High-resolution records of soil humification and paleoclimate change from variations in speleothem luminescence excitation and emission wavelengths

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ABSTRACT

Recent advances in the precision and accuracy of the optical techniques required to measure luminescence permit the nondestructive analysis of solid geologic samples such as speleothems (secondary carbonate deposits in caves). In this paper we show that measurement of speleothem luminescence demonstrates a strong relationship between the excitation and emission wavelengths and both the extent of soil humification and mean annual rainfall. Raw peat with blanket bog vegetation has the highest humification and highest luminescence excitation and emission matrix wavelengths, because of the higher proportion of high-molecular-weight organic acids in these soils. Brown ranker and rendzina soils with dry grassland and woodland cover have the lowest wavelengths. Detailed analysis of one site where an annually laminated stalagmite has been deposited over the past 70 yr during a period with instrumental climate records and no vegetation change suggests that more subtle variations in luminescence emission wavelength correlate best with mean annual rainfall, although there is a lag of ~10 yr. These results are used to interpret soil humification and climate change from a 130 ka speleothem at an upland site in Yorkshire, England. These data provide a new continuous terrestrial record of climate and environmental change for northwestern Europe and suggest the presence of significant variations in wetness and vegetation within interglacial and interstadial periods.

INTRODUCTION

Speleothem luminescence intensity variations have been recently developed as both a chronological tool and as a paleoclimate indicator. The luminescence predominantly derives from high-molecular-weight soil-derived organic matter (Shopov et al., 1994; Ramseyer et al., 1997) that is transported onto the speleothems; in northwest Europe this has been demonstrated to occur each winter at times of high discharge (Baker et al., 1993, 1997). As a paleoclimate indicator, the width and structure of the luminescent bands often correlate with proxies of paleoprecipitation (Genty and Quinif, 1996; Ming et al., 1997), and the long-term variations in luminescence intensity often correlate with long-term (10^3 to 10^6 yr) climate oscillations (Shopov et al., 1994). Techniques to stimulate luminescence have, until now, utilized a fixed excitation wavelength within the ultraviolet spectrum. However, recent developments in luminescence spectrophotometry permit the determination of both the excitation and emission wavelengths that generate the maximum luminescence, which may vary with changes in soil and vegetation type through time.

The luminescence properties of soil humic substances extracted from a wide range of soil types (from peat through to brown earth soils) and reference samples suggest that humic acids have a higher excitation and emission wavelength of luminescence than fulvic acids (Senesi et al., 1991), because of an increase in both the degree of aromacity, and the content of carboxylic groups and polycondensed aromatic and conjugated structures within the humic acid. Thus it might be expected that soils with a higher proportion of humic acid to fulvic acid would have a higher wavelength of luminescence excitation and emission that those with a low humic/fulvic acid ratio. It has also been long recognized that climate is one of the factors affecting soil humification; the rate of organic-matter breakdown increases with increasing temperature and soil moisture for many soil types (Heal and French, 1974; Meentmeyer, 1978). For example, temperate forests showed a linear relationship between actual evapotranspiration and humification rate (Meentmeyer, 1978). If climatically induced variations in the rate of organic-matter breakdown are reflected in changes in the composition (molecular weight or degree of aromaticity) of the organic acids (Zech et al., 1992, 1997), and thus their luminescence properties, then a climate signature may be preserved in this dissolved fraction after ground-water transport and entrapment within speleothem calcite.

Although climatic variations influence humification rate, this effect is moderated by the length of time that organic materials are held within the soil organic matter and ground-water reservoir. For example, Sanger et al. (1997) demonstrated that the soil organic matter decomposition rate increases from spruce woodland to ash woodland to grassland. By measuring changes in bomb-produced ^{14}C within soil profiles, Tegen and Dorr (1996) demonstrated that the soil-borne carbon reservoir can be modeled as a mixture of fast-decaying (lifetime of ~1 yr) and slow-decaying (lifetime of ~100 yr) components, and that the proportion of the fast-decaying component varies between vegetation types (e.g., it forms 60% of soil organic matter in deciduous forests and 40% of soil organic matter in coniferous forests. Genty et al. (1998) have observed similar vegetation-based differences in the bomb-produced ^{14}C contained within recently deposited stalagmites. These data show a lag between increased atmospheric ^{14}C and stalagmite ^{14}C of 4–10 yr, suggesting that any changes in soil organic matter humification in soils overlying limestone caves may take several years to be transported to and recorded in the underlying stalagmites.

In the study area in northwestern Europe (which has maritime continental climates), poorly humified soils such as histosols and peats, which are likely to have high wavelengths of luminescence excitation and emission, are typically found in limestone regions of high annual rainfall (>1500 mm) or where thin, impermeable strata overlie limestone. Well-humified soils such as dry grasslands and woodlands, which should have lower wavelengths of luminescence excitation and emission, are often found in regions of low (typically <1000 mm) annual rainfall. It should be possible to distinguish these two soil groupings for contemporary samples, as well as for Quaternary and older samples, through variations in dissolved organic matter washed from the overlying soil into cave speleothems. In addition, superimposed upon this signature may be more subtle variations in luminescence resulting from climatic influences on the rate of humification. Therefore lags may exist between changes in climate and the humification of the soil-derived organic fraction trapped within the speleothem calcite because (1) soil organic matter comprises different fractions with lifetimes of 1–100 yr and (2) there may be mixing of soil organic matter of different ages in both the soil water and ground water. With these complications in mind, careful contemporary calibration is required in order to determine (1) whether there is a relationship between wavelength of luminescence excitation and emission in stalagmites and the overlying soil type and climate and (2) the relative sensitivity of changes in this luminescence record to variations in vegetation and climate for recently deposited samples that have formed over a period of known vegetation and climate change.

METHODS

We collected 24 actively forming speleothem samples from sites within northwestern Europe for which the surface soil and vegetation have been relatively undisturbed by human influence over the past 150 yr. Samples were either from mine sites or from caves that have been disturbed by cavers or archaeologists, to ensure that the speleothems sampled were <150 yr old. Samples were analyzed with a Perkin-Elmer LS-50B luminescence spectrophotometer with a fiber-optic extension to permit the nondestructive analysis of solid samples. Fiber-optic width was 1.5 mm, limiting the spot size, and thus temporal resolution, available using this technique. Excitation wavelengths were increased from 320 to 400 nm in 2 nm steps; for each excitation wavelength, the emitted luminescence was detected at 0.5 nm steps from 390 to 500 nm. Slit width was set at 5 nm, which enabled the best compromise between signal intensity and background noise.

In addition to the contemporary calibration samples, one other site (Grotte de Villars, Dordogne, France; lat 45°30′N, long 0°50′E; elevation: 175 m) was analyzed; it contained a continuously annually laminated stalagmite that has been deposited over the past 70 yr. This analysis allowed a luminescence time series to be constructed for periods of instrumented climate records and known vegetation changes. This cave was chosen because it is below undisturbed vegetation (grassland) and because its stalagmites have a high growth rate (0.55 ± 0.35 mm · yr^{-1}; Baker et al., 1998). The area has a mean annual precipitation of 956 mm and a mean surface temperature of 11.7 °C. The stalagmite, Vil-stm1, was analyzed over the top 50 mm of a polished thick section of the sample, which on the basis of annual-laminae counting represents deposition from A.D. 1920 to 1993 (the time of sampling). Luminescence analyses were undertaken at 1.5 mm intervals as described herein; the fast growth rate of this sample gives a temporal resolution of 2.9 yr per sample.

CALIBRATION RESULTS

The contemporary calibration samples (Table 1) demonstrate a correlation between the luminescence properties, particularly in the form of the wavelength of the emitted luminescence, and the degree of humification of the overlying soil; samples overlain by poorly humified peat soils have a higher wavelength of excitation and emission than samples from more humified mineral soils. These results also partially reflect the different vegetation covers and the amount of rainfall at the sites. Sites that are overlain by blanket bog and that have the highest mean annual rainfall (>1900 mm if one excludes Faunarooska, Eire, which maintains an overlying

TABLE 1. SPELEOTHEM EXCITATION AND EMISSION WAVELENGTH OF MAXIMUM LUMINESCENCE, WITH SITE SOIL, VEGETATION, AND CLIMATE DATA

Site	Vegetation cover	Soil type†	Mean annual rainfall (mm)*	Excitation wavelength (nm)	Emission wavelength (nm)
Uamh an Tartair Tartair, Sutherland Scotland	Blanket bog	Raw peat	1900	370	444.0
				368	457.0
Faunarooska, Co. Clare, Eire	Blanket bog	Raw peat	1200	346	432.5
				352	444.5
Poole's Cavern, Derbyshire, England	Deciduous woodland	Brown ranker	1300	350	423.3
				336	408.5
				340	411.7
Stump Cross, Yorkshire, England	Moorland	Cambic stagnohumic gley soil	1200	350	422.0
				338	423.0
				348	423.0
				334	421.0
Sandford Levy, Mendip, Somerset England	Deciduous woodland	Brown ranker	950	350	418.5
Dolebury Levy, Mendip, Somerset England	Dry grassland	Brown ranker	950	348	415.5
				338	404.5
Grotte de Villars, Dordogne, France	Dry grassland^{+} and woodland$^{\#}$	Brown rendzina	870	328$^{\#}$	395.5$^{\#}$
				342^{+}	409.0^{+}
				318$^{\#}$	383.0$^{\#}$
La Faurie, Dordogne, France	Grassland with occasional deciduous wood	Brown rendzina	870	350	421.5
				352	424
				338	405
Brown's Folly Mine, Wiltshire, England	Deciduous woodland	Brown rendzina	800	346	415.0
				336	405.0
				344	413
				350	419.5

*Data rounded to nearest 10 mm when meteorological station is within 30 km; otherwise data are interpolated from nearby stations and quoted to nearest 50 mm.

†Data from United Kingdom Soil Survey and French soil survey 1:50 000 maps.

peat vegetation because a thin shale layer overlies the limestone rather than for climatic reasons) exhibit a higher wavelength of excitation and emission than those sites overlain by moorland, which have a higher peak-luminescence wavelength than dry woodland and grassland (mean annual rainfall <1000 mm). This result is in agreement with the published luminescence properties of organic acids extracted from various soil types (Senesi et al., 1991) and with existing data for stalagmite luminescence (Baker et al., 1996; Ramseyer et al., 1997).

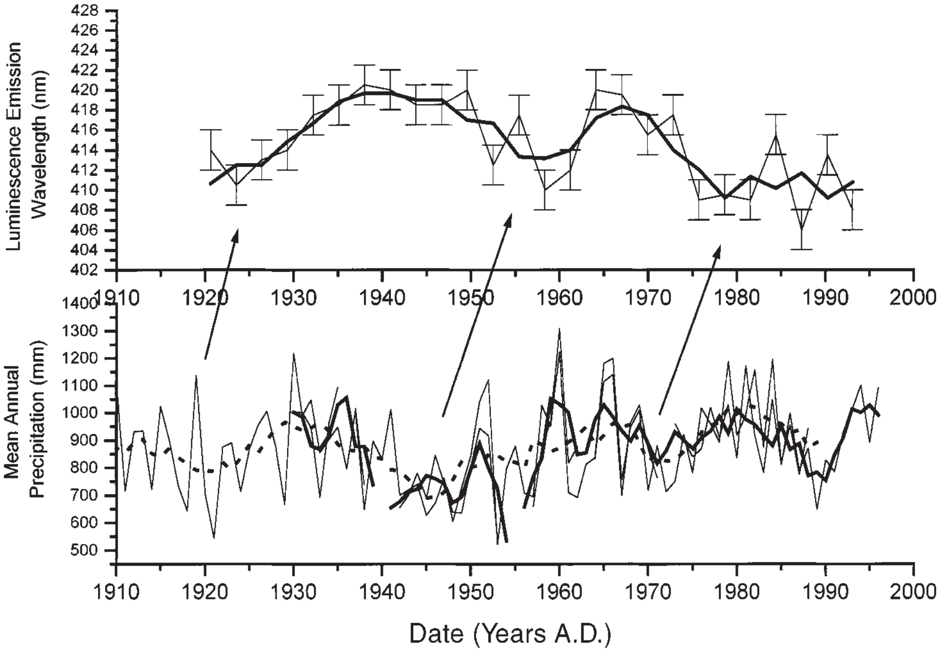

Figure 1. Luminescence of stalagmite Vil-stm1, Grotte de Villars, Dordogne, together with mean annual rainfall data from Bordeaux and Granges D'Ans, for period A.D. 1920–1995. Three-point smoothed data for all records are presented; duplicate luminescence analyses are not presented, but replicate within ±2 nm. Arrows indicate lag of luminescence behind rainfall.

Data for Vil-stm1 stalagmite deposition, and mean annual rainfall for the meteorological station at Bordeaux, Gironde (140 km distant, complete record), and Granges D'Ans, Dordogne (35 km distant, incomplete record) are presented in Figure 1. Mean annual temperature has not varied significantly over the past 70 yr from its mean of 11.7 °C; mean annual precipitation is 864 mm for Grange D'Ans and 865 mm for Bordeaux, and over the period of stalagmite deposition, the 3-yr-running-average mean annual rainfall has varied by 300 mm with a period of 20–40 yr. The mean stalagmite luminescence emission wavelength for the past 70 yr is 414.6 ± 4.5 nm, agreeing with that expected for grassland vegetation cover (Table 1). Over the 70 yr of deposition, the stalagmite luminescence exhibits 10 nm oscillations in emission wavelength that have a similar period but lag behind rainfall changes by 5–20 yr (indicated by arrows), agreeing with previous research suggesting a lag between soil organic matter production and transport onto speleothems (Genty et al., 1998). Hence this sample, overlain by grassland, seems to exhibit a luminescence response to relatively small climate variations over the past 70 yr, a period of comparative climate stability. Successful calibration of variations in luminescence excitation and emission wavelengths to speleothems from northwestern Europe deposited during the past 70 yr enables the application of luminescence-based paleoclimate technique over the late Quaternary time scale.

RECORD OF 130 ka SPELEOTHEM LUMINESCENCE WAVELENGTH VARIATIONS

A flowstone deposit from Lancaster Hole, Yorkshire, north England (lat 54°20′N, long 2°20′ W), an upland site at an altitude of 294 m above sea level and covered today by blanket bog, was chosen because it has been dated by thermal ionization mass spectrometry (TIMS) U-Th to have been deposited over short (<5 k.y.) intervals during the period 130–30 ka (Baker et al., 1995). This flowstone appears to have been highly sensitive to surface-moisture variations (although it is not possible to quantify this inference in terms of specific rainfall totals or extent of soil-moisture excess) because its water supply was through karst fissures that receive water only in periods of high rainfall intensity or duration (Smart and Friedrich, 1987). The 330-mm-long flowstone sequence was analyzed at a 3 mm sampling interval. The absolute growth rate of the flowstone is not determinable because it was faster than that resolvable by TIMS U-Th dating, but was always greater than 0.003 mm · yr^{-1}, giving a lowest sampling resolution of 1000 yr. Luminescence wavelength data (Fig. 2) suggest significant variations in the overlying soil and vegetation conditions over the past 130 ka.

During oxygen isotope stage 5e, flowstone was deposited (1) within the interval 128.8 ± 2.7 ka, suggesting that the period of maximum

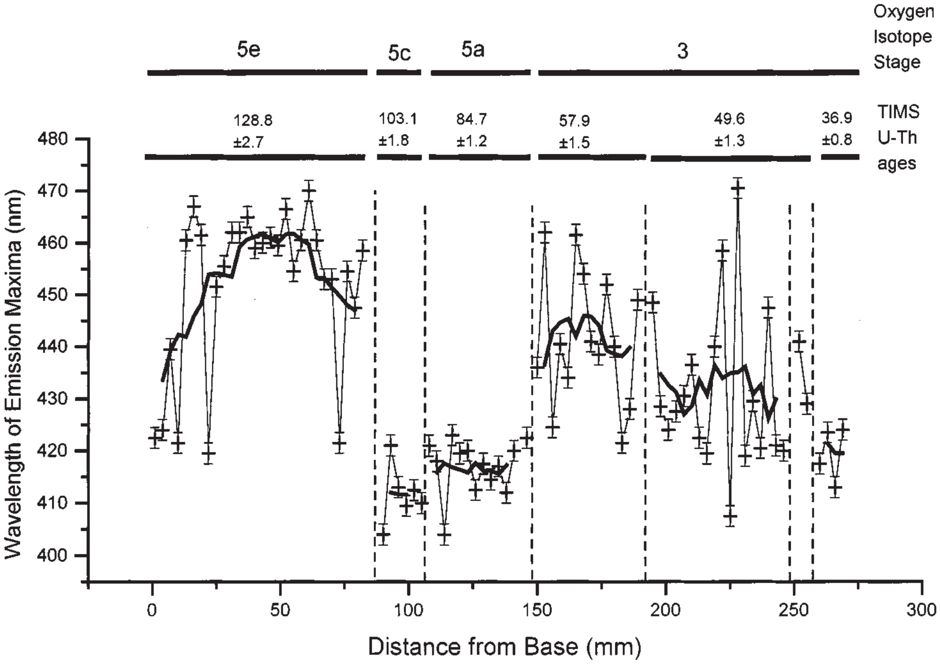

Figure 2. Wavelength variations of luminescence emission from Lancaster Hole flowstone, north England. Duplicate analyses are not shown but replicate within ±2 nm. Temporal constraint is provided by multiple thermal ionization mass spectrometry U-Th analyses (Baker et al., 1995; errors given are 2σ) generated by using standard techniques (Edwards et al., 1986); vertical dashed lines represent growth hiatuses within deposit.

moisture excess at this site was significantly less than that of the interglacial as a whole (~10 k.y.), and (2) at a time of deposition of organic matter with a high wavelength of emitted luminescence (452 ± 16 nm), suggesting an overlying peat soil. However, at the start and end of flowstone deposition, emission wavelengths were lower (420–440 nm), suggesting that the soil cover at these times was more humified. The full data set implies a shift from moorland to bog and then back to moorland as conditions became drier. Conditions within isotope stage 5e contrast markedly with those in the sections of isotope substages 5c and 5a preserved in the flowstone (101.1 ± 1.8 ka and 84.7 ± 1.2 ka, respectively), where emission luminescence is much lower (412 ± 6 and 417 ± 5 nm, respectively), suggesting that soil humification had increased and that conditions were not wet enough for bog development. Because flowstone deposition only occurs when soil moisture excess is at a maximum, both interstadial periods were probably relatively arid at the site. Evidence of aridity in northwestern Europe within isotope stage 5a has been observed in records of speleothem growth frequency (Baker et al., 1993) as well as the Grand Pile pollen record (Guiot et al., 1993), but has not previously been recognized in stage 5c. It is likely that if temperatures were within 1–3 °C of those during isotope stage 5e, then only a small increase in the continentality or seasonality of rainfall would prevent bog formation at the site. The luminescence record within isotope stage 3 exhibits a mean emission wavelength of 434 ± 15 nm, suggesting an overlying peat or gley soil. Throughout the period 58 to 36 ka, humification increased, suggesting a gradual increase in aridity and/or cooling as the onset of glaciation approached, and the periods of flowstone deposition represent wetter periods within isotope stage 3.

Data from Lancaster Hole suggest that the variations in speleothem luminescence wavelength enable us to clearly differentiate peat cover from other vegetation types. The technique therefore permits the investigation of climatic influences on bog humification, research that has previously been limited to Holocene deposits (Aaby, 1976; Barber et al., 1994) in which a cyclicity of between 76 and 400 yr has been observed. Within the Lancaster Hole record in isotope stages 3 and stage 5e, oscillations of the humification of the overlying soil can be observed; the lack of an absolute growth-rate determination for the flowstone constrains these oscillations to <1000 yr duration. Further research on high-growth-rate samples is required, especially to investigate whether other signals such as changes in soil thickness and transmission paths through soils are represented in speleothem luminescence. However, the data presented here, together with the existing Holocene bog humification records, suggest that the stability of interglacial climate periods in terms of atmospheric moisture variations may be investigated from variations in speleothem luminescence wavelength.

CONCLUSIONS

Speleothem analyses of luminescence wavelength variations can provide nondestructive, high-resolution, and precisely dated proxies of soil humification, which in some instances may provide a close correlation with climate and, in particular, soil moisture and temperature changes. The calibrations undertaken here have concentrated on periods of stable temperature and no vegetation change. Future research is needed to investigate the impact of both temperature and precipitation variations by calibrating speleothem records over longer time periods, as well as over periods during which vegetation has changed. In addition, the relationship between soil humification and climatic variations requires calibration for a wider data set: here we have concentrated on mid-latitude temperate maritime regions; sensitivity may be better in other regions. These studies are the focus of current research.

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