). Changes in δ¹³C values of –10.9 to –5.9‰ for speleothems deposited at 4 and 12 ka in Zaire have been interpreted as reflecting a transition from tropical rainforest (C₃ vegetation) to savannah grasslands (C₄ vegetation) (Brook et al., 1990), while a 3‰ shift in δ¹³C of a Holocene stalagmite from Iowa, U.S.A., was interpreted as reflecting changes in the proportion of C₄ plants in the overlying vegetation (Dorale et al., 1992).

In this study, we investigate the variation of δ¹³C in recently deposited speleothems to determine if δ¹³C falls within the expected range of values (–12 to –6‰) for the overlying C₃ vegetation for a cave site and samples which obey the criteria for equilibrium deposition listed above. In addition, δ¹³C data have been compiled for late Quaternary speleothems from the British Isles, including data from Gascoyne

(1992) and our own unpublished work. For both sets of data, it is believed that only a C₃ vegetation type has been present, as climatic conditions have not been warm and arid enough to support C₄ vegetation in the British Isles at any time over the late Quaternary time period. All the sites considered have a natural vegetation cover, unaffected by agriculture.

2. Experimental aims and methods

Forty-one actively forming speleothems were sampled from Stump Cross Caverns, Yorkshire, England. This site was chosen both for its natural upland grassland vegetation cover which has remained unchanged over the late Holocene, and the conditions of high humidity and near-constant air temperature which are maintained in the cave. Twenty-five samples comprised minimum-diameter stalagmites (all of <5-cm diameter); nine samples were low-discharge flowstones, and seven samples were straw stalactites. All samples were associated with slow-drip sources and had been deposited over the last 100 years. The data were supplemented by published and unpublished analyses from eight Quaternary high-discharge flowstone samples (all from caves in the Yorkshire Dales), and nine stalagmite samples (eight from the Yorkshire Dales, one from Sutherland). Details of all the samples, including speleothem type, location and period of deposition are presented in Tables 1 and 2¹.

Where δ¹³C analyses were performed, standard experimental techniques were used. Fifteen milligrams of calcite were reacted with 104% H₃PO₄ at 25°C and the evolved CO₂ gas was analysed using a Finnigan MAT delta E mass spectrometer. For the Stump Cross samples, as they were selected for their equilibrium deposition characteristics, no attempt was made to sample down an individual growth layer to test for kinetic fractionation. Instead, analyses were undertaken on sub-samples from beneath the location of drip impact to investigate if fractionation of ¹³C had occurred before deposition in the speleothem calcite. For the Quaternary high-discharge samples,

¹ Detailed sample location information may be attained from the authors upon request.

the amount of kinetic fractionation was determined, by taking subsamples of calcite from one individual growth layer as recommended in earlier work (Hendy, 1971). These data were used firstly to determine the extent of the change in $\delta^{13}\text{C}$ down individual growth layers due to kinetic fractionation, and secondly to calibrate a model of kinetic fractionation (see next section). All results were expressed in terms of the PDB standard.

3. Results

The results of the $\delta^{13}\text{C}$ analyses on all recently deposited samples from Stump Cross Caverns are presented in Table 1 along with $\delta^{18}\text{O}$ results. It is apparent that there is a wide range of $\delta^{13}\text{C}$, from -10.17 to -4.43% . In addition, there is a considerable variation for adjacent samples. For example, samples 10 and 11, which are < 2 m apart near the Jewel Box, have a 4.74% difference; and samples 21–23, all within a 1-m^2 area in the Clay Level, have a 3.52% range. Other samples exhibit less variability; samples 32–34, also sampled within 1-m^2 area within Raistrick's Cavern, only vary by 0.42% . There is no observed difference in mean $\delta^{13}\text{C}$ between stalagmite, stalactite and flowstone samples (using Student's t -test). For flowstones, mean $\delta^{13}\text{C} = -8.33$ ($\sigma = 1.62$; $n = 9$); for stalagmites mean $\delta^{13}\text{C} = -8.05$ ($\sigma = 1.45$; $n = 25$); and for stalactites mean $\delta^{13}\text{C} = -7.74$ ($\sigma = 0.82$, $n = 7$). For all samples, the mean $\delta^{13}\text{C} = -8.06$, $\sigma = 1.38$. The mean results and $\pm 1 \sigma$ bands thus fall within the field of $\delta^{13}\text{C}$ expected at a site overlain by C_3 vegetation (-12 to -6%), but 4 samples (9.8% of the total) from Stump Cross Caverns (3 stalagmites and 1 drip-fed flowstone) have $\delta^{13}\text{C}$ outside this range.

The $\delta^{13}\text{C}$ data for late Quaternary U.K. speleothem samples are presented in Table 2. Of the stalagmite samples, four of the seven have $\delta^{13}\text{C}$ greater than -6% for all or part of their deposition (57% of the samples). Of the eight flowstones, six (75%) also exhibit $\delta^{13}\text{C}$ greater than -6% for all or part of their deposition. Both stalagmites and flowstones exhibited $\delta^{13}\text{C}$ values as high as $+4\%$,

Table 1
Carbon and oxygen isotopic composition of Recent speleothems from Stump Cross Caverns, Yorkshire

No.	Location	$\delta^{18}\text{O}$ (‰ vs. SMOW)	$\delta^{13}\text{C}$ (‰ vs. PDB)
<i>Flowstones:</i>			
SC2	Bowling Alley	-4.74	-7.90
SC4	Bowling Alley	-4.67	-8.21
SC5	Cathedral	-4.98	-9.82
SC6	Policeman's Truncheon	-5.33	-9.14
SC7	Policeman's Truncheon	-4.88	-7.96
SC8	Sentinel	-5.39	-9.02
SC15	Main Passage	-3.97	-4.43
SC18	Main Passage	-4.39	-9.62
SC16	Main Junction	-5.19	-8.87
<i>Minimum-diameter stalagmites:</i>			
SC1	Bowling Alley	-4.30	-4.87
SC3	Bowling Alley	-5.28	-9.12
SC9	Bowling Alley	-5.15	-8.73
SC10	Jewel Box	-5.78	-9.22
SC11	Jewel Box	-3.93	-4.48
SC12	Main Passage	-5.36	-8.78
SC14	Main Passage	-4.68	-7.15
SC17	Main Passage	-4.72	-10.17
SC19	Steps	-4.99	-8.32
SC20	Clay Level	-4.64	-6.65
SC21	Clay Level	-5.19	-7.13
SC22	Clay Level	-4.24	-5.36
SC23	Clay Level	-5.63	-8.88
SC25	Long's Gallery	-5.68	-7.58
SC26	Long's Gallery	-5.78	-8.34
SC28	Long's Gallery	-5.63	-7.64
SC30	Fourth Level	-5.32	-9.03
SC31	Fourth Level	-4.37	-7.71
SC32	Raistrick's Cavern	-5.46	-8.60
SC33	Raistrick's Cavern	-5.45	-8.18
SC34	Raistrick's Cavern	-5.60	-8.54
SC35	Raistrick's Cavern	-4.50	-9.53
SC36	Raistrick's Cavern	-5.59	-9.58
SC37	Heartbeat	-5.66	-9.22
SC38	Heartbeat	-5.08	-8.36
<i>Stalactites:</i>			
SC13	Main Passage	-5.40	-8.00
SC39	Bowling Alley	-4.58	-6.12
SC40	Bowling Alley	-5.05	-7.76
SC41	Bowling Alley	-4.34	-8.43
SC42	Bowling Alley	-4.76	-7.87
SC43	Bowling Alley	-4.87	-7.49
SC44	Bowling Alley	-4.92	-8.52

significantly more positive than observed for Stump Cross samples fed by straw stalactites. Where information on the variation of $\delta^{13}\text{C}$ down an individual growth layer is available, the attainment of equilibrium fractionation defined by the criteria of Hendy (1971), i.e. uniform isotopic composition along growth layers, is also shown in Table 2. It can be observed that for the samples deposited in the late Quaternary, a proportion of both stalagmite and flowstone samples have been deposited in oxygen isotopic equilibrium with no significant fractionation effects (e.g., samples SU-80-11, 76127, 77143B and 77162). However, it is important to note that samples 76127 and 77162, which appear to have been deposited in oxygen isotopic equilibrium, have $\delta^{13}\text{C}$ values greater than that expected for C_3 vegetation. This has implications for the reliability of $\delta^{13}\text{C}$ down single growth layers as a test for fractionation. Where fractionation does occur, the data suggest that a fractionation rate of $0.8 \pm 0.3\text{‰}$ per 10 cm along the flow path is typical.

4. Interpretation

The observation that both stalagmites and flowstones exhibit values of $\delta^{13}\text{C}$ above those expected for a C_3 vegetation CO_2 source suggests that some form of fractionation has taken place previously along the flow path. When the relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measured in the samples from Stump Cross Cavern is considered, a weak but statistically significant correlation is observed; Fig. 1 ($r = 0.57$, $n = 41$; significant at the 99% confidence level). Such a correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ within a growth layer of an individual sample has been suggested as a test for kinetic fractionation effects (Hendy, 1971). Since all samples are of a minimum diameter, size being limited only by splash effects, then kinetic fractionation is unlikely over the growth surface. Therefore this relationship must be due to isotopic fractionation which has occurred before the waters were deposited on the stalagmite surface. Three explanations are possible: first, that significant

Table 2
Carbon isotope data for late Quaternary speleothems from the British Isles

Sample No.	Location	Source ^a	Type ^b	Time of deposition ^c (ka)	Range of $\delta^{13}\text{C}$ (‰ vs. PDB)	Deposition	
						Eqm? ^d	Frn? ^e
76122	Lancaster Hole, Yorks.	[1]	S	91–71	–5 to –1	N	0.65
76125	Lancaster Hole, Yorks.	[1]	S	38	–6 to +1	N	1.25
76210	Gaping Gill, Yorks.	[1]	S	38	–3 to –1	N	0.56
76190	Lost John's, Yorks.	[1]	S	< 10	–11 to –6	N	0.57
76128	Lancaster Hole, Yorks.	[1]	S	< 10	–3 to +5	N	1.27
79158	Lancaster Hole, Yorks.	[1]	S	?	–10 to –8	?	?
SU-80-11	Assynt, Sutherland	[2]	S	7–0	–12 to –10	Y	n/a
76201	Gaping Gill, Yorks.	[1]	F	< 7	–4 to +3	N	0.56
76127	Gaping Gill, Yorks.	[1]	F	240–225	–0.5 to 0.0	Y	n/a
77143B	Gaping Gill, Yorks.	[1]	F	128–108	–11.0 to –10.5	Y	n/a
77162	Gaping Gill, Yorks.	[1]	F	114–94	–6 to –3	Y	n/a
79151	Gaping Gill, Yorks.	[1]	F	290–190	–9 to –6	?	?
LH-90-2	Lancaster Hole, Yorks.	[2]	F	210–80	–10 to +4	N	?
H-90-5	Lancaster Hole, Yorks.	[2]	F	129–58	–6 to +4	N	?
SC-90-6	Stump Cross, Yorks.	[3]	F	78–52	–7 to +1	N	?

^a Source of data: [1] = Gascoyne (1992); [2] = Tillotson and Smart, unpublished data; [3] = this study, unpublished data.

^b Sample type: F = flowstone; S = stalagmite.

^c Time of deposition represents approximate time limits within which the sample was deposited. Sample growth was not continuous. Error bars are not shown but are typically 10% of the age analysis.

^d Y indicates that the sample was deposited in isotopic equilibrium as defined by Hendy (1971), N indicates that there is evidence for kinetic fractionation. Data are drawn from the sources listed in (^a) above; a question mark indicates that data were not available.

^e The value given is the average amount of fractionation of ^{13}C in ‰ for 10-cm distance down water flow direction for samples undergoing fractionation. Data are drawn from sources listed in (^a) above; a question mark indicates that data were not available; n/a = not analysed. The mean value is $0.8 \pm 0.3\text{‰}/10\text{ cm}$ ($n = 6$).

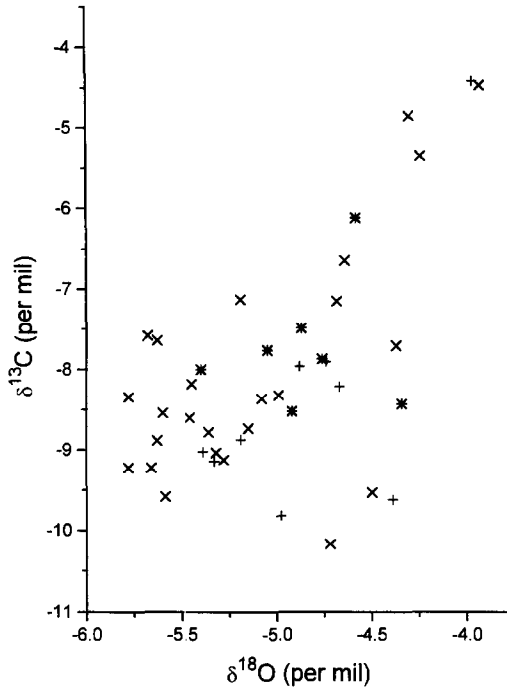


Fig. 1. Relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for the Stump Cross Cavern speleothem samples (*plus symbol* = drip fed flowstones; *cross symbol* = drip-fed stalagmites; *star symbol* = stalactites).

isotopic fractionation occurs within the cave between emission of the drip at the roof and the precipitation of the calcite. Under fast precipitation conditions with rapid loss of CO_2 , kinetic fractionation will occur between HCO_3^{2-} and $\text{CO}_2(\text{g})$ and the calcite precipitated will be enriched in ^{13}C (Hendy, 1971; Schwarcz, 1986). Second, degassing of the groundwaters may occur within the unsaturated zone above the cave, such that waters remain saturated with respect to calcium carbonate but become fractionated in $\delta^{13}\text{C}$. Third, soil-water residence times are sufficiently short that equilibrium between the soil CO_2 and water is not achieved, and a fraction of the water has an atmospheric CO_2 component.

4.1. Isotopic fractionation between stalactite and stalagmite deposition

Kinetic fractionation effects have been observed in a stalactite–stalagmite pair (Fantadis and Ehhalt, 1970). The extent to which fractionation occurs can be determined from theory. Initial studies of carbon isotope fractionation during precipitation were under-

taken using mass transfer considerations (Wigley et al., 1978). More recently an understanding of the chemical kinetics of the deposition process have been developed (Dreybrodt, 1980; Buhmann and Dreybrodt, 1985), and this kinetic theory has been used to develop a semi-dynamic model to explain $^{13}\text{C}/^{12}\text{C}$ isotope ratios in speleothems (Dulinski and Rosanski, 1990). The model distinguishes two phases in the precipitation process; initial outgassing of a solution to a critical threshold supersaturation, and the subsequent precipitation of CaCO_3 resulting from further outgassing. Model results suggest that the $\delta^{13}\text{C}$ of speleothems is dependent on temperature, chemical and isotopic composition of the initial solution, and the time elapsed since degassing commenced. This is highlighted in Fig. 2, which shows evolution of speleothem $\delta^{13}\text{C}$ modelled assuming an initial soil CO_2 of -25‰ (typical of a C_3 vegetation cover). Note that 10 minutes after the start of precipitation, calcite $\delta^{13}\text{C}$ is in the range -8 to -2‰ , depending on the temperature and P_{CO_2} , and

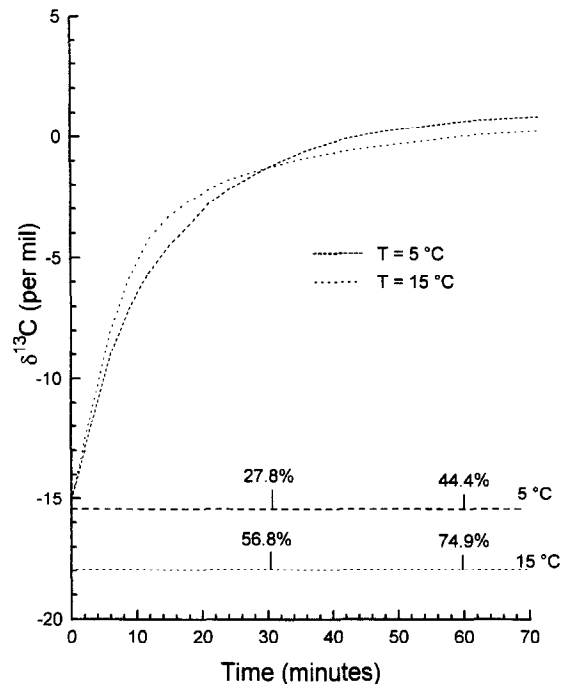


Fig. 2. Theoretically calculated variations of $\delta^{13}\text{C}$ with time since first deposition of calcite. Values are calculated for open-system conditions and a cave air P_{CO_2} of 0.05 atm. The x-axis also shows the percentage of total possible CaCO_3 that has been deposited by that time period. After Dulinski and Rosanski (1990).

only 10–30% of all the potential dissolved calcite has been deposited. After 30 minutes, between 30% and 60% of the potential calcite for deposition has been precipitated, and $\delta^{13}\text{C}$ is in the range -3 to 0‰ .

Such a variation should be observed between stalactite and stalagmite pairs for slow-drip-rate sources. For Stump Cross, paired samples were not analysed as the detailed hydrology was not known, but the $\delta^{13}\text{C}$ of stalactite and stalagmite calcite is not statistically different. However, comparison of the regression between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for all samples ($r = 0.57$, $n = 42$) with that for stalagmites and flowstones only ($r = 0.59$, $n = 35$; the relationship is maintained), and for stalactites only ($r = 0.17$, $n = 7$; the relationship breaks down) suggests, from a limited data set, that fractionation could be occurring in the cave environment. Further research from a larger number of paired samples is necessary to confirm this.

4.2. Degassing of groundwaters within the unsaturated zone

The second potential cause of elevated $\delta^{13}\text{C}$ in speleothems is the prior degassing of groundwaters within the aquifer, causing deposition of calcite and thus subsequent elevated values of $\delta^{13}\text{C}$ if the water remains saturated and deposits further calcite. Such a degassing process is particularly likely in karst aquifers, where many fissures may be both air-filled and linked to the cave void which has an atmospheric P_{CO_2} . Thus it will be “residual” calcite with an elevated $\delta^{13}\text{C}$ that is deposited when the water flow finally reaches a cave void. The extent of this process can be determined from the semi-kinetic model presented above, and could for instance be tested by sampling calcite or water along the flow path on a sequence of hydrologically linked actively depositing flowstones in different cave voids. However, no suitable sites were found in the course of this study. Data on the degree of kinetic fractionation observed along individual calcite growth layers in the late Quaternary samples have, however, been reported (Table 2), and averages $\delta^{13}\text{C}$ of $0.08 \pm 0.03\text{‰}$ per cm from the drip source (derived from data in Table 2). Fig. 2 suggests that a 1‰ increase in $\delta^{13}\text{C}$ will take < 2 minutes when the cave waters are in the initial stages of degassing. Over a 10-cm

length of a speleothem sample, this is equivalent to a minimum water velocity of 0.08 cm s^{-1} . Typical velocities for speleothem surface waters are in the range $0.03\text{--}2.0 \text{ cm s}^{-1}$ ($n = 11$; Baker and Smart (1995) and unpublished data). Although further measurements need to be made, the agreement between theoretically predicted and observed velocities again suggest that the semi-kinetic model gives a good prediction of speleothem $\delta^{13}\text{C}$, and demonstrates that prior degassing can occur in the karst groundwater system whilst leaving the waters supersaturated with calcite.

4.3. Disequilibrium with soil CO_2

Elevated $\delta^{13}\text{C}$ in speleothems could also be due to the presence of an atmospheric CO_2 component in the groundwaters. The possibility that soil waters may not reach equilibrium with soil CO_2 has not previously been considered; in semi-arid environments it has been demonstrated using pedogenic carbonates that equilibrium between soil water and soil CO_2 is reached (Cerling, 1984; Amundson et al., 1988; Quade et al., 1989), as soil-water residence time is much greater than the time taken for carbon isotope exchange between the gas and water. However, both the extent of redissolution and precipitation of carbonate, as well as exchange with atmospheric CO_2 , has been used to interpret the positive $\delta^{13}\text{C}$ observed in soil carbonate nodules and calcrete from various climate regimes (references cited in Salomons and Mook, 1986; Bishop and Lloyd, 1990). Few studies of equilibration between soil water and soil CO_2 in humid temperate karst areas similar to the British Isles have been undertaken. Rightmire and Hanshaw (1973), Rightmire (1978), Drever et al. (1982) and Haas et al. (1993) all observe seasonal variation in $\delta^{13}\text{C}$, with more negative values in spring and summer, reflecting the influx of biogenic CO_2 in the growing season, and positive values in winter due to an admixture of atmospheric CO_2 . Conversely, no seasonal variations in $\delta^{13}\text{C}$ were observed by Reardon et al. (1979). In any karst system, it may be possible for very rapid flows to occur within the soil system, and in the British case, with high annual precipitation, this is particularly important. This may be due to soil piping and macropore flows providing rapid flow routes through the soil; macropore flow velocities in the range of

10^{-3} – 10^{-2} m s⁻¹ and response times of 5–80 minutes have been reported (Beven and Germann, 1982; Mosley, 1982). In addition, immature soil cover is commonly found in karst areas of the British Isles, and this together with the many fissures typical of maturely developed karst could explain the disequilibrium between soil water and soil CO₂. Very thin soils (under 30 cm), together with a steep hydraulic gradient through the soil profile due to the highly permeable underlying karst geology, may cause a short residence time of water in the soil. Dye tracing studies on Magnesian Limestone in central England demonstrated a preferential soil throughflow when storm intensity exceeded 3 mm hr⁻¹ for > 2 hr (Trudgill et al., 1982), with rates of 30–50 cm hr⁻¹ (Trudgill et al., 1983). At GB Cave, Mendip Hills, the time between surface precipitation events and the first rise in the cave seep hydrograph for various high-discharge (10^{-1} – 10^3 l hr⁻¹) flows varies between 2 hr and 2–10 days (Smart and Friedrich, 1986); this lag time incorporates both the soil-water residence time and the time taken to pass through a 50–60-m-deep unsaturated zone. Similarly, lag times between precipitation events and cave drip feeds have been determined to range from between < 1 day to 2 weeks from comparatively low-discharge cave drips (10^{-2} – 10^{-1} l hr⁻¹) in Poole Cavern, Buxton (Pitty, 1966). All these investigations show that rapid recharge through the soil is possible; further research in this area is needed to determine whether this is sufficient to cause disequilibrium between soil CO₂ and soil water, and whether this in turn may generate elevated $\delta^{13}\text{C}$. Seasonal variations in $\delta^{13}\text{C}$ of 0.1–0.5‰ observed in one annually laminated Belgian stalagmite may have been generated by this mechanism (Genty et al., 1995).

5. Conclusions

The results presented here demonstrate that the $\delta^{13}\text{C}$ isotopic composition of speleothems cannot be interpreted solely in terms of changes in vegetation. Instead, degassing of groundwaters in the unsaturated zone of the karst aquifer, degassing between stalactite and stalagmite, or disequilibrium with soil CO₂, may be more important in controlling the $\delta^{13}\text{C}$ isotope composition. From the evidence presented above, it is not possible to distinguish between the

possible processes which may generate the observed elevated $\delta^{13}\text{C}$ in the speleothems. Elevated $\delta^{13}\text{C}$ is less frequently observed for all types of speleothems fed by low-discharge straw stalactite feeds. Only 10% of these samples were observed to have elevated $\delta^{13}\text{C}$, whereas over 50% of all higher-discharge stalagmites and high-discharge flowstones had greater than -6‰ $\delta^{13}\text{C}$. Furthermore, whilst the minimum $\delta^{13}\text{C}$ was similar for these two types of deposits, the maximum for the slow-flow samples was -4‰ compared to +5‰ for the higher-flow speleothems. As well as the presence of elevated $\delta^{13}\text{C}$, there is also a large variation in $\delta^{13}\text{C}$ between speleothems at Stump Cross Cavern. The average $\delta^{13}\text{C}$ was determined to be $-8.06 \pm 1.38\text{‰}$, a 1 σ variability of 17%, with adjacent samples varying in $\delta^{13}\text{C}$ by up to 4.74‰. This result is not site specific; two pairs of adjacent high-discharge stalagmite samples from G.B. Cave, Mendip Hills, England, differed in $\delta^{13}\text{C}$ by 2.90 and 0.10‰, respectively. This probably reflects the heterogeneity of flow routing within most karst aquifers and suggests that interpretation of the $\delta^{13}\text{C}$ record in speleothems in terms of vegetation change should be treated with caution unless the hydrology and soil cover of sample is known for its period of deposition. Furthermore, results from individual samples may be biased, and analyses from multiple samples deposited over the same time period are required to determine if a general $\delta^{13}\text{C}$ signal is present. Finally, the unambiguous derivation of changes in atmospheric $\delta^{13}\text{C}$ variations in speleothem $\delta^{13}\text{C}$ for a time of no vegetation change as suggested by Baskaran and Krishnamurthy (1993) is probably not possible, the 2‰ change in speleothem $\delta^{13}\text{C}$ over the last 50 years reported may equally be due to variations in the soil-water residence time or degassing within the aquifer or cave.

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References

- Amundson, R.G., Chadwick, O.A., Sowers, J.M. and Doner, H.E., 1988. Relationship between climate and vegetation and the stable carbon isotope chemistry of soils in the eastern Mojave Desert, Nevada. *Quat. Res.*, 29: 245–254.
- Baker, A. and Smart, P.L., 1995. Recent flowstone growth rates: Field measurements in comparison to theoretical predictions. *Chem. Geol.*, 122: 121–128.
- Baskaran, M. and Krishnamurthy, R.V., 1993. Speleothems as proxy for the carbon isotope composition of atmospheric CO₂. *Geophys. Res. Lett.*, 20: 2905–2908.
- Beven, K. and Germann, P., 1982. Macropores and water flow in soils. *Water Resour. Res.*, 18: 1311–1325.
- Bishop, P.K. and Lloyd, J.W., 1990. Chemical and isotopic evidence for hydrogeochemical processes occurring in the Lincolnshire Limestone. *J. Hydrol.*, 121: 293–320.
- Brook, G.A., Burney, D.A. and Cowart, J.B., 1990. Desert palaeoenvironmental data from cave speleothems with examples from the Chihuahuan, Somali–Chalabi, and Kalahari deserts. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 76: 311–329.
- Buhmann, D. and Dreybrodt, W., 1985. The kinetics of calcite solution and precipitation in geologically relevant situations of karst areas, 1. Open system. *Chem. Geol.*, 48: 189–211.
- Cerling, T.E., 1984. The stable isotopic composition of modern soil carbonate and its relationship to climate. *Earth Planet. Sci. Lett.*, 71: 229–240.
- Dorale, J.A., Gonzalez, L.A., Regan, M.K., Pickett, D.A., Murrell, M.T. and Baker, R.G., 1992. A high resolution record of Holocene climate change in speleothem calcite from Cold Water Cave, Northeast Iowa. *Science*, 258: 1626–1630.
- Drever, L., Durand, R. and Fontes, J.C., 1982. Géochimie et teneurs isotopiques des systèmes saisonniers de dissolution de la calcite dans un sol sur craie. *Geochim. Cosmochim. Acta*, 46: 1947–1956.
- Dreybrodt, W., 1980. Deposition of calcite from thin films of calcareous solutions and the growth of speleothems. *Chem. Geol.*, 29: 89–105.
- Dulinski, M. and Rosanski, K., 1990. Formation of ¹³C/¹²C isotope ratios in speleothems: a semi-dynamic model. *Radiocarbon*, 32: 7–16.
- Fantadis, J. and Ehhalt, D.H., 1970. Variations of the carbon and oxygen isotopic composition in stalagmites and stalactites: Evidence of non-equilibrium isotopic fractionation. *Earth Planet. Sci. Lett.*, 10: 136–144.
- Gascoyne, M., 1992. Palaeoclimate determination from cave calcite deposits. *Quat. Sci. Rev.*, 11: 609–632.
- Genty, D., Quinif, Y. and Keppens, E., 1995. Les variations saisonnières des lamines de croissance mises en évidence par le dosage des isotopes stables de l'oxygène et du carbone. *Spéléochronos*, No. 6, pp. 32–34.
- Haas, H., Fisher, D.W., Thorstenson, D.C. and Weeks, E.P., 1993. ¹³CO₂ and ¹⁴CO₂ measurements on soil atmosphere sampled in the sub-surface unsaturated zone in the western Great Plains of the USA. *Radiocarbon*, 25: 301–314.
- Hendy, C., 1971. The isotopic geochemistry of speleothems, I. The calculation of the effects of different modes of formation on the isotopic composition of speleothems and their applicability as palaeoclimatic indicators. *Geochim. Cosmochim. Acta*, 35: 801–824.
- Mosley, M.P., 1982. Subsurface flow velocities through selected forest soils, South Island, New Zealand. *J. Hydrol.*, 55: 65–92.
- Pitty, A.F., 1966. An approach to the study of karst water. Univ. of Hull, Occas. Pap. Geogr. No. 5.
- Quade, J., Cerling, T.E. and Bowman, J.R., 1989. Systematic variations in the carbon and oxygen isotopic composition of pedogenic carbonate along transects in the Southern Great Basin, United States. *Geol. Soc. Am. Bull.*, 101: 464–475.
- Reardon, E.J., Allison, G.B. and Fritz, P., 1979. Seasonal chemical and isotopic variations of soil CO₂ at Trout Creek, Ontario. *J. Hydrol.*, 43: 355–371.
- Rightmire, C.T., 1978. Seasonal variations in P_{CO₂} and ¹³C content of soil atmosphere. *Water Resour. Res.*, 14: 691–692.
- Rightmire, C.T. and Hanshaw, B.B., 1973. Relationship between the carbon isotope composition of soil CO₂ and dissolved carbonate species in groundwater. *Water Resour. Res.*, 9: 958–967.
- Salomons, W. and Mook, W.G., 1986. Isotope geochemistry of carbonates in the weathering zone. In: P. Fritz and J.Ch. Fontes (Editors), *Handbook of Environmental Isotope Geochemistry*, Vol. 2, The Terrestrial Environment, B. Elsevier, Amsterdam, pp. 239–270.
- Schwarcz, H.P., 1986. Geochronology and isotopic geochemistry of speleothems. In: P. Fritz and J.Ch. Fontes (Editors), *Handbook of Environmental Isotope Geochemistry*, Vol. 2, The Terrestrial Environment, B. Elsevier, Amsterdam, pp. 271–300.
- Smart, P.L. and Friedrich, H., 1986. Water movement and storage in the unsaturated zone of a maturely karstified carbonate aquifer, Mendip Hills, England. *Proc. Conf. on Environmental Problems of Karst Terrains and Their Solution*, pp. 57–87.
- Trudgill, S.T., Pickles, A.M., Smettem, K.R.J. and Crabtree, R.W., 1982. Soil-water residence times and solute uptake, 1. Dye tracing and rainfall events. *J. Hydrol.*, 60: 257–280.
- Trudgill, S.T., Pickles, A.M. and Smettem, K.R.J., 1983. Soil-water residence times and solute uptake, 2. Dye tracing and preferential flow predictions. *J. Hydrol.*, 62: 279–285.
- Wigley, T.M.L., Plummer, L.N. and Parson, Jr., F.J., 1978. Mass transfer and carbon isotope evolution in natural water systems. *Geochim. Cosmochim. Acta*, 42: 1117–1139.