[RADIOCARBON, VOL. 39, NO. 1, 1997, P. 33–48]

BOMB ^{14}C RECORDED IN LAMINATED SPELEOTHEMS: CALCULATION OF DEAD CARBON PROPORTION

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ABSTRACT. We performed radiocarbon measurements using accelerator mass spectrometry (AMS) on 6 stalagmites, 3 stalactites and 7 seepage waters from four different caves in Southwest France and Belgium in order to calculate the dead carbon proportion (dcp). All the speleothems studied are modern and annually laminated, which offers the advantage of an accurate chronology, with better than one-year resolution. Coupled with the fact that very little calcite is necessary for an AMS measurement (between 1.5 and 7 yr of calcite deposit), we obtained dead carbon values within an uncertainty limit of ± 1.5%. Results show that the dead carbon proportion varies from 9.2% to 21.9% for calcite deposits and from 3.6% to 21.9% for water. In each sampling site, the dcp is homogeneous. Although the inter-site dcp varies by >11%, its average value of 15.5% ± 4.4 still lies within the uncertainty range of the accepted value of 15% ± 5 (dilution factor of 0.85 ± 0.5). We compare the average dcp of each site with the local geology, vegetation and climate. Given similar geology and temperature, the highest dcp values are found under forest cover; dcp difference is up to 9%. However, the Belgian site, which is also under a forest, shows a dcp very close to the dcp found under grassland sites of Southwest France, which proves that other unknown factors may play an important role in dissolution processes. Secondary calcite deposition and redissolution in the soil zone or more likely in the fracture system before reaching the cave itself could also explain the inter-site differences. The IAEA isotopic model (Pearson model adapted for open systems) is in good agreement with the measured activities.

INTRODUCTION

Recent studies have shown that many speleothems possess annually deposited growth laminae; they can be visible (Genty 1993; Genty and Quinif 1996) or luminescent (Baker *et al.* 1993; Shopov and Dermendjiev 1990). The alternation of white porous and dark compact laminae represents the calcite deposit of one year, which gives modern laminated speleothems a very accurate chronology. It is not rare to have speleothems with continuous laminae for >100 yr, but in the case of longer durations, laminae are frequently interrupted by discontinuities. The search for paleoclimatic signals from these laminae has already started: correlation has been found between the laminae thickness and the pluviometry (Genty and Quinif 1996; Railsbak *et al.* 1994), and a stable isotopic seasonal signal has been observed in several stalagmites (Genty, Quinif and Keppens 1995).

Speleothem carbon has two principal sources: 1) the CO_2 of the soil above the cave; 2) the carbonate of the limestone where the cave developed and/or of secondary calcite deposits of the unsaturated zone. The soil CO_2 comes from root respiration and microbial decomposition of organic matter; it is thus linked to atmospheric CO_2 (Dörr and Münnich 1986). Carbon from limestone is generally so old as to have a negligible ^{14}C activity; however, if it comes from secondary deposits, its activity can be significant.

The determination of speleothem ^{14}C activity has at least two essential purposes:

1. To estimate the age of the deposit. Even if it is not now the most appropriate method precisely because of the unknown dead carbon proportion, it has been the only feasible method for a long time (Broecker and Olson 1960; Geyh and Franke 1970). It is still used because of its cost advantage over the U/Th mass spectrometric method and because it is a means of checking U/Th ages for the last 40 ky (Bastin and Gewelt 1986; Brook and Nickmann 1996; Genty *et al.* 1996; Gewelt, 1985; Geyh and Henning 1986; Goede and Vogel 1991; Holmgren, Lauritzen and Possnert 1994; Issar *et al.* 1992; Pazdur, Pazdur and Pawlyta 1995; Railsback *et al.* 1996; Talma and Vogel 1992; Vogel 1983).

2. To reconstruct atmospheric ^{14}C activity through time; in this case, the chronology is given by U/Th ages (Holmgren, Lauritzen and Possnert 1994; Vogel 1983). Atmospheric ^{14}C wiggles observed during the Holocene in tree-ring dated wood (Wigley and Kelly 1990) are probably due to the Earth's geomagnetic field changes (Bard, Hamelin and Fairbanks 1990; Mazaud *et al.* 1991; Vogel 1983), solar activity variations (Suess and Linick 1990) and the capacity of the ocean to absorb CO_2 (Goslar *et al.* 1995). During historical time, ^{14}C variations include an abrupt increase between AD 1500 and 1700 (the de Vries effect), a slight decrease of 2% since the beginning of the industrial period (AD 1850; the Suess effect), and finally, a massive production of ^{14}C in the atmosphere because of nuclear bomb tests (maximum increase of >100% in 1963–1964; Levin *et al.* 1992).

There are major problems in both cases: 1) the initial activity is not known; in other words the dcp must be estimated (or the dilution factor *q* that is its complement; Gewelt 1986); 2) the dcp possibly varies with time.

The dcp has been calculated in several different ways (Table 1):

- by measurement of the ^{14}C activity on the top of still-dripping stalagmites (Vogel 1983; Gewelt 1985, 1986; Bastin and Gewelt 1986); using the classical β-counting method, one must sample >20 g of calcite (more often between 30 and 100 g); thus, the error margin is large because sampling takes into account deposits of different ages (*e.g.*, a dcp of 30% was found on the top of three active Belgian stalagmites, whereas the value taken into account was 15% (Gewelt 1986));
- by age-distance interpolation up to the top of the stalagmite (linear least-square fit); the hypothesis of a constant growth rate must be considered critically here, because stalagmite growth rates are highly variable even over short periods (*i.e.*, from 0.1 to 1.0 mm yr^{-1}; Genty and Quinif 1996; Genty *et al.* 1996);
- by comparison with pollen extracted from the speleothem; this technique can be used in areas where the emergence or disappearance of a taxon is abrupt (*i.e.*, emergence of *Tilia* at the Atlantic in Belgium; Bastin and Gewelt 1986); but this is not an accurate method because there is very little pollen in speleothem calcite (up to 5 grains gm^{-1} of $CaCO_3$) and a great quantity of calcite is required (>100 g);
- by comparison with U/Th ages (Vogel 1983; Holmgren, Lauritzen and Possnert 1994); the accuracy depends on the U/Th errors, which are great for recent deposits (very little thorium).

In order to attempt more accurate dead carbon inferences we have combined these methods, using 1) annually laminated speleothems, which give an excellent chronology for the last few decades, and 2) AMS techniques that permit the analysis of *ca.* 10 mg of calcite, which is, in the most favorable cases, 1 yr of deposits, and more often, 2–7 yr.

Our purpose is to compare dcp's in modern deposits and water from four sites and to explain the observed variability in relation to the geology, vegetation and climate.

SITE AND SAMPLE DESCRIPTIONS

Samples come from caves at Han-sur-Lesse cave (Belgium; 50°08'N, 5°10'E, elevation 180 m); Villars (Dordogne, France; 45°30'N, 0°50'E, elevation 175 m), La Faurie (Dordogne, France; 45°08'N, 1°11'E, elevation 225 m) and Proumeyssac (Dordogne, France; 44°55'N, 0°56'E, elevation 155 m).

TABLE 1. Examples of Dilution Factors Found in Speleothems

Speleothem type, locale	Dilution factor q*	Method	Reference
Stalagmites – Belgium	0.85 ± 0.05	Pollen correlation	Bastin and Gewelt 1986
Stalagmite crust on a bone (called travertine) – Moaning Cave, California, USA	0.915	^{14}C age-distance interpolation (linear least square fit)	Broecker and Olson 1960
Stalagmites and stalactites – Red Spider Cave, Georgia, USA	0.85	Bibliography†	Brook and Nickmann 1996
Stalagmites and flowstones – Belgium	0.85	Pollen correlation, bibliography	Gewelt 1985
Stalagmites and flowstones – Belgium	0.85 (est.); 0.69; 0.72; 0.69 (measured)	Pollen correlation, bibliography	Gewelt 1986
Stalagmite – Central Europe	0.85	Bibliography	Geyh and Franke 1970
Flowstone – Heggen Cave, Germany	0.81	^{14}C age-distance interpolation (linear least square fit)	Geyh and Hennig 1986
Stalagmite – Tasmania	0.83 ± 0.05	Bibliography	Goede and Vogel 1991
Stalagmites – Galilee, Israel	0.89	Bibliography	Issar *et al.* 1990
Speleothems – Cracow-Wielun, Poland	0.83	Bibliography	Pazdur *et al.* 1995
Stalagmite – Drotsky's Cave, Botswana	0.86	^{14}C age-distance interpolation (linear least square fit)	Railsback *et al.* 1994
Stalagmite – Cango Cave, South Africa	0.83	^{14}C age-distance interpolation (linear least square fit)	Talma and Vogel 1992
Stalagmite – Cango Cave, South Africa	0.83	^{14}C age of the still active top, comparison with U/Th ages	Vogel 1983

*$q = 1 - $ (dead carbon proportion) / 100; note that all values are between 0.81 and 0.91, meaning that the dead carbon proportion is between 9 and 19%.

†"Bibliography" = author(s) used former works for their dilution factor q.

All these caves are horizontal and developed in hilly areas. Their entrances are on hill flanks, which explains the low thickness of the terrain above them (<50 m). Each site has characteristic geology, vegetation type and density, soil and limestone thicknesses and climate (Table 2). Examination of aerial photographs and of maps permitted us to estimate the grassland/forest ratio of the watershed above the caves; the Han-sur-Lesse and Villars caves are under forest while La Faurie and Proumeyssac are under grassland.

AMS ^{14}C activity measurements were performed on 6 stalagmites, 3 stalactites and 7 seepage waters. Except for Proumeyssac (station #1), waters and calcite deposits are from different systems (different places inside the cave). In the Han-sur-Lesse cave, the two stalactites studied correspond to the two stalagmites, which permits the comparison of the isotopic content of stalactite and stalagmite.

TABLE 2. Comparison of the Dead Carbon Proportion with the Geology, Vegetation and Climate Characteristics of the Four Studied Sites

Site	dcp (%) in: **speleothems** *(waters)*	Stratigraphy	Limestone thickness above cave (m)	Cave air pCO_2 (%)	Vegetation types and tree density of forest cover	Grassland/ forest ratio (%)	Soil thickness above cave (cm)	Mean annual precipitation (mm)	Mean temp., Jan, May, Sept (°C)
Han-sur-Lesse (Belgium)	**13.8 ± 1.5** (n = 4)	Givetian (Devonian)	50	0.03 (50 m near the entrance, large gallery)	Hornbeams, limes, oaks, hazels	0	5–30	787 (6 yr)	2.5 - 9.1 - 14.8
Villars (Dordogne, France)	**21.1 ± 1.5** (n = 3) *(20.0 ± 1.5; n = 3)*	Bajocian (Jurassic)	10–40	0.16 (n=2; 3 Jan 1997)	Oaks (13 oaks / 100 m^2; mean dia. = 17 cm), hazels, junipers, mosses, grass	5 ± 2	0–15	1048 (10 yr)	4.1 - 14.0 - 16.0
La Faurie (Dordogne, France)	**12.2 ± 1.5** (n = 1) *(3.7 ± 1.5; n=2)*	Bajocian (Jurassic)	15	0.08 (n=1; 31 Dec 1996)	Grass, mosses, oaks (20 oaks / 100 m^2; mean dia. = 10 cm)	90 ± 5	0–20	861 (10 yr)	4.6 - 14.1 - 16.2
Proumeyssac (Dordogne, France)	**9.2 ± 1.5** (n = 1) *(5.5 ± 1.5; n = 2)*	Maastrichtian (Cretaceous)	20	0.04 (n=1; 2 Jan 1997)	Grass, mosses, oaks (9 oaks / 100 m^2; mean dia. = 24 cm)	85 ± 5	10–30	889 (23 yr)	4.6 - 14.1 - 16.2

METHODS

Analytical Procedures

Between 19 and 82.3 mg of $CaCO_3$ were sampled with a microdrill for measurements on speleothems. This corresponds to 1.5 to 7 annual alternations. Laminae counting determined the exact date of the deposition of each sample (Table 3). Water analysis was performed on volumes of 100 to 200 ml.

Calcite powders were reacted with H_3PO_4 in order to obtain CO_2. The CO_2 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 accelerator mass spectrometer (Tandetron) at Gif-sur-Yvette (Centre des Faibles Radioactivités, France). Water samples were reacted with H_3PO_4 and degassed CO_2 was used as above for ^{14}C activity and $\delta^{13}C$ measurements.

Analytical errors, including laboratory errors, are $\pm 0.1\%$ for $\delta^{13}C$ and between 0.6 and 0.9 pMC for ^{14}C activity. Calcite powders are from seasonal laminae, and because two laminae deposit in one year, accuracy of sampling is less than one year.

Dead Carbon Calculation

Dead carbon calculation requires three values: 1) the deposit ^{14}C activity; 2) the deposit age; 3) the atmospheric ^{14}C activity during the deposit formation. Because the latter has varied greatly during recent decades, due to nuclear bomb tests, it is necessary to have the most accurate date for the calcite deposits ($\Delta^{14}C$ varied from 200‰ in 1960 to >1000‰ in 1963 in the Northern Hemisphere; Levin *et al.* 1992). This is possible with annually laminated speleothems. One must be cautious in attributing an age to a karst water because the latter may be composed of waters of different residence times: typically, a rapid transit occurs a few hours to a few days after a storm event, whereas in dry periods water comes mostly from porous media storage whose age is difficult to know (Ford and Williams 1989). Spring hydrographic analysis can tell us about the storage characteristics of an aquifer (Mangin 1975). Models with different water flow characteristics have been developed: porous (or diffuse), fissure and conduit flows permit plotting of a karst aquifer on a three end-member diagram (Atkinson 1985; Hobbs and Smart 1986). However, very little is known about stalactite flow characteristics; the few published measurements also show the existence of a fast and a slow component (Pitty 1966; Baker *et al.* 1997; Destombes *et al.* 1997; Genty *et al.* in press; Reicher and Trimborn 1995), but only the continuous dripping flow rate and the chemistry under several stalactites will permit quantification of these two components (work in progress). For all the waters, it is assumed that the sampling date corresponds to the water age because of the low thickness of the terrain above the caves and because it has been observed that after a rain storm, flow rate increases in the caves after a few hours or a few days. However, we must keep in mind that dilution with older water is possible.

Because the calcite samples correspond to a depositional time span between 1.5 and 7 yr, we have considered the mean atmospheric ^{14}C activity of the corresponding period. No direct atmospheric ^{14}C activity measurements near the studied sites are available. This is why we used the published results of European sites, particularly those from Germany (Levin *et al.* 1992; Levin, Graul and Trivett 1995). For the most recent years, we have extrapolated data from the modeling, with an exponential representation of the decrease of the atmospheric ^{14}C activity measured at Schauinsland (Germany; Levin, Graul and Trivett 1995).

TABLE 3. ^{14}C Activity and ^{13}C Results of Speleothems and Seepage Waters*

Sample	Type	Position	Quantity	Duration covered by sample	$a^{14}C_m$ (pMC)	Error (pMC)	$\delta^{13}C$ (‰ PDB ±0.1)
Vil-stm1 14C-C	Stalagmite	Under the top	19 mg	1985–1992; 7 alternations	96.6	0.6	–8.9
Vil-stm5 14C-A	Stalagmite	Growth surface	59.9 mg	1991–1995; 3–4 alternations	91.1	0.6	–9.7
Vil-stm4 14C-A	Stalagmite	Under the top	31.5 mg	1958–1965 (?); 7 alternations	118.6	0.6	–10.1
Vil-eau 14C-A	*Water*	*Station #1B*	*200 ml*	*2 Sep 1995; <3 h*	*89.7*	*0.6*	*–11.8*
Vil-eau 14C-B	*Water*	*Station #4*	*100 ml*	*22 Aug 1996; < 3 h*	*93.7*	*0.8*	*–9.7*
Vil-eau 14C-C	*Water*	*Station #1B*	*100 ml*	*22 Aug 1996; < 3 h*	*91.6*	*0.8*	*–10.9*
Fau-stt1 14C-A	Stalactite	Tip (6 mm), thin wall	59 mg	1990–1996; 6 alternations	102.6	0.8	–10.9
Fau-eau 14C-A	*Water*	*Station #2*	*120 ml*	*24 Aug 1996; < 48 h*	*110.3*	*0.8*	*–11.7*
Fau-eau 14C-B	*Water*	*Station #12*	*120 ml*	*24 Aug 1996; < 48 h*	*110.0*	*0.7*	*–11.7*
Prou-pot1 14C-A	Stalagmitic crust	Growth surface, station #1	63 mg	Apr 1996 – Aug 1996	104.0	0.9	–11.2
Prou-eau 14C-B	*Water*	*Station #1*	*120 ml*	*26 Aug 1996; < 0.3 h*	*108.2*	*0.7*	*–10.7*
Prou-eau 14C-A	*Water*	*Station #2*	*120 ml*	*26 Aug1996; < 0.5 h*	*108.2*	*0.7*	*–14.0*
Han-stm4 14C-A	Stalagmite	Growth surface	72.8 mg	Jan 94 – Jun 95; 1.5 alternations	98.9	0.8	–9.3
Han-stm5 14C-A	Stalagmite	Growth surface	44.1 mg	Jun 94 – Nov 95; 1.5 alternations	100.5	0.6	–9.1
Han-stt4 14C-A	Stalactite	Tip (6 mm), thin wall	56.2 mg	1989–1995; 6 alternations	102.1	0.9	–10.2
Han-stt5 14C-A	Stalactite	Tip (4 mm), soda-straw 2/3 filled	62.3 mg	1991–1995; 4 alternations	99.6	0.8	–10.8

TABLE 3 – *continuation*

Sample	$\Delta^{14}C_{atm}$ (‰)	$a^{14}C_{atm}$ (pMC ±0.7)	dcp (% ±1.5)	$\delta^{18}O$ (‰ PDB ±0.1)	$a^{14}C_g$ (pMC)	CO_2/DIC frac. (pMC)	$a^{14}C_{DIC}$ (pMC)	Avg. cave temp. (°C ±0.2)	CO_2/DIC frac. (‰PDB ±0.1)	IAEA model (pMC ±1.5)
Vil-stm1 14C-C	171.0	121.2	20.3	–4.8	117.4	3.0	120.4	--	--	--
Vil-stm5 14C-A	127.0	116.7	21.9	–5.1	112.9	2.8	115.8	--	--	--
Vil-stm4 14C-A	450.0	150.1	21.0	–4.1	145.3	2.7	148.1	--	--	--
Vil-eau 14C-A	*109.0*	*114.8*	*21.9*	--	*111.1*	*2.3*	*113.5*	*11.3*	*–9.45*	*104.7*
Vil-eau 14C-B	*106.0*	*114.5*	*18.2*	--	*110.8*	*2.8*	*113.7*	*11.3*	*–9.45*	*85.4*
Vil-eau 14C-C	*106.0*	*114.5*	*20.0*	--	*110.8*	*2.6*	*113.4*	*11.3*	*–9.45*	*95.8*
Fau-stt1 14C-A	129.0	116.9	12.2	–4.8	113.1	2.6	115.7	--	--	--
Fau-eau 14C-A	*106.0*	*114.5*	*3.6*	--	*110.8*	*2.4*	*113.2*	*12.9*	*–9.26*	*101.5*
Fau-eau 14C-B	*106.0*	*114.5*	*3.9*	--	*110.8*	*2.4*	*113.2*	*12.9*	*–9.26*	*101.5*
Prou-pot1 14C-A	106.0	114.5	9.2	–5.3	110.8	2.5	113.3	--	--	--
Prou-eau 14C-B	*106.0*	*114.5*	*5.5*	--	*110.8*	*2.6*	*113.4*	*13.0*	*–9.25*	*92.8*
Prou-eau 14C-A	*106.0*	*114.5*	*5.5*	--	*110.8*	*1.8*	*112.7*	*13.0*	*–9.25*	*121.7*
Han-stm4 14C-A	116.0	115.5	14.4	–5.9	111.8	2.9	114.8	--	--	--
Han-stm5 14C-A	116.0	115.5	13.0	–4.9	111.8	3.0	114.8	--	--	--
Han-stt4 14C-A	137.0	117.7	13.2	–5.5	114.0	2.7	116.7	--	--	--
Han-stt5 14C-A	128.0	116.8	14.7	–5.9	113.0	2.6	115.6	--	--	--

*$a^{14}C_m$ = sample measured ^{14}C activity; $a^{14}C_{atm}$ = atmospheric ^{14}C activity (calculated with $\Delta^{14}C$ published data and an atmospheric CO_2 $\delta^{13}C$ = –8.2‰); $a^{14}C_g$ = soil CO_2 ^{14}C activity; CO_2/DIC frac. = soil CO_2 / DIC fractionation factors; $a^{14}C_{DIC}$ = DIC ^{14}C activity, IAEA model = initial DIC ^{14}C activity calculated with the IAEA model.

The dcp is calculated using the measured ^{14}C activity of the deposit ($a^{14}C_m$) and the mean atmospheric ^{14}C activity of the period covering the calcite formation ($a^{14}C_{atm}$; Table 3):

$$\mathrm{dcp} = \left(1 - \frac{a^{14}C_m}{a^{14}C_{atm}}\right) 100\,\% \;. \tag{1}$$

Because we compare only groundwaters, no normalization (for a $\delta^{13}C$ of –25‰; Stuiver and Polach 1977; Mook 1980) was done (Wigley and Muller 1981).

The dilution factor (q) connected to the "hard water effect" and used by several authors (Thorpe, Otlet and Sweting 1980; Vogel 1983; Gewelt 1985; Bastin and Gewelt 1986; Fontes 1992) is

$$q = (100 - \mathrm{dcp}) / 100\,. \tag{2}$$

From $a^{14}C_m$ and $\delta^{13}C$ uncertainties (average uncertainty of ±0.7 pMC and ±0.1‰, respectively) and assuming an average error of ±0.7‰ for the $a^{14}C_m$, we estimated the total dcp error at ±1.5%.

Dead carbon calculation, as presented above, is actually an apparent proportion because it is deduced from direct atmospheric and carbonate or water ^{14}C activity measurements and does not take into account fractionation processes. The decrease of the seepage water ^{14}C activity due to limestone dissolution (the actual "dead carbon effect") should lie between the dissolved inorganic carbon (DIC) ^{14}C activity of the water before and after dissolution. Before dissolution, DIC activity is in equilibrium with the soil CO_2; after dissolution, DIC activity is similar to the measured activity of water bicarbonates and of calcite, within uncertainties due to fractionation processes. Thus, it would be more rigorous to consider isotopic fractionations that occur at different stages (Fig. 1):

1. exchange between atmospheric and soil CO_2;
2. CO_2 dissolution and bicarbonate formation;
3. limestone dissolution (dead carbon injection);
4. seepage;
5. CO_2 degassing and $CaCO_3$ precipitation at the time of seepage into the cave.

Based on this simplified course, the dead carbon arrives in the water during the third stage and it is necessary to know the processes during the two previous stages.

Exchange between Atmospheric and Soil CO_2

A global formula takes into account ^{14}C fractionation due to photosynthesis, decarboxylation and diffusion (Fontes 1992):

$$a^{14}C_g = a^{14}C_{atm}\left(\frac{1 - 2.3(\delta^{13}C_{atm} - \delta^{13}C_g)}{1000}\right) \mathrm{pMC}\;, \tag{3}$$

where "g" signifies soil CO_2 and "atm" atmospheric CO_2. The latter is known ($a^{14}C_{atm}$ is variable and $\delta^{13}C_{atm} = -8.2$‰, from Levin, Graul and Trivett (1995)), so we must estimate $\delta^{13}C_g$. Above the caves studied, vegetation consisting of oak trees and Graminaceae is typical of the C_3 type (Calvin-Benson photosynthetic pathway) which produces a $\delta^{13}C_g$ between –20 and –25‰ (Fritz *et al.* 1978; Dörr and Münnich 1986, etc.). Direct measurements on soils above limestone yield values between –20.8 and –23.1‰ for Moulis (Pyrenees, France; Fleyfel 1979) and –22‰ for the Champagne area

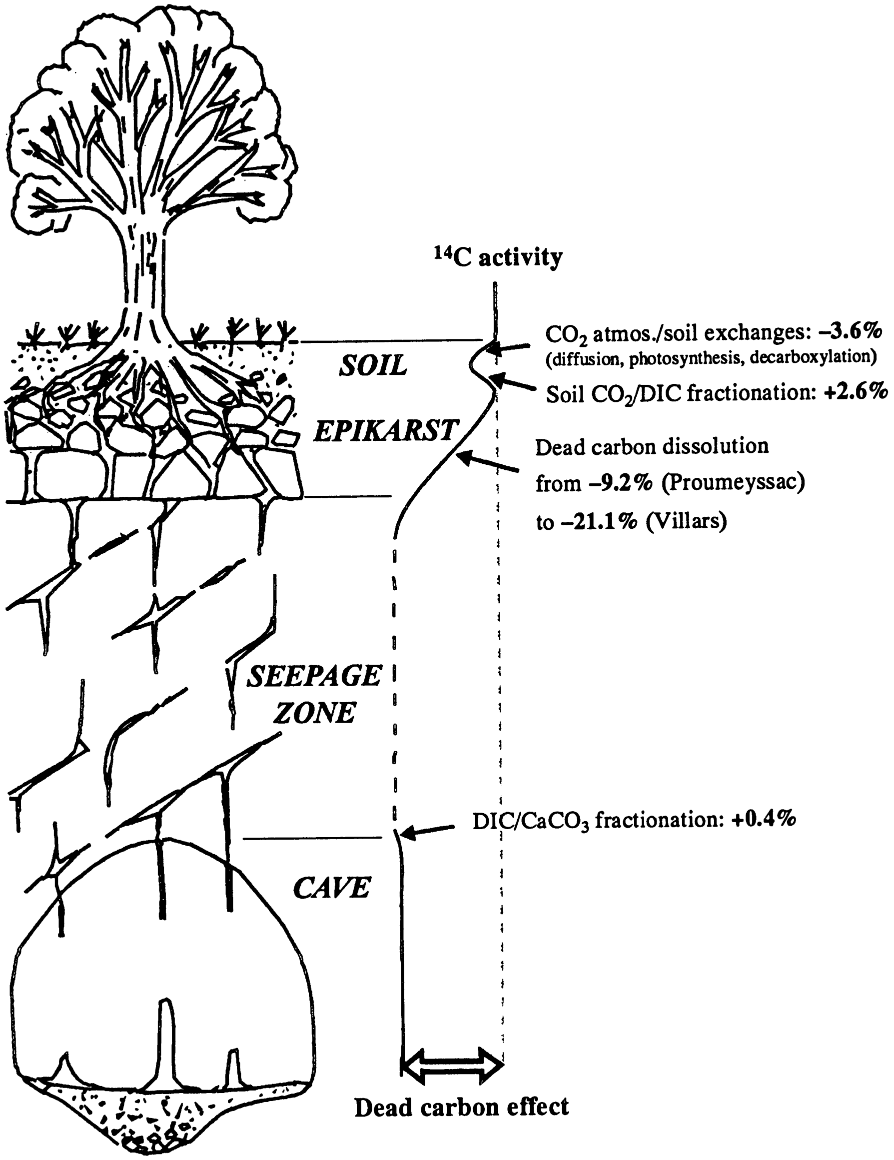

Fig. 1. Schematic ^{14}C activity evolution from atmosphere toward cave deposit. Numbers in % represent the average relative ^{14}C activity variations due to fractionation processes (see text and Table 3). Note that the ^{14}C activity decrease due to soil/atmosphere exchange is compensated by the CO_2/DIC fractionation within the uncertainty limits (± 1.5%).

(France; Dever *et al.* 1982). We can reasonably consider a mean value of −22‰. Results show that soil CO_2 activity is, on average, 3.6 pMC lower than atmospheric activity (Table 3). Karstic soils are generally very thin, and it can be assumed that there is no significant delay between atmosphere and soil CO_2 (Dever *et al.* 1982).

CO_2 Dissolution and Bicarbonate Formation

Assuming equilibrium between soil CO_2 and the DIC, the activity of the latter is given by (Saliège and Fontes 1984):

$$a^{14}C_{DIC} = a^{14}C_g + 0.23(\delta^{13}C_{DIC} - \delta^{13}C_g)\ \text{pMC}\ . \tag{4}$$

Results show an average $^{14}C_{DIC}$ enrichment of 2.6 pMC (Table 3).

The net isotopic balance of stages 1 and 2 is a decrease of about 1 pMC between atmosphere and DIC activities, which is similar to the uncertainty range ±1.5 pMC. Thus, depending on whether we consider atmospheric activity or DIC activity, it is very likely that we will obtain similar values for the dead carbon proportion.

Several models have been developed in order to estimate the hard water effect (connected to the dead carbon effect by Equation (2)) by the calculation of correction for initial water activity: *e.g.*, Tamers's chemical model (1967), Pearson's isotopic model (1965), the IAEA isotopic model (Salem *et al.* 1980), Plummer's chemical and isotopic model (1977) and Fontes and Garnier's chemical and isotopic model (1979). We have applied the IAEA model, which corresponds to the Pearson model corrected by the CO_2/DIC fractionation factor εg-b. This authorizes its use for open systems, which is more adapted to the karstic unsaturated zone:

$$a^{14}C_{DIC} = (a^{14}C_g - a^{14}C_c) \cdot (\delta^{13}C_{DIC} - \delta^{13}C_c) / (\delta^{13}C_g - \varepsilon g\text{-}b - \delta^{13}C_c)\ \text{pMC}\ , \tag{5}$$

where $a^{14}C_c$ and $\delta^{13}C_c$ relate to the limestone of the rock formation,
and $\varepsilon g\text{-}b = -9483\ T^{-1} + 23.89‰$
with T = temperature in K (Mook, Bommerson and Staverman 1974).

RESULTS AND DISCUSSION

^{13}C Results

Measured $\delta^{13}C$ values (Table 3) are typically in the range of published results for speleothems and demonstrate that the main source of carbon from dissolved inorganic carbon comes from an equilibration with soil CO_2 (*i.e.*, with $\delta^{13}C_g = -22‰$ and $T = 15°C$, the enrichment factor = $-9‰$, then $\delta^{13}C_{DIC} = -13‰$; Mook, Bommerson and Staverman 1974; Schwarcz 1986; Dulinski and Rozanski 1990; Gascoyne 1992). Calcite values are slightly higher than water values. Average differences are 1.2‰ for Villars, 0.8‰ for La Faurie and 1.1‰ for Proumeyssac. For the cave temperatures (between 10.5 and 15°C), the enrichment factor between DIC and calcite is much lower than the observed difference (between 0.41 and 0.18‰; Mook 1980). However, these differences cannot be interpreted in terms of isotopic equilibrium because waters and calcite do not come from the same systems, and we know that variations from place to place in the same cave can be very great, as noticed in Lower Cave in England (variations up to 4.7‰ between modern deposits; Baker *et al.* 1996). Another possibility is seasonal variation: because calcite develops over several years, mostly in winter when the drip rate is high (Genty *et al.* 1996, 1997), and because all the waters studied were sampled in summer, it may be possible that the observed differences reflect seasonal variations in the isotopic content of seepage water. Similar variations have been observed in the seasonal growth laminae of stalagmites in Belgium, possibly due to the isotopic content variation of the seepage water (Genty, Quinif and Keppens 1995). The other possibility is that water is lighter than calcite because of a slight kinetic fractionation due to a fast CO_2 degassing during $CaCO_3$ precipitation; however, if this is the case here, it would provoke a negligible ^{14}C fractionation (Hendy 1971).

In the Han-sur-Lesse cave, analyzed samples consist of two pairs of stalagmites and stalactites; each pair belongs to the same system. A ^{13}C enrichment of 0.9‰ and 1.7‰ is observed between stalactites and stalagmites for both stations, respectively. Differences up to 2.8‰ have been observed between stalactites and stalagmites of Lower Cave, England (Baker, Barnes and Smart 1996); evaporation could be one of the causes. Here, the $\delta^{18}O$ results do not testify in favor of evaporation, at least for the Han-stt4/Han-stm4 couple where the difference is –0.4‰ (Table 3); then kinetic isotopic fractionation due to a fast CO_2 escape could explain these differences (Hendy 1971). In any case, differences here are small and will have no important consequences on ^{14}C fractionation (*i.e.*, if we assume a ^{14}C fractionation twice that of the ^{13}C fractionation, maximum ^{14}C enrichment will be 3.4‰, which is within the ^{14}C activity measurement uncertainty).

^{14}C Results

Calcite and DIC AMS ^{14}C contents are between 89.7 and 118.6 pMC (Table 3). These high values confirm the continued importance of bomb ^{14}C contamination. The dead carbon proportion is between 9.2% and 21.9% for the calcite deposits and between 3.6% and 21.9% for the DIC of seepage waters. From these results we can make two important inferences: 1) for the same sampled site, waters have a systematically lower dead carbon proportion than calcite; 2) for the same site and where we analyzed several calcite samples, the dead carbon proportion is homogeneous.

^{14}C Activity Comparison between Water (DIC) and Calcite

Villars cave samples show the lowest dcp difference between water and calcite (avg. = 1.1%), which is within the uncertainty limits (± 1.5%). For the La Faurie and Proumeyssac caves, the difference is greater: 8.5% and 3.7%, respectively. Table 4 includes factors capable of having an influence on ^{14}C content in water. These show that:

- Neither the time elapsed between sampling and analysis, nor the time during which water was sampled, has any effect on dcp: *i.e.*, similar dcp is found for a low drip rate (La Faurie) and for a high drip rate (Proumeyssac);
- $\delta^{13}C$ values do not show any possible equilibrium with cave air, whose composition must be similar to that of the atmosphere, but are characteristic of DIC that has been in equilibrium with soil CO_2 (according to the pCO_2, which is close to that of the atmosphere; however, measurements will be necessary to verify this);
- pH values are typical of karstic waters; note, however, the higher pH (8) in the Proumeyssac cave.

Explanation of water-calcite ^{14}C activity differences must be found elsewhere. Seasonal variations in the ^{14}C content of soil CO_2 have been detected in Germany: it is lower in winter because of more intense organic matter decomposition and it is higher in summer because plant root respiration is the dominant factor; the winter/summer $\Delta^{14}C$ variation varies from 50‰ under grassland to 100‰ under forest (Dörr and Münnich 1986). Water that feeds speleothems in temperate areas like Europe infiltrates mostly in winter between November and March (Genty *et al.* 1997); then it is likely that calcite deposits more closely reflect the winter season. Conversely, water that has been collected in August must reflect the summer season. Thus, the differences observed between the ^{14}C activity of water and calcite could be explained by a simple seasonal variation in the ^{14}C content of the soil above the cave; but more measurements are needed to confirm this hypothesis.

TABLE 4. Factors Capable of Influencing Content of ^{14}C in Water

Sample and station numbers	dcp (%)	Type of bottle	ND*	TE†	MFR‡	pH	δ^{13}C (‰ PDB)	Cave air pCO_2 (%)§
Vil-eau 14C-A - #1B	21.9	Plastic 250ml	10	<3	4.7	?	−11.8	0.16
Vil-eau 14C-B - #4	18.2	Plastic 250ml	49	<3	3.8	7.5	−9.7	0.16
Vil-eau 14C-C - #1B	20.0	Plastic 250ml	49	<4	6	7.5	−10.8	0.16
Fau-eau 14C-A - #2	3.6	Glass 150ml	47	<48	95	7.1	−11.7	0.08
Fau-eau 14C-B - #12	3.9	Glass 150ml	47	<48	100	7.1	−11.7	0.08
Prou-eau 14C-B - #1	5.5	Glass 150ml	47	<0.3	continuous water flow	8.0	−10.7	0.04
Prou-eau 14C-A - #2	5.5	Glass 150ml	47	<0.5	<2	8.0	−14.0	0.04

*ND = No. of days between sampling and analysis
†TE = Time elapsed during dripping sampling, hours
‡MFR = Mean flow rate, seconds/drip
§Measured January 1997

Inter-Site ^{14}C Activity Comparison

For each site, and where at least several analyses have been made, it appears that the calcite dcp is homogenous (Fig. 2). Villars shows the highest values (avg. = 21.1%, σ = 0.8%; n = 3), followed by Han-sur-Lesse (avg. = 13.8%, σ = 0.8%; n = 4), La Faurie (12.2%; n = 1) and Proumeyssac (9.2%; n = 1). Comparison of these results with environmental conditions—vegetation type and density, soil thickness, geology and limestone formation thickness, pluviometry and temperature (Table 2)—leads to the following remarks:

- Rock formation thickness does not correlate with dcp; moreover, in the same cave a similar dcp was found for two samples taken at a 10 m altitude difference (Villars, #1B and #4);
- soil thicknesses, which are typical of karstic areas, also do not correlate with dcp;
- the lowest dcp (calcite and water) is found under grassland (La Faurie and Proumeyssac), whereas the highest is found under forest (Villars and Han-sur-Lesse);
- however, the Han-sur-Lesse site (Belgium), also covered by a continuous forest, shows a calcite dcp close to the dcp found under grassland in Southwestern France sites; note also that this site is about 3°C colder than the French ones;
- the difference observed between La Faurie and Villars, which are 60 km apart and have similar geology and climate, is possibly due to the forest cover of the Villars site.

The dcp is theoretically linked to the dissolution intensity: the more intense the dissolution, the higher the dcp. Factors that control carbonate dissolution are temperature and, most importantly, soil CO_2 partial pressure (Dever *et al.* 1982; Dörr and Münnich 1986, *etc.*). Soil CO_2 has two major sources: root respiration and microbial organic matter decomposition. Both sources will be higher in a forest soil than under a grassland. This can explain, for the most part, why dcp is higher under forest covers like the Villars and Han-sur-Lesse caves. It is possible that the 3°C lower temperature of the Belgian site yields a lower vegetation activity and thus a lower dissolution and dcp.

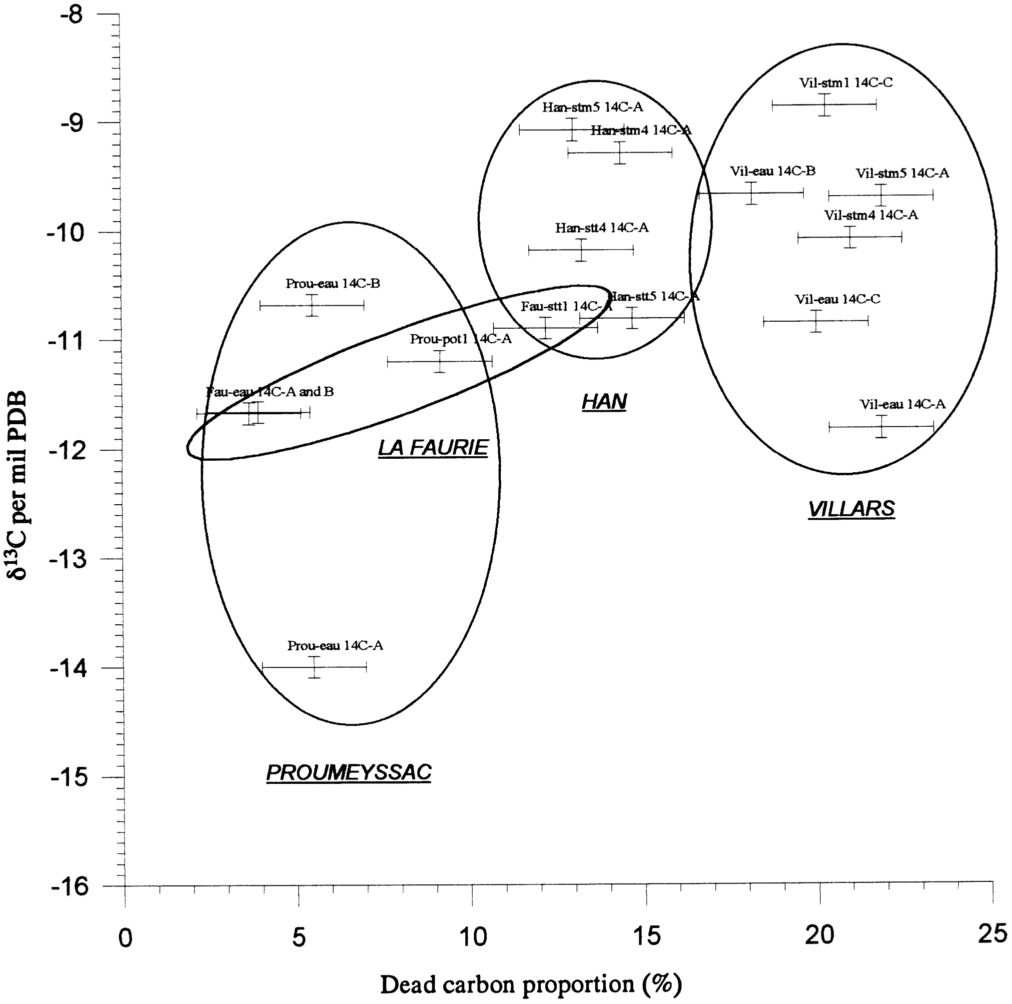

Fig. 2. Dead carbon proportion (dcp) *vs.* $\delta^{13}C$. Note that all samples from the same site are grouped together; Villars cave has the highest dcp, followed by Han-sur-Lesse cave, both under a forest cover. La Faurie and Proumeyssac, which are under grassland, show the lowest dcp.

But we must consider that other unquantified factors may possibly intervene. The possible mixing of fast and slow transit waters can change the theoretical ages that we have considered; only the hydrographic analysis of stalactite dripping flows in the different sites studied will inform us as to the possible age spectrum of the waters (work in progress). Another complicating factor can be the fracture density in the rock formation through which water infiltrates. During seepage, both water and gas infiltrate (two-phase seepage) as has been shown in a Southern France karstic area (Mangin 1975; Fleyfel 1979; Fleyfel and Bakalowicz 1980). Such a flow, combined with an intense fracture system, will favor dissolution-reprecipitation processes and thus secondary calcite deposits before reaching the cave itself (not to mention the higher possibility of isotope exchanges). This will have major consequences on speleothem isotope measurements, particularly in modern deposits. For example, a period of intense dissolution will have opposite effects on dcp:

- a decrease in the DIC ^{14}C activity, and consequently a higher dcp, if the dissolved carbonate is old limestone;
- an increase in the DIC ^{14}C activity, and consequently a lower dcp, if the dissolved carbonate is a secondary calcite deposit that was precipitated in the 1960s, when the atmospheric ^{14}C activity was very high.

The actual process probably occupies a midpoint between these two hypotheses: both old limestone with 0 pMC activity and secondary calcite deposits with a significant ^{14}C activity are dissolved during infiltration.

Comparison Between Measured ^{14}C Activity and the IAEA Model Initial Activity Calculation

Water mixing models could be helpful in understanding dissolution processes. Because we do not have enough chemical data, we have only tested the corrected Pearson isotopic model, known as the IAEA model (Salem *et al.* 1980), on three sites: La Faurie, Villars and Proumeyssac (Table 3). Because the original Pearson model is designed for closed systems (Pearson 1965) and because the karstic unsaturated zone cannot be considered as a closed system (CO_2 is mostly dissolved in the presence of carbonates, at least in our sites where the soil thickness is only a few centimeters; Krajcar-Bronić *et al.* 1986, 1992; Ek, Hilaire-Marcel and Trudel 1981; Fontes 1992), it must be corrected by the CO_2/DIC fractionation factor. Considering a soil CO_2 $\delta^{13}C = -22‰$ and a 0 pMC ^{14}C activity for the limestone formation, the average calculated DIC activities show quite good agreement (±15 pMC) with measured activities (Table 3). The average difference between the IAEA and the measured activities is −1.2 pMC ($\sigma = 12.0$), which confirms the validity of this model in different geological contexts (Fontes, 1985).

CONCLUSIONS

1. Thanks to annually laminated speleothems, the dcp due to old limestone dissolution can be calculated within an uncertainty range of ±1.5%.
2. The dcp varies from 9.2% to 21.9% for calcite deposits and from 3.6% to 21.9% for DIC in water.
3. At the same sampling site, and where several measurements were made, the dcp is homogeneous.
4. Inter-site dcp variations are up to 11%; the average dcp in our sites is 15.5% ± 4.4, within the uncertainty range of former measurements and assumptions (15% ± 5; equivalent to a dilution factor of 0.85 ± 0.5).
5. For the same site, water has a lower dcp than calcite deposits (mean differences are between 1.1 and 8.5%); this could be because all the waters studied were sampled in summer, when soil CO_2 activity is higher, while speleothems mostly develop in winter and spring when soil CO_2 activity is lower; but more measurements are needed to confirm this hypothesis.
6. For a similar environment, the dcp is higher under forest cover (*e.g.*, at the Dordogne sites, dcp = 21.1% under forest and dcp = 12.2% under grassland); this may be the consequence of more intense dissolution processes due to root respiration and microbial organic matter decomposition. However, the Belgian site, also under a forest cover, shows a dcp very close to Southwestern France sites that are under grassland; the 3°C lower temperature may be one of the causes. The possible mixing of rapid and slow (old) water flows must also be considered as playing a role in dcp results; only stalactite hydrographic analyses in each site will bring insight into the nature of the drainage.

7. The IAEA isotopic water mixing model (Pearson model corrected for an open system) is in good agreement with measured activities.

If dcp is as varied as we observed from one site to another, and if those variations are due to vegetation and soil conditions, it is very likely that dcp changed at any given site during the past when vegetation altered because of human activities and/or climate changes. From our study, dcp can vary by 11%; this yields an age difference of 970 yr, which is not negligible for the Holocene or Late Glacial chronology. Thus it is highly recommended to calculate the dcp at the sample site first before doing any age calculation based on ^{14}C method.

If vegetation seems to be a factor that influences the dcp, it is likely that environmental factors that favor secondary calcite precipitation in the unsaturated zone, such as fracture density, also play an important role. The high measured activities could accordingly be explained by the dissolution of secondary calcite deposits that precipitated in the 1960s or 1970s, when the atmospheric activity was very high. Thus, the dcp can be tied both to vegetation and to the local potential of secondary calcite deposit. The possible existence of such a process greatly complicates the interpretation of the dcp; work in progress on a single laminated stalagmite will help shed light on the importance of dissolution-precipitation processes above a cave.

ACKNOWLEDGMENTS

This study was funded by specific research programs of the Centre National de la Recherche Scientifique: DBT, DYTEC and GDR 970. It is part of IGCP 379 and PAGES PEPIII programs. We are grateful to Thierry Baritaud, Yves Quinif and Guy Deflandre, who helped us in sampling, and to the cave owners, Hubert Versaveau, Alain Frances, and Mesdames Duret and Trapp. All AMS measurements were performed at the Tandetron at the Centre des Faibles Radioactivités, Gif-sur-Yvette, France. We thank Andy Baker for his help in pCO_2 measurements and are grateful to Bogomil Obelić and Niel L. Plummer for helpful comments.

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