LUMINESCENCE VARIATIONS IN FAST-GROWING STALAGMITES FROM UPPSALA, SWEDEN

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ABSTRACT: Two fast-growing stalagmites from a cellar vault in Uppsala, southeast Sweden, are analysed for their luminescent properties. The results indicate that variations in luminescence intensity in the stalagmites are annual. Due to problems in finding a suitable absolute dating method this assumption cannot yet be firmly tested; however, results from radiocarbon dating of one of the stalagmites do not contradict the proposal that the laminae are annual. If so, the speleothems have been growing for 10–15 years with a growth rate of 3–8 mm per year, which is a similar rate to other fast-growing speleothems in Great Britain that have formed from the reaction of lime mortar and carbon dioxide. It is likely that the assumed annual laminae of the luminescence record represent a flush of organic material.

Key words: stalagmites, luminescence, Sweden

Introduction

Many speleothems exhibit luminescence (light emission) when exposed to ultraviolet light sources. Speleothem luminescence is predominantly generated by organic acids which are formed in the overlying soil by the breakdown of plant material (Baker *et al*. 1993; Shopov *et al*. 1994). The organic acids can be divided chemically into two groups: fulvic and humic acids. Fulvic acids tend to be of lower molecular weight, are more readily soluble in water, and are expected to enter speleothem feed waters preferentially during the growing season compared to humic acids, which are often more hydrophobic and of higher molecular weight. Studies of soil extracts suggest that fulvic acids have a more intense luminescence and shorter wavelengths of excitation and emission than the humic acids (Senesi *et al*. 1991). Together, these two groups can be taken as indices of organic productivity in the overlying soil and plant cover, and therefore as a proxy measure of palaeoclimate (Shopov *et al*. 1994; McGarry and Baker 2000).

Research in speleothem luminescence has focused on two properties. The first property is the intensity of luminescence, which for samples with constant crystallographic fabric and texture can provide a proxy of the concentration of luminescent organic material (Baker *et al*. 1993, 1996; Shopov *et al*. 1994). The second property is, luminescence wavelength variations, which can provide a measure of organic acid molecular weight and structure, and thus distinguish between humic and fulvic acid luminescence (Baker *et al*. 1998, 1999b; Baker and Genty 1999; McGarry and Baker 2000; Perette *et al*. 2005).

In caves in Great Britain, luminescence intensity varies seasonally, with a late autumn/winter peak caused by a flushing of dissolved organic matter from the soil zone by high winter rainfall (Baker *et al*. 1993, 1997; Genty *et al*. 1997). This has led to the deposition of yearly luminescent lamina. The distance between laminae represents the yearly growth rate. In northern Norway, however, the main luminescence lamina is inferred to be deposited in the spring when the snow melts (Linge *et al*. 2001).

Most methodological studies of luminescence wavelength variations have focused on changes in the excitation and emission wavelength of the luminescence intensity maximum (Baker *et al*. 1998, 1999b). For many speleothems the dominant luminescence maxima (excitation wavelength 330 to 390 nm; emission wavelength 390 to 460 nm) can be resolved into two luminescence maxima (Baker and Bolton 2000; Proctor *et al*. 2000; van Beynen *et al*. 2001). Baker and Bolton (2000) claim that for samples with small varia-

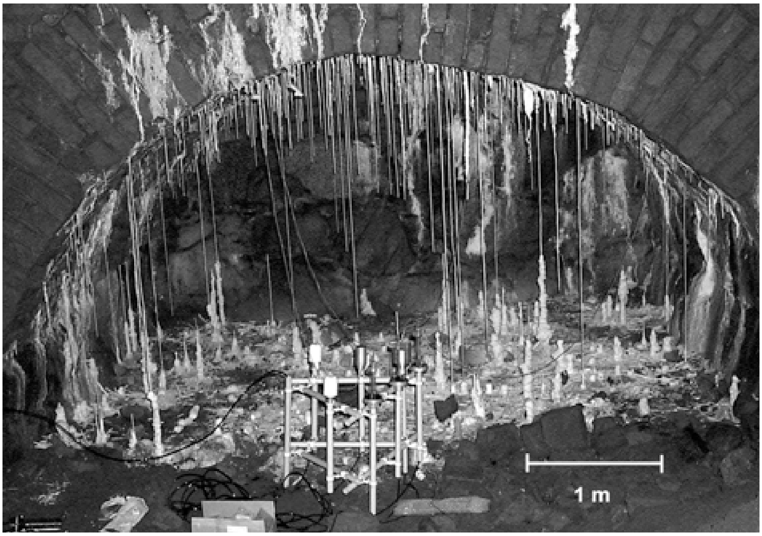

Fig. 1. Stalagmites and stalactites growing inside the cellar vaults in Uppsala

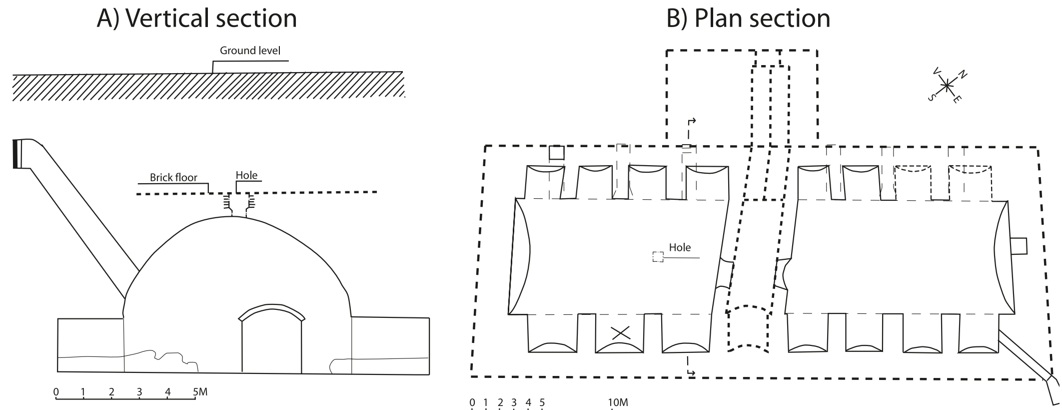

Fig. 2. Sketch of the cellar vaults next to Uppsala castle. The niche from where the stalagmites were collected is marked with a cross

tions in luminescence wavelength maximum it appears that the use of a luminescence ratio might provide a more precise measure of variations in luminescent matter.

In this study, two fast-growing stalagmites from a cellar vault in Uppsala, southeast Sweden, are analysed for their luminescence properties. Variations in luminescence lamination structure are independent of the deposition mechanism and can therefore be investigated as for 'normal speleothems' formed in limestone caves (Baker *et al*. 1999a). The objective is to test if variations in luminescence intensity and wavelength can be used to identify and measure annual laminae and if variations in luminescence and growth rate can be calibrated against the detailed meteorological record available from Uppsala (Bergström 1990). The hypothesis was that the stalagmites have been growing continuously for the past 300 years since the house above the cellars was burned down and the roof above them was covered with soil. The results indicate that the variations in luminescence intensity are annual and that the stalagmites have been growing for 10–15 years sometime during the last 300 years. The luminescent laminae are believed to have been deposited in late autumn when luminescent material could have been washed out from the soil above the cellar by high rainfall.

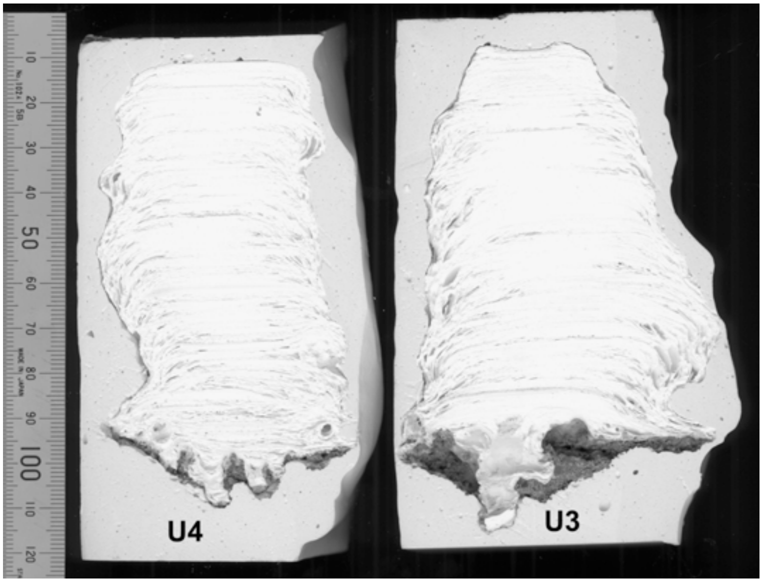

Fig. 3. Stalagmites U3 and U4

Site and sample description

The two stalagmites studied come from one of two cellar vaults situated below a grass field, next to the southern tower of Uppsala castle. The cellars used to be connected to a house that, together with parts of the castle, was destroyed in a fire in 1702. The cellars were thought to have been completely demolished until, in 1976, a motorised roller preparing the ground almost fell through the roof of the western cellar vault (Figs 1 and 2). The cellar vaults together with the house were probably erected in the 1560s.

Above the cellar vaults there is a layer of soil 4–9 m thick, which contains construction materials from the rebuilding of the castle after the fire, and the surrounding vegetation consists of cultivated grass. A number of oaks in the vicinity might have root systems reaching the area above the cellar. Inside the cellars, both stalagmites and stalactites of considerable size (5–50 cm) are found. These speleothems probably formed after the fire when the house above was gone and ground water could penetrate through the roof. But it could be that lateral flow allowed the movement of water into the cellars before then. The cellars are closed to the public and are only opened every five years for inspection of ground subsidence. This has ensured a constant climate and environment (8°C and 100% relative humidity).

Uppsala has an average annual precipitation of 545 mm and an annual average temperature of 5.7°C (1961–1990; unpublished data, Swedish Meteorological and Hydrological Institute). The highest precipitation amounts occur from July to September, but there is also a small peak in November. The mean monthly temperature is below zero from mid-November to mid-March. The castle and the cellar vaults are situated on top of an esker. Water reaching the cellars originates from meteoric water directly above them.

The speleothems are deposited from hyperalkaline waters (pH>10) by the reaction

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1)$$

which is generally termed ‘concrete carbonation’ (Pinsent *et al*. 1956; Barnes *et al*. 1982; Liu and He 1998). The speleothems are most likely a result of the dissolution of the calcareous mortar, slaked lime ($Ca(OH)_2$), between the bricks in the roof. Slaked lime is prepared by reacting calcium oxide and quicklime with water. Quicklime is prepared by combustion of calcium carbonate (e.g. limestone). Under natural conditions in limestone caves CO_2 escapes from water and $CaCO_3$ precipitates by the reaction

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \text{ r.r.} \qquad (2)$$

Speleothems deposited by concrete carbonation have accelerated growth rates, of 1–20 mm yr^{-1} (Liu and He 1998; Baker *et al.* 1999a). The fast growth rate of this type of speleothem is determined by the kinetics of hydroxylation of aqueous CO_2 ($CO_{2(aq)}$ + OH^- reaction), which is also accompanied by a depletion of ^{13}C (Clark *et al.* 1992; Liu and He 1998). Variations in luminescence are independent of the deposition mechanism (Baker *et al.* 1999a) and can, therefore, be investigated as for normal speleothems formed inside limestone caves.

In this study, two stalagmites, referred to as U3 and U4 (Fig. 3), are examined for their luminescence properties. The stalagmites were collected in September 2000 from a niche in the western cellar (Fig. 2). Above this niche the soil cover is about 9 m thick. U3 is 80 mm long and was probably actively growing (drips were falling down on it) when collected. U4 is 83 mm long and was not actively growing; it was found overturned on the floor. Both stalagmites exhibit some visible laminar structure. Two types of visible laminar exist: 'master' laminae with large-scale (*c.* 0.5–1 cm) alternations from porous to compact calcite, within which are thinner (*c.* 1 mm) laminae composed of compact calcite.

Methods

The stalagmites were cut in half along the central axis of growth and polished. Complete representations of the luminescence properties (an excitation–emission matrix, or EEM) along the central axis were collected every 3 mm, using a Perkin-Elmer LS-50B luminescence spectrophotometer with a Perkin-Elmer fibre-optic extension and moving stage. The excitation luminescence wavelength was varied from 315 to 411 nm at 3 nm steps, and the emission wavelength was recorded from 340 to 500 nm at 0.5 nm steps, in order to construct EEMs (Figs 4 and 5). In an EEM, luminescence intensity is presented as a function of excitation wavelength on one axis and emission wavelength on the other. For each EEM, the wavelength maximum was reported (as in Baker *et al.* 1998, 1999b), and the ratio of the two intensity peaks (longer wavelength peak, as in Proctor *et al.* 2000), if they were present.

Continuous luminescence intensity records were obtained by scanning the stalagmites at fixed excitation (339 nm) and emission (420 nm) wavelengths. To avoid problems with laser light scattering, which can cause the emitted signal to reflect calcite porosity, at least three scans were performed along and parallel to the central axis of the sample. The final record is an average of all scans.

Dating

Two 1-mg samples were extracted from the top and the bottom of stalagmite U3 for AMS radiocarbon dating. The samples were dated at the Ångström Laboratory of Uppsala University and calibrated with INTCAL98 (Stuiver *et al.* 1998).

Results and discussion

Luminescence wavelength variations

The luminescence maximum is observed as a double peak throughout U4 and in most of U3 (Fig. 4) except for in the top 17 mm that only exhibits the shorter wavelength intensity peak (Fig. 5). The longer wavelength peak is most likely the humic component of the organic acids and the lower the fulvic component. The humic component could be a result of the breakdown of wooden construction materials in the soil and the reason for its absence in the upper part of U3 could be that the construction material had been broken down completely at the time of deposition, or that this part represents a colder, wetter period.

No similarities in the wavelength ratio pattern between the two stalagmites can be seen, but the common variations are of the same magnitude: U3, ±0.16; U4, ±0.17. Variations in the intensity ratio of the same magnitude are found in a 1000 year-old Scottish speleothem (Proctor *et al.* 2000). The ratios of the higher emission wavelength peak to the lower wavelength peak are shown in Fig. 6. The intensity of the higher wavelength sub-peak is extremely high, between 8 and 18 mm, in U4. It is so high that the ratio becomes close to zero and the intensity value of the fulvic peak is impossible to measure. The reason for these high intensity values in the humic peak is unknown.

The luminescence lower wavelength intensity maximum (fulvic peak) variations of U3 and U4 can be seen in Fig. 7. As for the wavelength ratio pattern, no similarities between the two records can be observed, indicating that they probably do not cover the same period of time. The fulvic peaks of the stalagmites have a variability of ±6.25 and ±5.75 nm.

Luminescence intensity variations

The variations of luminescence intensity from the continuous scan, are shown in Fig. 8. While it is

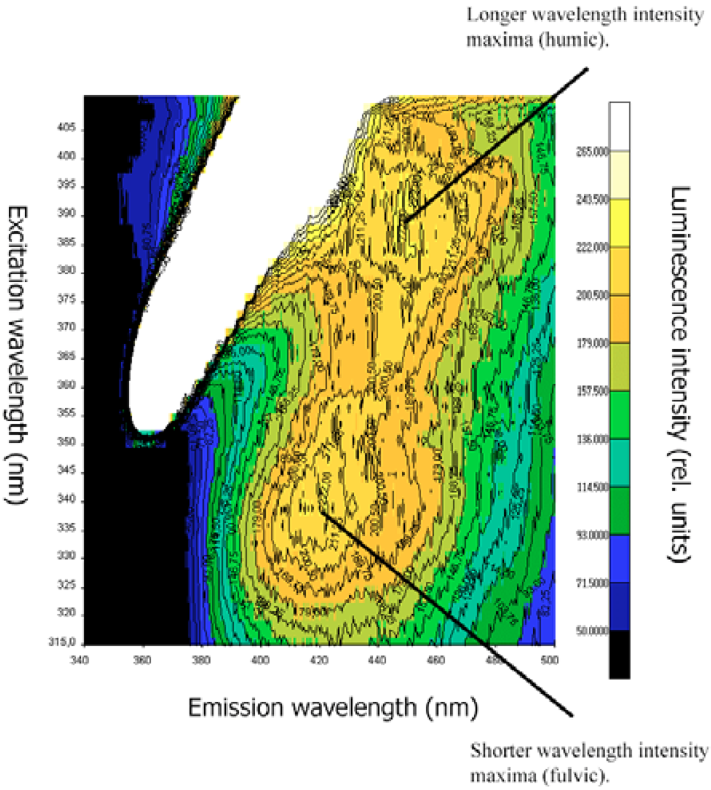

Fig. 4. Luminescence excitation–emission matrix (EEM) from the older (80 mm from the top) part of U3 demonstrating the two (humic and fulvic) luminescence maxima. The white diagonal area is caused by Rayleigh–Tyndall scattering

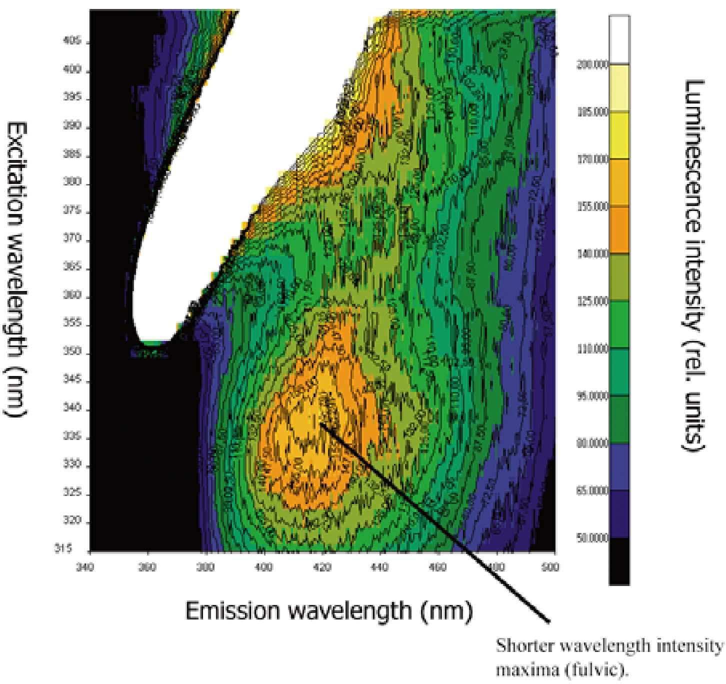

Fig. 5. Luminescence excitation–emission matrix (EEM) from the younger (6 mm from the top) part of U3 with the lower (fulvic) luminescence maxima

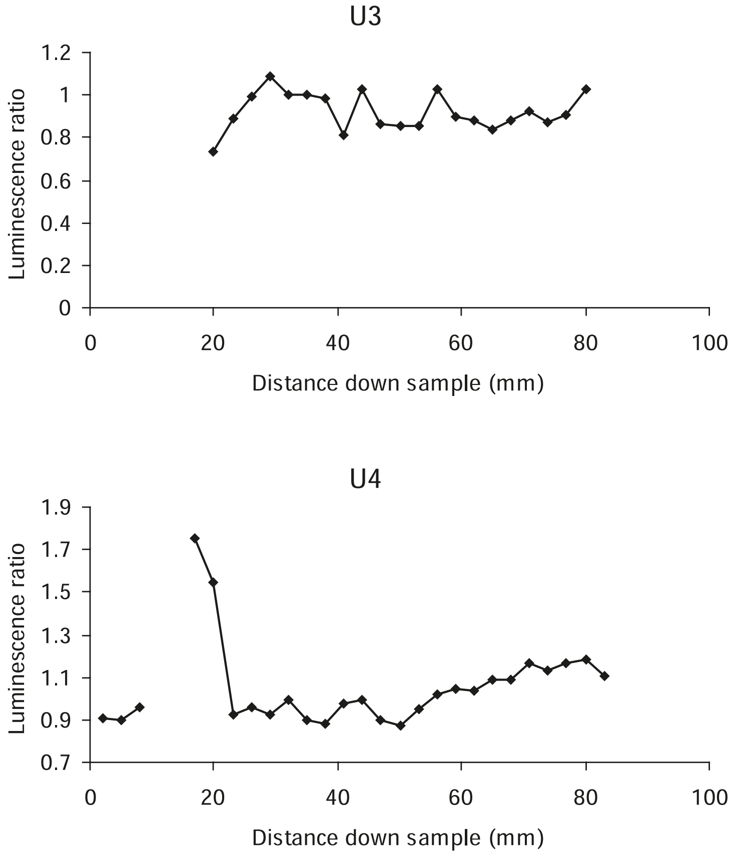

Fig. 6. Humic to fulvic (higher wavelength peak to lower wavelength peak) luminescence intensity ratio variations of U3 and U4

easy to identify the luminescence intensity peaks for U3, it is more difficult to do so for U4. The numbers of peaks are around 10–15 for each sample which is about the same as for the visible laminae (Fig. 3). The hypothesis of continuous deposition with annual lamina peaks since 1702 must therefore be rejected. Rather, it seems that the two stalagmites have been deposited under short time periods at different time intervals somewhere between 1702 and 2000. Perhaps a 'flush' of lime (from corroding mortar?) allows a stalagmite to grow for 10–20 years and then the mortar is used up and growth stops.

Since Uppsala experiences its highest amounts of precipitation during summer and autumn, it is likely that this is the time of year when the luminescent lamina is deposited, as was the case in stalagmites studied in Great Britain (Baker and Genty 1999). The distance between the peaks should therefore represent one year. This assumption of annual deposition is supported by the fact that the luminescence intensity maxima are evenly distributed. If this is the case, U3 would have been growing for about 14 years with a growth rate of 3.5 to 8 mm yr^{-1}, agreeing with growth rates expected for lime-based stalagmite growth (Baker *et al*. 1999a). U4 has four distinct peaks and up to six less distinct peaks, so there is less certainty in the growth rate but it is of a similar magnitude to U3.

Three of the luminescence intensity maxima of stalagmite U3 exhibit a double peak structure (numbers 6, 14 and 15 from the top). In a stalagmite from England, double laminae were found to occur in years with high monthly or daily precipitation totals (Baker *et al*. 1999a). In a stalagmite from northern Scotland double laminae are believed to represent both an autumn signal and a second spring meltwater-generated influx of organic matter after extremely cold winters (Baker *et al*. 2002). In northern Norway the occurrence of an extra lamina

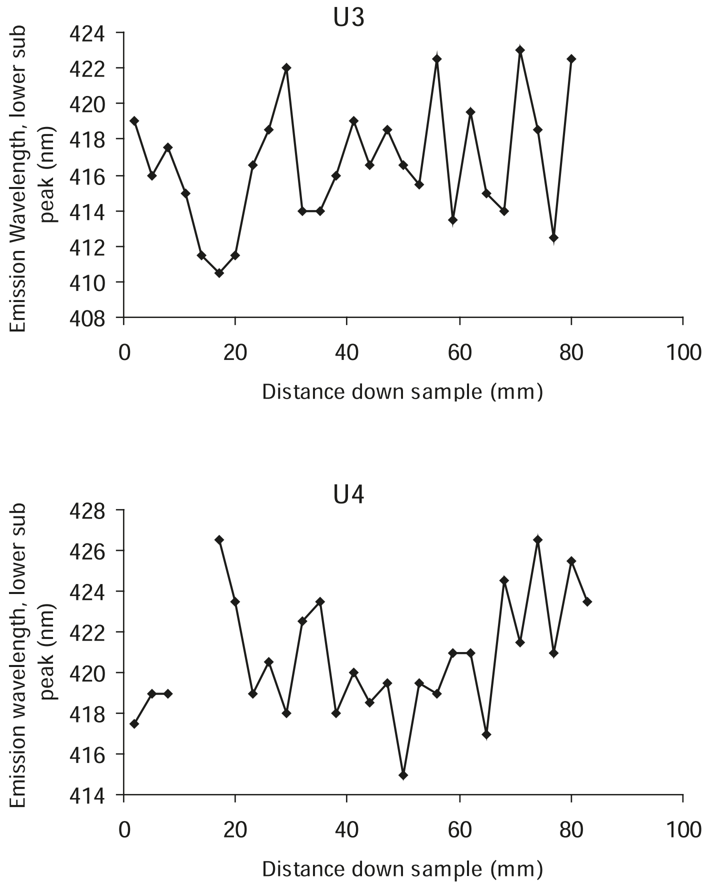

Fig. 7. Luminescence emission wavelength data, lower wavelength intensity maxima of U3 and U4

is proposed to be caused by heavy autumn rainstorms (Linge *et al*. 2001). Whether the double laminae in U3 are due to high monthly or daily precipitation totals or extremely cold winters is difficult to say.

The luminescence intensity records for both stalagmites show an increasing trend from bottom to top. This could indicate increasing organic activity in the soil during the time period of their growth.

Dating

The results of the ^{14}C dating reveal 'ages' within the time span of about AD 1300–1400 (Table 1). Since the ages of U3 are older than AD 1702, when the house above the cellar disappeared, and even predate the construction of the cellars themselves, they are not realistic ages of the speleothem.

According to the chemical equation (1) the stalagmites will receive all the carbon from the carbon dioxide in the cellar atmosphere, and should therefore be accompanied by an anomalously negative δ^{13}C. Should deposition occur by equation (2), carbon will include a contribution from both soil and bedrock, as is the 'normal' case: in this case a 15% 'dead carbon' proportion would be expected (Genty and Massault 1999), the ^{14}C ages will be too old and δ^{13}C would be typical of that for cool climate speleothems (–14 to –6‰; Baker *et al*. 1997). This suggests that the calcite deposition is not the result of concrete carbonation only, but that carbon must also have been brought to the stalagmite from another (older) source than the cellar atmosphere. Some old carbon could have come from calcitic sand used as aggregate in the mortar and/or remains from incomplete conversion of calcium carbonate to calcium oxide. Also parts of the mortar that were in contact with air during the hardening process would have been retransformed into calcium carbonate (Heinemeier *et al*. 1997).

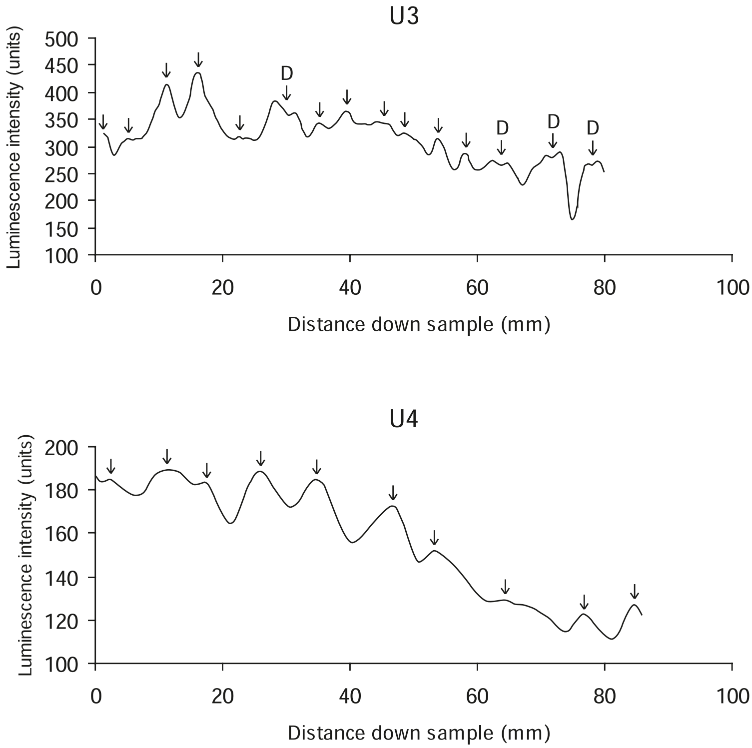

Fig. 8. Luminescence intensity variations of U3 and U4, continuous scanning (mean of three scans; 339 Ex, 420 Em). Arrows indicate intensity peaks, possible late autumn flush; 'D' indicates double laminae

However, the high pH (>10) of the drip water, the abnormally negative $\delta^{13}C$ (Table 1) and the fast growth rate indicate that the stalagmites have been mainly deposited from dissolved $Ca(OH)_2$ by the uptake of atmospheric CO_2. Even though absolute determination of the age period of stalagmite growth has not been possible, the absolute age difference between the dated bottom and top of the stalagmite does not exclude the possibility that the peaks are annual. Experiments in progress will soon confirm this hypothesis.

Conclusions

The patterns of variation in luminescence intensity ratios of the stalagmites indicate that these variations are annual and sometimes even sub-annual (double laminae). If the laminae are annual, the stalagmites would have been growing for 10–15 years with growth rates of 3–8 mm yr^{-1}, which is similar to other fast-growing speleothems. It is suggested that the peaks of the record represent a flush of organic material in the late autumn reflecting the yearly peak in precipitation.

Since neither the wavelength nor intensity records show any obvious similarities, it is most likely that the stalagmites have been growing during different time periods sometime between 1702 and 2000. The carbon dioxide consumption and deposition process dominates stalagmite formation resulting in fast growth rate, high pH of the drip water and low $\delta^{13}C$ values. Due to the difficulties of dating these stalag-

Table 1. AMS ^{14}C-dates of stalagmite U3, Uppsala cellar vault, Sweden. Calendar years (and ranges) listed are the intercepts (INTCAL 98, Stuiver *et al*. 1998) of the ^{14}C dates

Sample	Length (mm from base)	$\delta^{13}C$	(years BP) ^{14}C age,	AD (1σ) Calendar year
U3–1	79–80	–39.0	555 ± 40	1328 (1404) 1420
U3–2	0–1	–39.8	655 ± 40	1291 (1300, 1373, 1377) 1389

mites it was not possible to compare the luminescence data with available meteorological data.

Fast-growing speleothems have been found at many historical sites, including an old train tunnel in Belgium, a lime-affected cave in Great Britain, a coal mine adit in Wales. When available they can provide an opportunity for studying luminescence properties in speleothems in greater detail than otherwise possible. Some of the sites might have high resolution records for the last 100–200 years which could yield important information about history and variation in climate.

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