

Speleothem organic acid luminescence intensity ratios: a new palaeoenvironmental proxy

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Abstract: One area of recent speleothem research has been the analysis of luminescence variations. Here we present luminescence data for the dominant luminescence centre (excitation wavelength 330 to 390nm; emission wavelength 390 to 460nm). For many speleothems this peak can be resolved into two luminescence maxima. Data presented here, from a variety of speleothems and a wide range of cave locations, suggest that in many cases the ratio of luminescence intensity of these two luminescence intensity sub-centres can provide a more sensitive record of luminescence variations. Also, in some cases, it can provide a palaeoenvironmental proxy.

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INTRODUCTION

Organic acids are commonly entrapped within speleothems, and their luminescence is readily observed (O'Brien, 1956; Baker *et al.*, 1993; Shopov *et al.*, 1994). Forty to sixty per cent of all total organic carbon luminesces (Senesi *et al.*, 1993). Most of the luminescent material consists of humic and fulvic acids and protein, and this organic matter has a source in the soil overlying the cave. Recent research into speleothem luminescence has focused on two properties. Firstly, the intensity of luminescence, which for samples of constant crystallographic fabric and texture can provide a proxy of the concentration of luminescent organic material (Shopov *et al.*, 1994; Baker *et al.*, 1996). Secondly, luminescence wavelength variations, which can provide a measure of organic acid molecular weight and structure, as well as distinguish between humic/fulvic acid luminescence and that of protein (Baker *et al.*, 1998, 1999; Baker and Genty, 1999; McGarry and Baker, 2000).

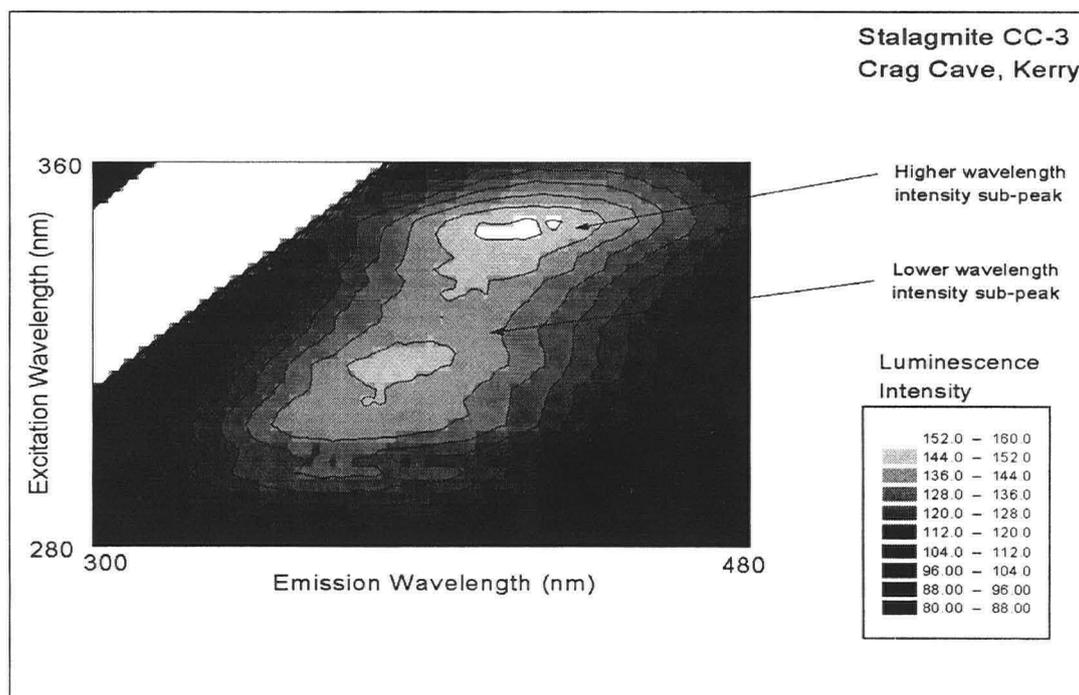
Most studies of luminescence wavelength variations have focused on changes in the excitation and emission wavelength of the luminescence intensity maximum (Baker *et al.*, 1998, 1999). However, this luminescence centre is commonly observed to be a double peak

(Fig.1), with two clear luminescence sub-peaks. Analysis of just the maximum luminescence therefore omits additional information that could be obtained from the luminescence centre as a whole. Recently, Proctor *et al.* (2000) demonstrated that the ratio of the two observed sub-peaks can provide a high resolution palaeoenvironmental proxy (Fig.2). By comparing the luminescence ratio against a separate climate proxy (that of mean annual rainfall/mean annual temperature, derived from growth rate variations, which is historically calibrated), a strong correlation is observed, with an increased proportion of high wavelength (high molecular weight) luminescence in wet and cold climate phases. Such a correlation agrees with our existing understanding of the effects of climate on soil humification (Christ and David, 1996; Martin-Neto *et al.*, 1998; Baker *et al.*, 1999), and suggests that further investigation is required into the sub-peaks of the organic acid luminescence centre.

METHODS

Eleven cut and polished speleothem samples were analysed for their luminescence properties, at 1mm intervals down their central axis of growth. Samples were chosen to represent a wide range of surface environments (climate, vegetation) as well as age ranges (Table 1).

Figure 1. Typical speleothem luminescence excitation-emission matrix (EEM), demonstrating the presence of two luminescence sub-centres.



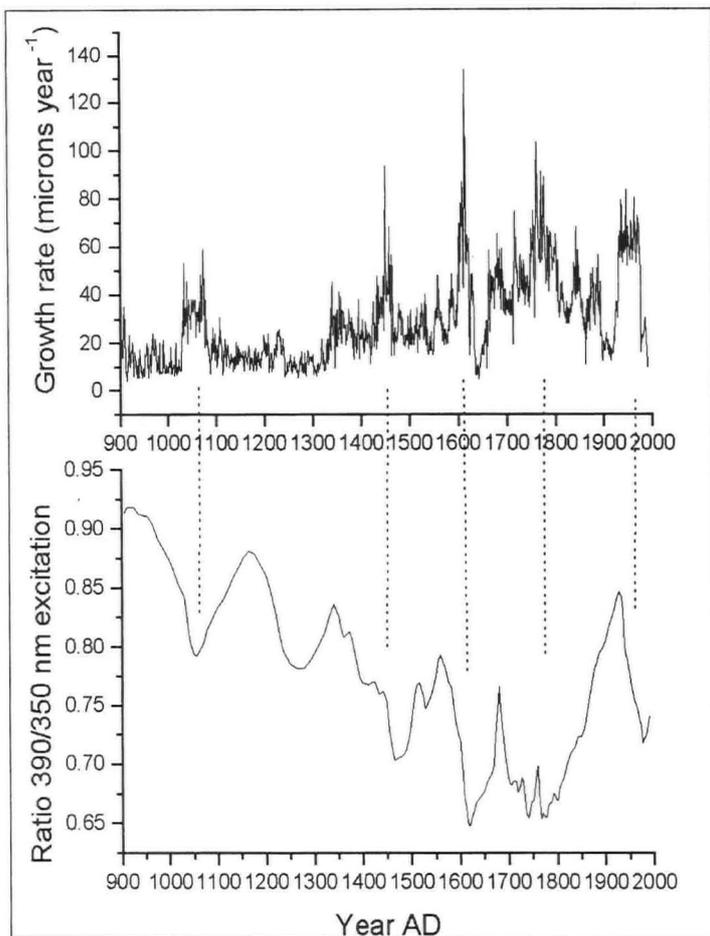


Figure 2. Growth rate (top) and ratio of luminescence intensity sub-centres (base) at excitation wavelengths of 350 and 390nm for stalagmite SU-96-7, Uamh an Tartair, Assynt. The inverse relationship demonstrates that at this site the high luminescence intensity ratio is equivalent to poorly humified soil conditions.

Luminescence data were collected using a Perkin-Elmer LS-50B luminescence spectrophotometer and Perkin Elmer fibre-optic extension. Excitation luminescence was varied from 260 to 420nm at

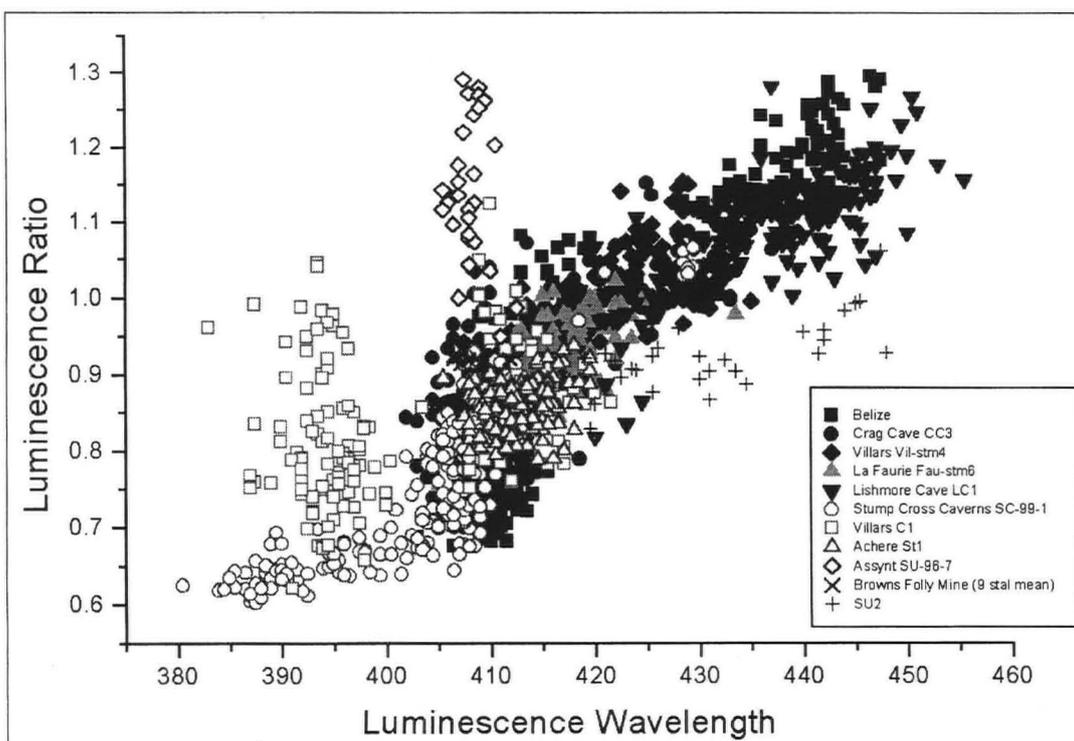


Figure 3. Mean luminescence wavelength of the lower wavelength luminescence centre vs. luminescence ratio for 11 speleothems. Sample details can be found in Table 1.

between 3 and 5nm steps, and the emission recorded from 360 to 550nm at 0.5nm steps, in order to construct an excitation-emission matrix (EEM; Fig.1). For each EEM, the wavelength of maximum luminescence was reported (as per Baker *et al.*, 1998, 1999), as well as the ratio of the intensity of the two sub-peaks (higher wavelength peak / lower wavelength peak, as per Proctor *et al.*, 2000), if they were present.

RESULTS

Results are presented in Fig.3 and Table 1. Fig.3 demonstrates a wide range of wavelengths of maximum luminescence emission, from 380nm to 460nm. There appears to be no obvious environmental control on this parameter, with sites of similar rainfall and temperature and recently deposited speleothems having widely differing mean luminescence wavelengths (e.g. Stump Cross Caverns, Yorkshire, having some of the lowest wavelengths and Lishmore Cave, County Kerry, Ireland, having some of the highest). Such results are not surprising, given the fact that luminescence wavelength variations reflect both molecular weight and aromaticity of organic acids, and that non-climatic factors such as vegetation type, soil clay content, etc. will influence the luminescence properties (Baker and Genty, 1999; McGarry and Baker, 2000). Similar results are observed for the ratio of the luminescence intensity of the two sub-peaks, with considerable inter- and intra-site variability. A statistically insignificant relationship is observed between intra-site mean luminescence wavelength and mean ratio ($r = 0.48$; $n = 11$, significant at the 80% confidence level).

Comparison of the wavelength of the maximum luminescence with the ratio data demonstrates that some samples have a strong correlation between the wavelength of maximum luminescence intensity and the ratio of the two sub-peaks (e.g. samples SU-2, Bel-1 and Vil-4). However, other samples exhibit no correlation between the two variables. Close inspection of the data suggests that these samples are those that exhibit a very small variability in the luminescence wavelength maximum ($< \pm 3\text{nm}$), which is the same as the analytical error of the technique. Hence, for these samples, it appears likely that use of the luminescence intensity ratio data may provide a more precise measure. This is demonstrated by data for SU-96-7, for which the ratio data have already been demonstrated to reflect soil humification (Proctor *et al.*, 2000 and Fig.2), and yet has only a weak correlation between luminescence peak wavelength and ratio data (Table 1).

Table 1. Location, sample type, deposition period and luminescence properties of speleothems analysed in this study.

Sample ID	Location and type ^a	Deposition Period	Mean and 1 σ wavelength of lower luminescence intensity sub-peak	Mean and 1 σ intensity ratio	Correlation between wavelength of lower ^b luminescence peak and intensity ratio (r)
Bel-1	Belize, S	~ 180-10 ka	420.4 \pm 13.2	0.933 \pm 0.199	0.93
CC-3	Kerry, Ireland, S	10-0 ka	413.4 \pm 7.8	0.879 \pm 0.107	0.71
LC-1	Kerry, Ireland, S	10-0 ka	437.9 \pm 7.5	1.103 \pm 0.070	0.75
Vil-stm4	Dordogne, France, S	4-0 ka	419.4 \pm 6.7	0.974 \pm 0.063	0.75
Vil-C1	Dordogne, France, F	~ 100-0 ka	401.4 \pm 9.9	0.840 \pm 0.090	- ^b
Fau-6	Dordogne, France, S	last 100 yrs	417.2 \pm 3.9	0.929 \pm 0.050	0.52
SC-99-1	Yorkshire, UK, S	10-0 ka	404.2 \pm 8.7	0.763 \pm 0.098	0.86
Ach-1	Ethiopian Central Highlands, S	6-0 ka	412.8 \pm 2.9	0.856 \pm 0.033	0.31
BFM-B	Wiltshire, UK, S	last 100 yrs	408.1 \pm 1.7	0.920 \pm 0.004	-0.21
SU-96-7	Sutherland, UK, S	1.1-0 ka	408.2 \pm 1.6	1.146 \pm 0.094	-0.10
SU-2	Sutherland, UK, S	2.5-0 ka	432.1 \pm 9.7	.930 \pm 0.053	0.70

^a S stalagmite; F flowstone;

^b Correlation is Spearman's Product coefficient between the mean wavelength of luminescence of the lowest wavelength sub-peak, and the luminescence ratio. The bimodal distribution of the lowest wavelength centre for Vil-C1 makes correlation an inappropriate statistic, and so no coefficient is reported for this sample.

DISCUSSION AND CONCLUSION

The luminescence intensity ratio of two sub-peaks typically observed in the organic acid luminescence centre appears to provide a more precise measure of luminescence variations. This is particularly true for speleothems that exhibit little variability in the wavelength of the peak luminescence. For stalagmite SU-96-7, the use of an independent proxy has permitted the interpretation of the luminescence ratio data as a palaeoenvironmental proxy. Further work is required to investigate the palaeoenvironmental information contained within the ratio data for other sites and different soil covers.

Stalagmite SU-96-7 is overlain by thin peat, and the luminescence of the stalagmite reflects a relatively simple record of water table depth in the peat. For other sites, ratio data may reflect more complex soil processes. In addition, as the time period of study increases, so the complexity of the luminescence may increase, reflecting changes in the peak luminescence wavelength due to, for example, vegetation changes. Results presented here also suggest that considerable within-site variability may occur. Duplicate samples were analysed from the Grotte de Villars (flowstone Vil-C1 and stalagmite Vil-stm4) and Uamh an Tartair (stalagmites SU-96-7 and SU-2). At Villars, the flowstone sample exhibits a switching in wavelength of the two luminescence centres, yet for each centre there is no relationship between wavelength and the ratio due to the invariance of the former. For stalagmite Vil-stm4, a good relationship exists between the wavelength of maximum luminescence and the ratio. Both samples are from the same cave system although c. 200m apart. Given the variability of the ratio data in Vil-C1, such differences between samples are unlikely to be due to hydrological effects (mixing of waters of different ages or sources) and suggest that local variations in soil type and/or vegetation cover are important.

A similar effect can be seen between SU-2 (with strong correlation between maximum luminescence and ratio) and SU-96-7 (with a weak correlation); both samples grew over the same time period and were located less than 10m apart. Again, local soil conditions can be the most likely explanation: Uamh an Tartair is overlain by karstified dolomite with numerous small (< 2m-diameter) dolines that may affect the soil drainage and localised emplacement of glacial till affects the soil type. Despite this variability, both stalagmites exhibit variability in luminescence that has been correlated to surface environmental change (Baker *et al.*, 1999; Proctor *et al.*, 2000).

Further research is needed into the nature and cause of luminescence wavelength variability. However, preliminary results suggest that the ratio of the two luminescence sub-peaks that are typically observed commonly provides a more precise measure of luminescence properties of a given stalagmite. Partly this is due to the increased analytical precision of measuring luminescence intensity (typically <0.2% at 100 intensity units) as opposed to wavelength (\pm 2 to 3nm). But it also appears to reflect changes in the composition of the organic acids trapped within the speleothems.

One implication of this research is the ability to obtain high precision and automated luminescence ratio data. Providing the wavelength of the two luminescence sub-centres does not change through time, then the relative luminescence intensity can be obtained through the continuous scanning of each sub-peak in turn, using a fixed excitation-emission wavelength pair and a moving stage. Using this technique as shown in Fig. 2, Proctor *et al.* (2000) presents a luminescence intensity ratio timeseries with a 1mm-wide luminescence spot and with the intensity recorded every 0.1s. This gives an effective sample resolution of 150 μ m (with 1mm spot size this is effectively 8 overlapping spots). With future developments in fibre-optic technology likely to reduce the fibre-optic bundle required to perform such automated analyses, this resolution can only improve and provide approximately annual to decadal scale luminescence data.

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Comparison of the luminescence intensity of speleothem feed waters from six cave systems

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Abstract: Feed waters that are associated with active stalagmite and flowstone deposition in six cave systems were sampled over individual hydrological years for their luminescence intensity. Luminescence intensity of cave waters has been demonstrated to derive from luminescent organic acids that are transported from the overlying soil. Sample sites include Sharkham Point Adit, Devon, a coastal site where luminescence may be quenched by marine derived salts; Lower Cave, Bristol; Brown's Folly Mine, Wiltshire; Grotte de Villars, Dordogne; Uamh an Tartair, Assynt and Stump Cross Caverns, Yorkshire. Comparison of the mean annual luminescence intensity within sites demonstrates that flowstone-depositing waters have higher luminescence intensity than stalagmite waters. Inter-site comparison demonstrates increasing luminescence intensity in the order Sharkham Point Adit < Lower Cave < Uamh an Tartair < Stump Cross Caverns < Brown's Folly Mine << Grotte de Villars. Villars has statistically higher luminescence intensity than all the other sites at a 95% confidence level. A higher flowstone water luminescence intensity than that of stalagmites agrees with results previously observed and may be explained by: (1) a greater transport capacity at higher mean discharge; (2) short groundwater residence time, which decreases the potential for absorption of organic acids within the karst aquifer; (3) possible wider fissures that optimise the transport of high molecular weight organic acids.

The significantly higher luminescence intensity observed at Grotte de Villars correlates with the high dissolved calcium concentration in the dripwaters at this site, and high stalagmite growth rate. It is suggested that further investigations from a range of sites with differing dripwater calcium and soil CO₂ productivity would discover if changes in luminescence intensity correlate with soil productivity, and hence can be used as a palaeoenvironmental proxy when preserved in speleothems.

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INTRODUCTION

Considerable research into the luminescence intensity of stalagmite dripwaters has taken place in recent years. Results have been published from Lower Cave, Bristol (Baker *et al.*, 1997; Baker and Barnes, 1998), Grotte de Villars, Dordogne; Uamh and Tartair, Assynt; Poole's Cavern, Derbyshire, and Brown's Folly Mine, Wiltshire (Baker *et al.*, 1999; Baker and Genty, 1999). Previous research has demonstrated significant differences in both inter-site mean annual luminescence intensity, and in intra-annual luminescence fluxes for individual drips or sites. Luminescence intensity of natural waters correlates with the total organic carbon of those waters (Senesi, 1993) and, hence, dripwater luminescence can be used as a proxy for this variable. Given the observation of variations in luminescence intensity, which is related to the drip water organic matter trapped within the speleothem sample calcite (Shopov *et al.*, 1994; Baker *et al.*, 1996), an understanding of dripwater luminescence is important in our understanding of the speleothem record.

METHODS

Dripwaters in six cave sites were sampled at regular intervals throughout the hydrological year during the period 1994 to 2000. Data and site descriptions for Brown's Folly Mine, Wiltshire, Grotte de Villars, Dordogne and Uamh an Tartair, Derbyshire, have been published in Baker and Genty (1999) and for Lower Cave, Bristol in Baker *et al.* (1997) and Baker and Barnes (1998). Here we add data from two additional sites, Stump Cross Caverns, Yorkshire and Sharkham Point Adit, Devon. Stump Cross Caverns is located on Greenhow Hill, North Yorkshire, at an elevation of 361m asl (grid reference: SE 089634). Four sites at a depth of c.12m, where speleothems is being deposited actively, were sampled between January 1999 and January 2000. Overlying vegetation is a mixture of upland grasses; heather and peat species. At Sharkham Point Adit, Devon, five drip sites (four feeding stalagmites and one feeding a

flowstone) were sampled over the period August 1994 to August 1996. This abandoned mine working, at an elevation of 4m asl (grid reference: SX 737546) contains actively forming speleothems. Due to its coastal location, its dripwaters have high concentrations of marine salts (sodium ranging from 6 to 12 mmol l⁻¹; unpublished data) that may quench the organic luminescence (Buhmann and Dreybrodt, 1987). Overlying vegetation is bracken-dominated grassland.

Data for Stump Cross Caverns were analysed using a Perkin-Elmer LS-50B luminescence spectrophotometer using standard techniques (Baker and Genty, 1999); those for Sharkham Point Adit were analysed using a UV (HeCd, 325nm) laser, as per Baker *et al.* (1997). In order to compare between data collected by laser (Sharkham Point and Lower Cave) and spectrophotometric techniques (Brown's Folly Mine, Stump Cross, Grotte de Villars, Uamh an Tartair), data were standardised to a Raman peak intensity at an excitation wavelength of 350nm of 16.9 intensity units. The latter figure was the mean laboratory blank intensity during the period 1997-1998.

RESULTS

Luminescence intensity results presented in Table 1 are for just the stalagmites sampled at the six sites. Flowstone dripwater luminescence intensity has previously been demonstrated to be significantly higher than that of stalagmites at the same site at Lower Cave (Baker and Barnes, 1998). Results from the one flowstone sampled at Sharkham Point Adit demonstrate a similar relationship, having a higher mean luminescence intensity than the four stalagmites (flowstone luminescence intensity = 5.6 times mean stalagmite luminescence intensity).

The data in Table 1 demonstrate that stalagmite dripwaters in Grotte de Villars have significantly higher luminescence intensity than those at all the other sites, at a 95% confidence level. All other sites have statistically similar luminescence intensity.

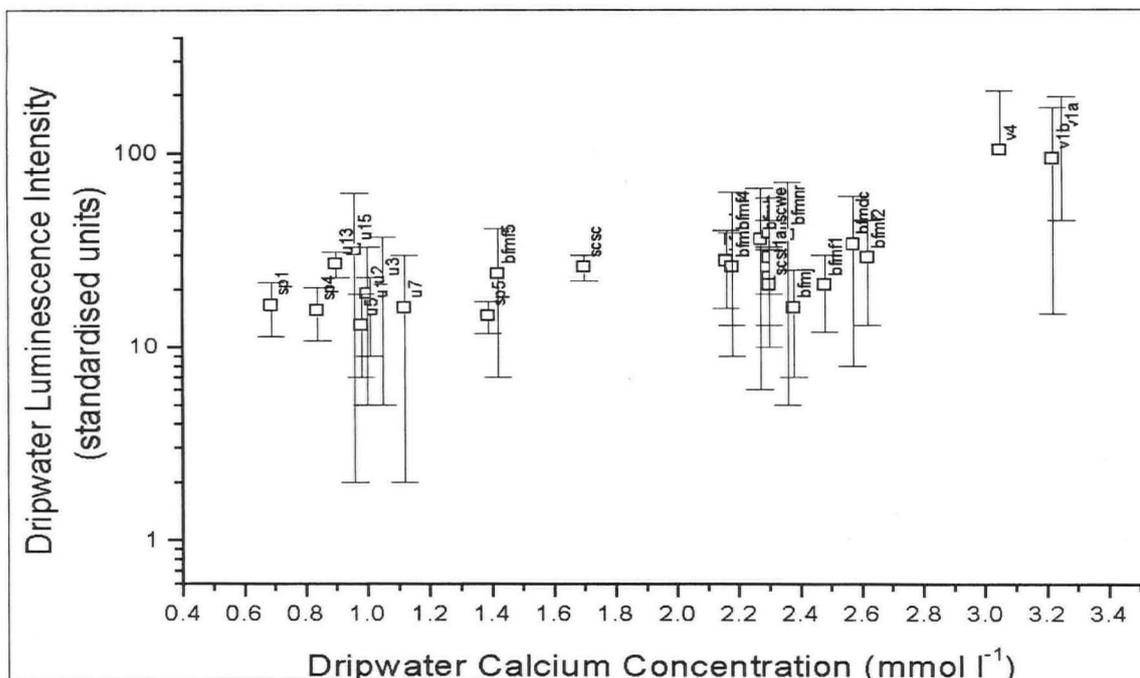


Figure 1. Mean annual calcium ion concentration vs. log mean annual luminescence intensity for dripwater sites where both parameters have been determined. Errors on the calcium concentrations are not shown for clarity, but range between 10-20% and reflect seasonal variations in this parameter.

INTERPRETATION AND CONCLUSIONS

The analysis of flowstone feed water at Sharkham Point Mine, together with the data from a flowstone at Lower Cave, Bristol (Baker and Barnes, 1998) suggest that, from this very limited dataset, flowstone waters are significantly more luminescent than stalagmite waters. This difference is as great as the inter-site variability in stalagmite luminescence intensity. It is suggested that flowstone feedwater is sourced through wider fissures, has a shorter residence time and has higher discharge than dripwaters feeding stalagmites. All three factors may affect the transport of luminescent organic carbon, given its high molecular weight and affinity to adsorb onto limestone surfaces. Stalagmite dripwater luminescence is similar between sites in the British Isles, but statistically higher at Grotte de Villars. Sharkham Point dripwaters were not significantly lower than other British Isles sites, suggesting that quenching effects of marine salts are not significant and that quenching cannot be used as a palaeoenvironmental proxy of sea-level rise in near-coast stalagmites.

A graph of mean dripwater calcium ion concentration against mean luminescence intensity is presented in Fig.1; a good correlation is observed ($r = 0.74$ against log intensity, significant at the 99.9% confidence level). Grotte de Villars, Dordogne, is noted for its high dripwater calcium ion concentrations and rapid growth rate (Baker *et al.*, 1998), both caused by elevated soil PCO_2 . The results presented in Fig.1 suggest that further research is required for a range of cave sites with differing soil productivity and climate. Luminescence intensity could be used as a palaeoenvironmental proxy within stalagmite samples, if it can be demonstrated that it increases with soil CO_2 production.

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Sample site	Number of dripwater sample sites	Luminescence Intensity	Calcium Ion Concentration			
			1σ	95% t-interval	mean	1σ
Lower Cave, Bristol	5	18.1	1.5	16.3-20.0	-	-
Sharkham Point Adit, Devon	5	15.2	1.5	13.3-17.0	0.97	0.37
Brown's Folly Mine, Wiltshire	11	28.8	6.9	24.2-33.4	2.27	0.32
Grotte de Villars, Dordogne	5	82.2	33.3	40.8-123.6	3.17	0.11
Uamh an Tartair, Sutherland	7	20.6	6.8	14.3-26.8	1.00	0.07
Stump Cross Caverns, Yorkshire	4	27.3	8.1	14.4-40.1	2.15	0.30

Table 1. Stalagmite luminescence intensity data.