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Speleothem luminescence intensity and spectral characteristics: Signal calibration and a record of palaeovegetation change

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Abstract

The intensity and spectral characteristics of speleothem luminescence are investigated for signs of any potential palaeoenvironmental signals. Luminescence in speleothems has been demonstrated to have an organic acid source, acids being transported from the overlying soil to the speleothem via the groundwater system. Luminescence spectral characteristics confirm a humic/fulvic acid source of the luminescence, but are unable to distinguish between plant acids derived from different vegetation systems. Spectral characteristics also differ between solid and dissolved speleothem calcite. The influence of six factors on luminescence intensity are considered; changes in organic acid concentration, organic acid structural type, depth of the sample below the surface, dilution effects through changes in water discharge rate, dilution effects through changes in speleothem growth rate, and the effects of luminescence quenching due to the presence of metal ions. In a Holocene stalagmite sample from Sutherland a period of low luminescence intensity is observed, which is demonstrated to correlate with periods of blanket bog expansion recorded in the regional pollen record. This suggestion is supported by a study of 18 recently deposited samples from Northwest Europe and 5 cave water samples feeding stalagmites in a British cave, where a relationship to vegetation is evident, with very low luminescence intensity observed from sites overlain by blanket bog deposits. This is thought to be due to both low organic acid concentrations in feedwaters, and also the low luminescence efficiency of the humic acids from bog sites due to their structural characteristics.

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1. Introduction

Speleothems are secondary carbonate deposits which form in cave systems and consist of several forms such as stalagmites, stalactites and flowstones. Speleothem deposition is typically caused by the degassing of groundwaters which contain elevated carbon dioxide concentrations (Holland et al., 1964; Ford and Williams, 1989), the carbon dioxide is derived from the high partial pressures of CO_2 in the soil atmosphere, generated by microbial processes and root respiration (Dorr and Munnich, 1986). Stalagmites and stalactites are formed by the degassing of groundwaters from drip sources within caves, flowstones are formed by the same mechanism but in higher-discharge cave seeps and streams.

A variety of indicators of terrestrial palaeoenvironmental and palaeoclimatic change have been obtained from speleothems. In particular, using α-spectrometric uranium series dating, speleothem growth

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has been demonstrated to correlate with interglacial and interstadial periods (Gordon et al., 1989; Baker et al., 1993a), while oxygen and carbon isotope studies, fluid inclusions and pollen analysis have been used to obtain information on palaeotemperature and plant community variations (Hendy, 1971; Thompson et al., 1976; Bastin and Gewelt, 1986; Brook et al., 1990). Most recently, advances have been made in the precision of the records available. The development of thermal ionisation mass spectrometric $^{238}U-^{234}U-^{230}Th$ (TIMS ^{230}Th) dating (Edwards et al., 1987) and its application to speleothems (Li et al., 1989; Dorale et al., 1992; Baker et al., 1993b), have allowed the dating of samples to a precision of ± 1% from samples of smaller than 1 g.

The most recently discovered signal held within speleothems is that contained in their luminescence properties. When examined under 253.7 and 365 nm ultra-violet light, it has been observed that they emit a blue-green fluorescence (White and Brennan, 1989). This was attributed to the presence of humic and fulvic acids, which are known to be present in speleothem (Lauritzen et al., 1986), and are luminescent in the blue spectral region (Senesi et al., 1991). These organic acids could be introduced from the overlying soil and vegetation by the percolation waters feeding the speleothem. A more detailed investigation of the causes of variations in luminescence intensity and spectral characteristics is presented in this study. A luminescence intensity record is then examined from a Holocene stalagmite which is calibrated against luminescence variations in recent speleothem and cave water samples.

2. Speleothem luminescence

A molecule in a high energy or excited state may relax to a lower energy by emitting a photon in a process known as luminescence. In the case under consideration, the humic and fulvic acids are excited by UV light, and relax through luminescence to give a photon in the blue/green part of the visible spectrum.

A variety of palaeoenvironmental signals have been determined from speleothem luminescence. Luminescence has been observed to be annually banded in some samples (Baker et al., 1993b); this has been used to give a record of changes in growth rate for one sample from northwest Scotland, where growth rate increased at the time of the Hekla 3 volcanic eruption in Iceland (Baker et al., 1995). Where annual bands are present, an 11-yr cyclicity of intensity correlated with the sunspot cycle has been observed (Shopov et al., 1994). In addition, the latter workers observed significant (± 50%) long-term variations in luminescence intensity in a unbanded flowstone from Jewel Cave, South Dakota, U.S.A., which was deposited over the period 250–100 ka and which demonstrated broad correlations with ocean core foraminifera ^{18}O and speleothem ^{13}C. Hence a potential palaeoenvironmental signal is present in at least this flowstone sample: detailed investigations are now required to interpret the cause of this long-term luminescence variation and any potential palaeoenvironmental signal.

Two potential speleothem luminescence records are considered in this study. The first is that of variations in luminescence spectral characteristics. Fulvic and humic acids extracted from different soil types exhibit differences in spectral characteristics (Senesi et al., 1991). A summary of their results for soil types likely to be found within the British Isles over the Quaternary time period is presented in Table 1. It is apparent that the peak emission wavelength can vary with both organic acid type and soil cover. These variations in organic acid spectral characteristics should also be visible in speleothem if the organic matter gets transported by the dripwaters onto the sample.

The second record is that of speleothem luminescence intensity variations. Six factors can be considered to affect speleothem luminescence intensity, the first three of which have been previously recognised (Shopov et al., 1994).

(a) The concentration of humic and fulvic acids in the water feeding the speleothem, which are affected by changes in the overlying plant community and the rate of organic matter breakdown.

(b) The discharge of the water feed onto the speleothem; under high flow rates a lower humic and fulvic acid concentration may be expected due to a dilution effect.

(c) Changes in speleothem growth rate. This will affect luminescence intensity, as, for example, feed water with high calcium ion concentrations will de-

Table 1
Spectroscopic characteristics of various soil humic and fulvic acids (from Senesi et al., 1991)

Humic or fulvic acid	Soil type	Location	Emission maximum wavelength (nm)	Relative luminescence intensity (units)
HA	Brown Mediterranean Soil	Sardinia, Italy	514	4–5
HA	Mollic Epipedon	Illinois, U.S.A.	507	5
HA	Terra Rosa	Puglia, Italy	470–511	5–18
HA	Loamy soil	California, U.S.A.	457–514	2–29
HA	Peat	Florida, U.S.A.	511	3
FA	Brown Mediterranean Soil	Sardinia, Italy	446–465	10–50
FA	Peat	Florida, U.S.A.	461	59

posit speleothem faster than those with low concentrations (Buhmann and Dreybrodt, 1985), and hence luminescence intensity will be lower per unit volume of calcite in the former despite feed water humic and fulvic acid concentrations remaining the same.

(d) A previously unconsidered control on speleothem luminescence is that of variations in luminescence intensity between humic and fulvic acids due to variations in their molecular weight and chemical structure. The luminescence intensity of the emission maxima for several humic and fulvic acids extracted from different soil types have been characterised (Senesi et al., 1991); these data are presented in Table 1, together with luminescence emission wavelength maxima detailed earlier. It can be observed that there is a wide range of relative luminescence intensities, with fulvic acids in general having a greater luminescence (a maximum of ×20) than humic acids. This variation in relative luminescence intensity between humic and fulvic acid types may be equally significant to the factors suggested earlier.

(e) A fifth factor is that luminescence intensity will decrease with depth in the aquifer, as the humic and fulvic acids will be filtered out of the groundwater system. Organic acids have molecular weights of 500–300,000 daltons, and thus will not be transported easily through the narrow fissures of diameter 0.01–0.05 cm which typically feed stalagmite samples (Dreybrodt, 1988). This factor is not significant for individual samples which are deposited at a constant depth below the surface, but is important when comparisons of luminescence intensity are attempted between different sample sites.

(f) A final factor affecting luminescence intensity is the presence of complexed metals within the humic substances. Both theoretical and empirical studies have been undertaken, which demonstrate the importance of metal ion–humic and fulvic acid interaction (Mountney and Williams, 1992; Higgo et al., 1993). Several studies have investigated the effect of metal ions on luminescence intensity, and demonstrate a wide variety of quenching and enhancing effects (Cabaniss, 1992; Tam and Sposito, 1994). However, in a study of the complexation of Co^{2+}, Ni^{2+}, UO_2^{2+} and Ca^{2+} with humic and fulvic acids, it has been demonstrated that all metal complexation sites are taken up by calcium and magnesium when groundwater concentrations reach 1 mmol l^{-1} (Higgo et al., 1993). Since the calcium concentration of speleothem forming dripwaters is typically 50–200 mmol l^{-1} (Buhmann and Dreybrodt, 1985), metal ion uptake is probably outcompeted as demonstrated by Cao et al. (1995). Hence complications in the luminescence intensity record caused by metal ion interactions are not thought to be significant, an assumption tested later.

Thus speleothem luminescence intensity is a function of several factors, which may combine to give a complex palaeoenvironmental signal. Luminescence intensity may be dependent on plant community variations, speleothem growth rate, metal ion interactions, depth in aquifer, temperature (affecting organic matter decomposition rate) and precipitation. The relative importance of these different controls, as well as analyses of luminescence spectral characteristics, are determined in the following section for a Holocene stalagmite from Assynt, northwest Scotland, which is close to areas for which relatively detailed Holocene vegetation records are available (Pennington et al., 1972), and whose record can be calibrated against speleothem and cave water samples which have been collected under a variety of growth conditions today.

3. Sample descriptions and experimental method

A stalagmite sample was chosen for the investigation of the potential palaeovegetation signal contained in speleothem luminescence. Sample SU-80-11, a 170-mm-high stalagmite consisting of a single growth phase of dense, cream/brown coloured calcite, was collected at a depth of ~ 10 m from Uamh an Tartair Cave, Sutherland. The annual luminescence banding record has already been presented for this sample (Baker et al., 1993b), and has been precisely dated by TIMS ^{230}Th analyses (Baker et al., 1993b, 1995) and known to have been deposited between 7000 ± 750 yr ago and present. In addition, the sample is from the upper Traligill Basin, Assynt, a location for which the regional pollen record for the period of sample growth is well known from the record of Loch Sionascaig (Pennington et al., 1972). This record suggests that northwest Scotland underwent a period of pine/birch decline at around 4500 calibrated radiocarbon years ago, with consequent expansion of *Calluna eriphorum*-dominated blanket bog.

The luminescence intensity record for sample SU-80-11 was obtained using a UV (HeCd, 325 nm) laser. This was used to excite the luminescence which was collected with a lens, wavelength selected at 480 nm with a spectrometer and detected with a photomultiplier. The incident UV light was focused onto the sample with a spot diameter of 250 μm. Luminescence intensity data were recorded as the sample was scanned in front of the laser beam; three scans were made down the central axis of the sample in order to ensure the reproducibility of the intensity record. No significant difference was observed between scans, and a luminescence intensity record compiled from the average of all scans. The luminescence intensity of SU-80-11 at a distance 3 mm from the tip was used to calibrate all the speleothem samples used in this study and for use as a future standard. Luminescence emission spectra were also obtained at fixed distances down the sample, by analysing both solid samples and solutions of dissolved calcite. The latter were obtained by dissolving calcite in a minimum quantity of 10% HNO_3, adjusting the pH to the range 6.0–7.0, and placing the solutions in a 5-ml UV transparent quartz cuvette for laser analysis.

In order to calibrate this Holocene luminescence record, the luminescence intensity was determined for eighteen stalagmite and low-discharge flowstone samples that are actively forming under a wide range of depositional conditions in different regions of Northwest Europe (England, Scotland, Wales, Ireland and Belgium). The luminescence intensity data for the speleothem calcite were obtained using the method detailed earlier. A constant spot size was used to allow the investigation of the effects of growth rate variations, data being collected for the most recent 5–10 mm of growth (equivalent to the last 10–500 yr of deposition depending on sample growth rate). In addition, luminescence emission spectra were collected for each sample for both solid and dissolved calcite as detailed earlier.

A relatively small number of samples were collected in order to conserve the cave sites from which they were derived. Samples originated from sites with differing vegetation cover and limestone geology, and the samples had a wide range of water discharges and growth rates. Such sample selection permits determination of the relative importance of the factors which may determine speleothem luminescence intensity [Section 2, (a)–(f)]. Sample identity, type (flowstone or stalagmite), location, geology, trace-metal concentration, drip discharge onto the sample, sample growth rate and overlying vegetation type are all detailed in Table 2.

A final calibration data set was obtained from the luminescence properties of five dripwaters feeding stalagmite samples in Lower Cave, Bristol, England. Water samples and discharge data were collected over the period 1994–1995, with 16 samples obtained from each site over the course of a year, in order to determine the effect of flow dilution on luminescence intensity [see Section 2, (b)]. Water samples were analysed in 5-ml UV-transparent quartz cuvettes as detailed earlier, the intensity signal was calibrated against the 365-nm Raman peak in blank samples of double-distilled water.

Table 2

Speleothem data and luminescence characteristics

Sample name	Sample type[a]	Location	Vegetation type	Geology[b]	Zinc conc. (ppm)	Sample growth rate (mm yr^{-1})	Drip discharge[d] (l s^{-1})	Luminescence intensity (mean ± 1σ)	Luminescence wavelength of intensity maxima: solid (nm)	Luminescence wavelength of intensity maxima: dissolved (nm)
FR-94-1	S	The Burren, Co. Clare	blanket bog	CAR	22.6	?	[3.6×10^{-7}]	5.7 ± 0.4	517	424
FR-94-2	S	The Burren, Co. Clare	blanket bog	CAR	1.8	?	[1.9×10^{-7}]	4.9 ± 0.3	507	n.d
SU-80-11	S	Assynt, Sutherland	blanket bog	CA-OR	0.8	0.010 ± 0.04	?	3.2 ± 0.6	495	415
DL-91-1	F	Mendip Hills, Somerset	unimproved grass	CAR	1286	> 0.020	$(2.7 \pm 1.9) \times 10^{-4}$	31.2 ± 2.8	501	n.d
CC-93-1	F	Black Mountains, S. Wales	unimproved grass	CAR	8.2	?	?	9.2 ± 2.2	511	431
LC-92-1	S	Bristol, Avon	light scrub	CAR	21.8	> 0.040	$(5.7 \pm 1.9) \times 10^{-7}$	36.7 ± 19.5	491	n.d
BFM-92-8	S	Bath, Avon	semi-mature	JUR	1.6	> 0.080	[5.4×10^{-7}]	10.9 ± 1.4	490	421
BFM-92-6	S	Bath, Avon	secondary woodland	JUR	n.d	> 0.080	[1.0×10^{-6}]	13.5 ± 3.3	491	415
SL-92-2	S	Mendip Hills, Somerset	ancient deciduous	CAR	550	> 0.081	?	45.8 ± 2.7	498	416
SL-92-3	S	Mendip Hills, Somerset	woodland	CAR	106.3	> 0.081	?	5.4 ± 2.3	492	422
GodStm5	S	Godarville, Belgium	woodland	YPR	n.d	1.38 ± 0.07	[5×10^{-5}]	10.4 ± 1.5	510	n.d
GodStm8	S	Godarville, Belgium	woodland	YPR	n.d	0.59 ± 0.03	?	10.4 ± 2.6	508	n.d
KC-92-1	S	Torquay, Devon	gardens and light secondary woodland	DEV	n.d	> 0.041	[5×10^{-5}]	10.2 ± 4.3	495	416
KC-91-8	F	Torquay, Devon	gardens and light secondary woodland	DEV	10.0	> 0.036	$(11.0 \pm 6.7) \times 10^{-5}$	16.6 ± 3.6	501	n.d
KC-91-11	F	Torquay, Devon	gardens and light secondary woodland	DEV	20.5	> 0.045	$< 1 \times 10^{-8}$	9.3 ± 2.9	502	424
KC-91-6	F	Torquay, Devon	gardens and light secondary woodland	DEV	n.d	> 0.020	$(6.9 \pm 11.0) \times 10^{-4}$	8.3 ± 2.6	503	n.d

n.d. = not determined.

[a] S = stalagmite; F = flowstone. All samples were fed by a drip source.

[b] DEV = Devonian limestone; CAR = Carboniferous limestone; JUR = Jurassic limestone; CA-OR = Cambro-Ordovician dolomites; YPR = Ypresian calcareous sandstone.

[c] Absolute growth rate data for SU-80-11 are the average of the last 800 ± 150-yr growth from TIMS ^{230}Th data (Baker et al., 1995). Absolute growth rates from Godstm5 and Godstm8 are the average of growth from 1976–1992 determined from annual visible bands (Genty, 1992). Other minimum growth rates are from cave and mine sites where the earliest time of formation was the date of mine or cave excavation, all samples have formed over the last 100 yr (Baker, 1993).

[d] Drip discharge data is the mean and 1σ error of measurements taken over the course of a year's field cycle in 1991–1992 (Baker, 1993). Figures in square brackets are the drip discharges on sample collection where annual data were not obtained and gives an order of magnitude estimate of discharge.

[e] Absolute values of luminescence intensity data tabulated here cannot be directly compared with that of relative intensity of Senesi et al. (1991) in Table 1; see text for details.

4. Results and interpretation

4.1. Luminescence spectral characteristics

Typical spectra obtained from both solid and dissolved calcite are presented in Fig. 1, and the wavelengths of the luminescence maxima of all the calibration samples and stalagmite SU-80-11 in Table 2. Fig. 1 and Table 2 both demonstrate that there is a significant difference between the wavelength of the luminescence emission maxima between solid and dissolved calcite, with solid samples having a longer peak wavelength. The reason for this is uncertain, but as there is no significant difference between the dissolved calcite spectra and the cave dripwater spectra, it is probably due to the influence of the calcite crystal lattice. There was no observed variation in the wavelength of the emission luminescence maxima either within sample SU-80-11 (mean wavelength of emission maxima = 414.5 ± 8.7 nm; $n = 8$, 1σ errors) or between the calibration samples and sample SU-80-11; Table 2 (mean wavelength of emission maxima = 419.9 ± 5.2 nm; $n = 10$, 1σ errors). These results suggest that the spectral characteristics of speleothem luminescence cannot be used to derive data on vegetation change in the British

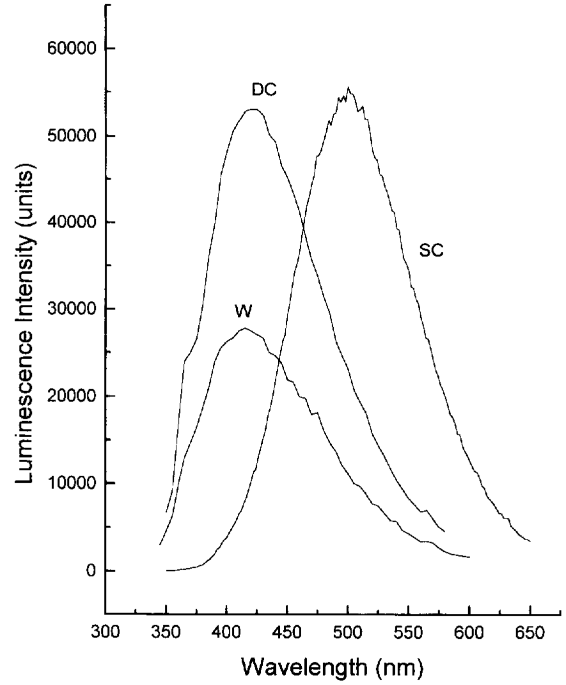

Fig. 1. Typical luminescence emission spectra for speleothem calcite (*SC*), dissolved speleothem calcite (*DC*) and cave drip water (*W*).

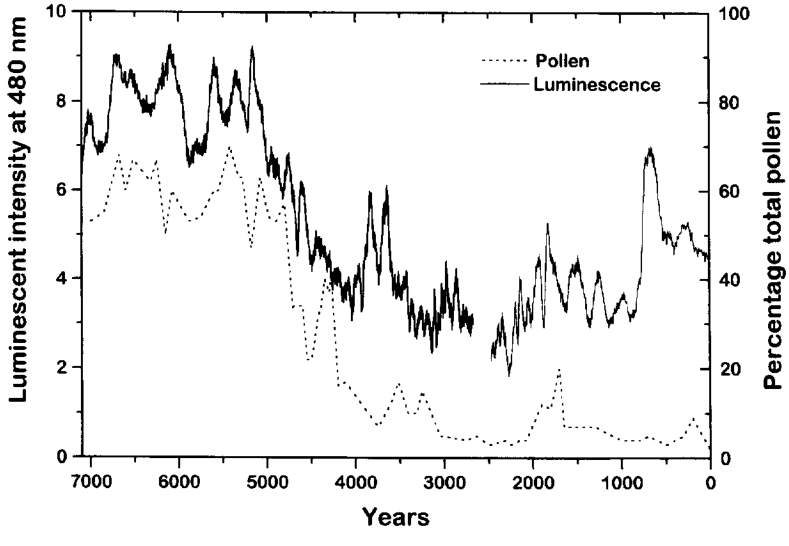

Fig. 2. The speleothem luminescence intensity record of stalagmite SU-80-11 and the regional *Pinus* record from Loch Sionascaig (Pennington et al., 1972) for the last 7000 yr. Seven TIMS ^{230}Th analyses on the speleothem at 6970 ± 750, 4540 ± 160, 3270 ± 110, 3000 ± 100, 2670 ± 70 and 800 ± 150 yr BP were used to correct the luminescence record for variations in growth rate (Baker et al., 1993b); ^{14}C dates on the pollen record from 5930 ± 160 radiocarbon years BC to present demonstrate constant deposition rate (Pennington et al., 1972). Stalagmite luminescence data were collected at 250-μm intervals (20 points/100 yr), pollen data have a resolution of ~ 110 yr.

Isles; close inspection of Table 1 suggests that this result may have been expected as there is both a wide range and large overlap in the peak luminescence wavelengths of soil humic and fulvic acids. However, there is a good agreement between speleothem and soil humic and fulvic acid spectral characteristics; the lower-wavelength maxima observed here compared to the results of Senesi et al. (1991) (Table 1) are due to the dependence of emission maxima of organic acids on the excitation wavelength; with a laser of lower excitation wavelength used in this study (325 nm compared to 360 nm).

4.2. Luminescence intensity records

4.2.1. The Holocene luminescence record from the Sutherland stalagmite

The luminescence intensity record for SU-80-11, together with that of the total pollen percentage of *Pinus* from Loch Sionascaig (Pennington et al., 1972), is presented in Fig. 2. Both records have been converted to calendrical years; the radiocarbon ages having been converted using the calibration of (Pearson and Stuiver, 1993; Stuiver and Pearson, 1993), and have an average error of ± 100 yr. The TIMS ^{230}Th ages have an average error of ±50 yr (all errors 1σ), except for the commencement of growth which is precise to only ±380 yr; Baker et al., 1993b). The TIMS ^{230}Th ages have been used to correct the luminescence data for variations in stalagmite growth rate.

Fig. 2 demonstrates a remarkable correlation between luminescence intensity and the record of *Pinus* decline. In particular, although the timing of the commencement of growth of SU-80-11 is less well constrained than the other periods of growth, the mid-point of the time of the luminescence decline in the stalagmite has been precisely determined to 4540 ± 160 yr from the TIMS ^{230}Th analyses (Baker et al., 1993b), which correlates within 95% confidence levels with the calibrated ^{14}C date of on the *Pinus* decline of 4300 ± 200 yr (all errors are 2σ). Radiocarbon dates on preserved pine stumps beneath peat bogs which are widely preserved through northwest Scotland (Birks, 1975), as well as the increase in Cyperacae, Gramineca, *Calluna* pollen and *Sphagnum* spores in the sediments at Loch Sionascaig from 4300 yr ago (Pennington et al., 1972), both demonstrate the subsequent peat development and spread of blanket bogs in the region. This is reflected in the low luminescence intensity in the stalagmite over the period 4540 yr ago until present. As well as the general correlation, close inspection of Fig. 2 reveals that several of the major oscillations within the luminescence intensity record can be correlated with oscillations in the *Pinus* record, particularly the peaks between 7000 and 4540 years ago, and the double peak at ~ 3700 yr ago in the luminescence record, which may correlate within dating errors with that at 3400 yr ago in the *Pinus* record. Not all peaks correlate, which suggests that the speleothem is reflecting local vegetation changes which may not reflect changes in the region as a whole; one example of this is the recent luminescence peak at ~ 700 yr ago which may have only a local cause.

4.2.2. Luminescence intensity of the calibration samples

Luminescence intensity data for each of eighteen calibration samples are presented in Table 2, the range of values reflecting the range observed over the last 5–10 mm of sample growth. Time series data have not been presented as this would not be meaningful for samples with variable growth rate and thus poor temporal control. All samples were obtained from within 30 m of the surface, in order to limit the effects of filtering of organic acids with depth [Section 2, (e)]. Fig. 3 shows the luminescence intensity of actively forming stalagmite samples from G.B. Cave, Mendips. Active speleothem deposition is occurring in the range 25 to 140 m below the surface, and Fig. 3 demonstrates that luminescence intensity declines significantly with depth. In the calibration data set, consisting of samples taken from the depth range 0 to 30 m, and similar to that of the sample SU-80-11 (~ 10 m), it is apparent that there is a wide range in observed luminescence intensity, but that samples from several different vegetation covers have similar luminescence intensity except for those overlain by blanket bog deposits which have consistently low luminescence intensity.

The effect of dilution on luminescence intensity [Section 2, (b)] can be investigated with the dripwater data from Lower Cave, Bristol. Fig. 4 presents the relationship between luminescence intensity and drip discharge for water sample sites LC-2 to LC-6.

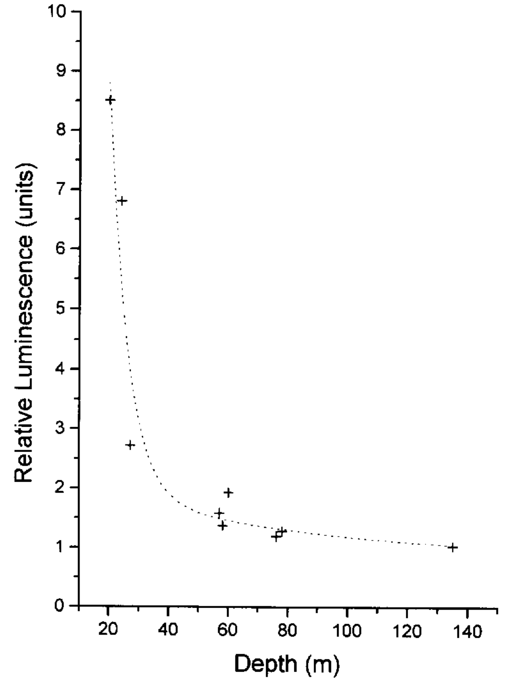

Fig. 3. Relationship between luminescence intensity and depth below surface for currently forming stalagmites from G.B. Cave, Mendip Hills, England. Luminescence intensity is calibrated to allow comparison with the data in Table 2; the site is overlain by grassland. The *dashed line* is the best-fit three-component exponential decay equation.

At only one site is the relationship between discharge and luminescence statistically significant at a 99% confidence level (LC-2 with a correlation coefficient of 0.93); two other sites are significant at a 95% confidence level (LC-3 and LC-4 with correlation coefficients of 0.538 and 0.519, respectively). Surprisingly, these results show that if there is any relationship between luminescence intensity and discharge, that it is a positive one with humic and fulvic acids being flushed through the groundwater system with increasing discharge, the opposite to that postulated by Shopov et al. (1994). It is apparent that with increases in discharge of up to ×10, luminescence intensity increases by between 4.6% and 39.9%. For example, LC-2 (the site with most significant relationship being luminescence and discharge) has a relationship:

$$(\text{luminescence intensity}) \\ = 10.69 + 99.17 * (\text{discharge}) \quad (r = 0.93)$$

demonstrating that there is a ×1.8 increase in luminescence intensity with a ×10 increase in discharge. The maximum annual variability of drip rate from the sites presented in Fig. 4 is ×20 (that of LC-2); this would suggest that the maximum effect of drip rate variability would be a ×2.6 increase in luminescence intensity. No relationship between discharge and luminescence intensity can be observed in the calibration data set. For example, in samples from Kent's Cavern, Torquay, which have differing drip discharge rates yet similar vegetation cover and geology; no difference in luminescence intensity can be observed between low-discharge sample KC-91-11 and the high-discharge samples KC-91-8 and KC-91-6. This is due to both the weakness of the relationship between drip discharge and luminescence intensity for most sites as noted above, and also the fact that dripwater data were collected on an intra-annual basis, when the flushing of organic acids may be a more significant process than when drip discharge

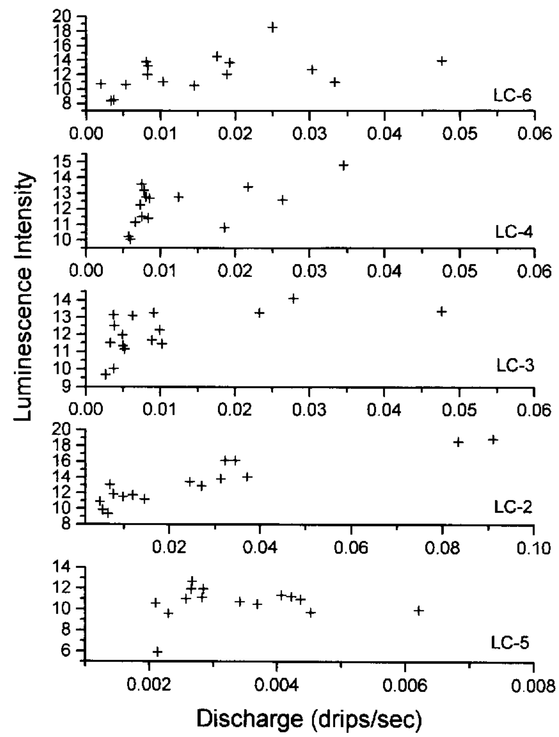

Fig. 4. Relationship between luminescence intensity and discharge for five drip waters feeding actively depositing stalagmites in Lower Cave, Bristol.

varies with inter-annual or inter-sample variations in drip discharge.

The effect of growth rate variations on luminescence intensity [Section 2, (c)] can also be observed to be unimportant. Sample SU-80-11 has a very low luminescence intensity and yet the slowest growth rate of 0.010 ± 0.04 mm yr^{-1}. If growth rate effects are significant, then samples with such low growth rate should have the highest luminescence intensity, with a greater number of years of humic and fulvic acid deposition excited by the laser beam. The fact that this is not observed here, especially in comparison with samples Godstm5 and Godstm8 which have a growth rate × 100 faster, suggests that other factors are more important in limiting luminescence intensity.

The effect of metal ion–humic and fulvic acid interactions [Section 2, (f)] is demonstrated to be unimportant through samples formed within different limestone geology. Trace-element analyses were performed on the calibration samples using standard atomic absorption spectrometric (AAS) techniques; the results for zinc are tabulated in Table 2. Samples with equal drip discharges and growth rates from woodland sites from both Jurassic limestone (a former Bathstone mine with high-purity limestone) and Carboniferous limestone (an ochre mine which may be expected to have high groundwater iron and zinc concentration) have similar luminescence intensities, despite zinc concentrations being over × 1000 higher in the latter (1.6 ppm vs. 1286 ppm). This is an expected result, and provides a further line of evidence to confirm that calcium and magnesium ions dominate the complexing of the humic and fulvic acids in karst systems.

4.3. Interpretation

The data presented in Tables 1 and 2 suggest that most vegetation types generate comparable luminescence spectral characteristics and intensity in speleothems. Depth below the surface is important in limiting luminescence intensity, and to eliminate this variable samples were taken from the top 30 m of the limestone. The effects of variations in discharge, growth rate or metal–organic acid interactions were observed to be insignificant. When samples from within 30 m of the surface are compared, samples overlain by blanket bog do appear to exhibit a consistently low luminescence intensity. This provides corroboratory evidence for the decline in luminescence of stalagmite SU-80-11 after the transition from pine to blanket bog in northwest Scotland. Two lines of evidence exist which give an explanation for this low luminescence with blanket bog cover. Peat humic acids are known to have a lower luminescence intensity than humic acids derived from other soil types (Senesi et al., 1991). The latter authors attributed this to their complex structural components, high degree of aromatic polycondensation and a high molecular weight fraction. This is a product of the poor break down of humic substances in peatlands, which by definition have high concentrations of undegraded biotic material due to the predominantly anaerobic conditions (Moore et al., 1992). Hence as well as the low luminescence intensity of the humic acids, they may also be present in a lower concentration due to the low organic matter breakdown. These factors confirm that a change in palaeovegetation to or from blanket bog cover should be observable in long-term variations in speleothem luminescence intensity.

5. Discussion

The oscillations in the luminescence intensity record can be analysed in further detail for the periods for which the stalagmite is most precisely dated (Baker et al., 1993b). In particular, between 4540 ± 60 and 3270 ± 110 yr ago, 9 oscillations occur (a frequency of 140 ± 20 yr); between 3270 ± 110 and 2670 ± 70 yr ago there are 13 oscillations (a frequency of 46 ± 14 yr); Fig. 2. Similar oscillations have been observed in plant macrofossil variations in blanket bogs (Aaby, 1976; Barber, 1981; Barber et al., 1994), but at a lower frequency (260 and 800 yr). These have been attributed to changes in surface wetness and hence climate change, perhaps through an ocean driven signal in regions of maritime climate (Barber et al., 1994). A similar cause could be attributed to the oscillations in luminescence, with increasing temperature leading to increased drying of the upper layers of the peat, increasing biodegradation and thus humic acid production and subsequent luminescence intensity. It can also be noted that

76–88-yr oscillations have been observed in recent climate change records for the North Atlantic, North America and European regions (Schlesinger and Ramankutty, 1994), which are attributed to an ocean–atmosphere coupling and have a frequency of the same order of magnitude as the oscillations in the luminescence record. Further studies from cores taken from above the cave site would ascertain whether there are correlations between the luminescence oscillations and plant macrofossil distributions.

An interesting observation is the correlation between the presence of annual luminescence banding and the periods of low luminescence intensity (interpreted as blanket bog cover). Annual banding is only observed in the section of sample from 3270 ± 110 yr ago to present (Baker et al., 1993b), a section which has low luminescence intensity and blanket bog cover. It has been suggested that limitations on the preservation of annual luminescence banding may be caused by the strict requirements of the type of percolation flow feeding the speleothem, soil water and unsaturated zone storage needing to be adequate to maintain flow during the summer, while residence times overall remain sufficiently short that waters are not completely mixed (Baker et al., 1993b). Results obtained here suggest that peat cover may allow the seasonal differentiation of water which will permit banding to be preserved. A possible explanation is that in summer, with the drying of the upper layers of the peat, increased organic matter breakdown and humic acid production occurs (Latide, 1972). Increased summer organic matter concentrations have been observed in a surface stream draining a subarctic peatland (Moore, 1987), and could explain the annual luminescence banding preservation if seasonally differentiated water is also transported into the groundwater system. Downward seepage is minimal in blanket bogs, and water balance is mainly characterised by relatively large, horizontal, surface runoff (Streetkerk and Casparie, 1989). Organic matter in this water would be sensitive to the variations in humic matter breakdown rate near the surface of the bog, and could enter the limestone through fissures and sinks within the blanket bog. In contrast, soil sites are more likely to buffer organic matter variations; for example, there has been observed a decrease in dissolved organic carbon with depth in the soil in a study of 48 soil types (Moore et al., 1992), organic matter sorption in various soil horizons buffer the seasonal variations in humic acid production. This in turn would prevent seasonally differentiated waters from entering the groundwater system, and thus may explain the lack of luminescence banding in the section of stalagmite SU-80-11 deposited between 7000 to 4500 yr ago, when there was probably a pine or birch cover with associated soil development.

6. Conclusions

The evidence presented here suggests that a blanket bog vegetation cover over a cave system should be reflected in a low luminescence intensity signal in stalagmites. Other vegetation types cannot be distinguished, limiting the overall usefulness of the signal for the British Isles, although other regions with more extreme variations in vegetation and soil types may produce more significant results. However, where low luminescence intensities are determined over the period for which radiocarbon dated pollen records are available, then the luminescence intensity record can be used to provide a high-resolution record of the timing and causes of oscillations in the blanket bog system. In addition, the precise dating of the speleothem can in itself provide more detailed palaeoenvironmental information. For speleothem deposited over the Quaternary period, the determination of the timing of blanket bog cover by TIMS ^{230}Th or α-spectrometric uranium series analyses may provide unique records which provide further evidence of changes in vegetation type in the late Quaternary British pollen stratigraphy.

Further research into the luminescence intensity record is necessary. The record from Sutherland has demonstrated that speleothem luminescence does not reflect global ^{18}O variations as proposed previously (Shopov et al., 1994), but instead a local, palaeoenvironmental record. In addition, three areas of immediate research potential can be highlighted. Firstly, calibration of the intensity signal needs to be undertaken for regions outside Northwest Europe with different vegetation covers. Secondly, no work has been undertaken on high-discharge flowstones which may have a greater flow rate and growth rate variability and which may contain a luminescence intensity signal less dominated by palaeovegetation changes. Finally, further investigation as to the occurrence of 40–140-yr oscillations in luminescence intensity within periods of blanket bog cover is required from other samples. Comparison of the record obtained from SU-80-11 with pollen cores overlying the cave site is the focus of current research.

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