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Visualisation of luminescence excitation-emission timeseries: palaeoclimate implications from a 10,000 year stalagmite record from Ireland

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Abstract. Stalagmite luminescence excitation emission wavelength timeseries can provide high-resolution palaeoclimate records. Here, we employ multidimensional visualisation techniques in order to interpret a 10,000 year luminescence record from a stalagmite from Crag Cave, SW Ireland. Our results demonstrate three periods of distinct luminescence properties: (1) 0-4,000 BP, when they are affected by overlying agriculture. (2) 4,000-9,600 BP, where there is a strong correlation between luminescence and ^{13}C isotopic variations; we suggest the correlation demonstrates a vegetation response to climate change. (3) Before 9,600 BP, where a strong early Holocene transition is visible. Our results suggest that it took about 400-600 years for soils above the cave to stabilise after significant climate or environmental change, and that there was a complex vegetation response between 8,000 and 7,100 BP that my have been a lagged response to the "8.2 ka event".

1. Introduction

Recent advances in luminescence spectrophotometry permit the rapid generation of 3-D geological and hydrological datasets (excitation-emission matrices or EEMs) within optical space [Coble, 1996; Baker et al., 1998a; Baker and Genty, 1999]. Such data provide high resolution geological and hydrological information concerning: (1) algal production, total organic carbon (TOC) fluxes and organic acid humification in marine and lake sediment and surface waters [Coble et al., 1990; 1996; Del Castillo et al., 1999; Baker and Genty, 1999], (2) palaeovegetation and soil humification changes in stalagmites [Baker et al., 1998a; 1999] (3) humification of peat [Caseldine et al., in press]. An EEM typically consists of a regular spatial grid of 10^3-10^5 data points taken at a given point in time. Each data point represents the intensity of luminescence for an excitation-emission wavelength pair. A typical time series of EEMs will comprise from 365 (for daily sampling within a hydrological year) to upwards of 10,000 (for Quaternary and geological samples) such grids. Such datasets are difficult to display and analyse, given the large amount of data that is present in four dimensions (x,y,z,t). This in turn can lead to significant loss of useful data for this reason we have utilised the techniques described below.

Data in two-dimensions, such as luminescence and time, may be visualised on a scatter-plot, so that we may view the relationship between these two phenomena. However, the luminescence variation is also dependant on the excitation and emission wavelengths and intensity, and all three respond to temporally changing soil derived organic acids that are transported to the stalagmite. We might visualise the relationship between excitation and emission wavelengths and intensity in some form of contour plot (such as an EEM), but adding the desire to explore this variation over time raises problems of visualisation in only two dimensions. One technique which could easily be applied to these data is dynamic visualisation [Meisner et al., 1999]. This adds one further dimension (time) to the visualisation scheme. Such a visualisation is primarily exploratory in nature, and although they provide little in the way of formal models to help us draw inference about the underlying processes, they do enable the visualisation and analysis of the full time series.

Therefore in this paper we present appropriate visualisation techniques for the analysis of luminescence excitation-emission wavelength timeseries. Firstly, we employ a three-dimensional isosurface detecting routine to identify a set of two-dimensional surfaces in three-dimensional space which join together points of equal luminescence. Then we utilise POVRay, a freeware ray-tracing tool to visualise the isosurfaces (POVRay, 1999). Working with ray tracing-based visualisation software enables high quality graphical representations of surfaces to be created. As an example, we present a visualisation of a luminescence excitation-emission matrix (EEM) timeseries that comprises 440 data points covering the period 10,000 years bp to present (giving an effective mean resolution of 2.5 yrs/ EEM) for stalagmite CC3. This stalagmite sample, from Crag Cave, W. Ireland, has already undergone extensive research in the form of isotope

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and crystal structure variations [McDermott et al., 1999]. We therefore present our luminescence visualisation in comparison to existing data to provide a high resolution record of palaeoclimate change for the last 10,000 years.

2. Method

A luminescence timeseries was obtained for stalagmite CC3 using standard techniques [Baker et al., 1998a]. 440 excitation-emission matrices were obtained, which each comprised luminescence emissions of 390 to 480 nm and excitations from 300 to 380 nm; the 440 matrices covered the period 10,000 years bp to present, giving an effective mean resolution of 2.5 yrs per matrix. In order to visualise and interpret this dataset, methods involving projections of data from four dimensions to lower dimensional spaces were applied (see for example Brunsdon et al. [1998]). In particular, techniques involving isosurfaces were employed here. Thus an isoline for some function f(x,y) is a contour line joining all (x,y) pairs having the same value of f. In this study, x corresponds to excitation wavelength, and y to emission wavelength, and f to the luminescence intensity. Using contour lines, as on a map, the three dimensional surface f(x,y) can be represented on a plane. Now suppose that we add a third variable to the function, giving f(x,y,t). Here t can be thought of as a time dimension. In this situation, the equivalent to the isoline is the isosurface, a curved surface joining all (x,y,t) pairs having the same value of f. In the f(x,y) case it is not always necessary to draw contours - it is possible to visualise three-dimensional surfaces using techniques such as perspective drawing. However, the function f(x,y,t) is a four dimensional entity and so cannot be visualised directly: using some dimension reduction technique such as isosurface drawing is essential.

Here the isosurfaces are approximated as a collection of triangular plates using a FORTRAN77 program adapted from Young (1996). The POVRay ray-tracing program then uses these to produce the final images.

3. Results

Results of our visualisation techniques are applied to stalagmite CC3 from Crag Cave, Ireland. Figure 1 demonstrates the luminescence timeseries based on the presentation of the luminescence emission wavelength of maximum luminescence intensity, and the maximum luminescence intensity, following the presentation style of Baker et al. [1998a; 1999], together with isotope data for CC3 from McDermott et al. [1999]. Figure 1 does show significant variations in luminescence emission wavelength through time, including periods of predominantly high wavelength from 0-4000 BP and from 9,600 BP, and a period of relatively unstable luminescence emission wavelengths around 7500-8500 BP. However, significant amounts of interpretable data could not be presented in this simple diagram. A 3-D visualisation of this dataset as undertaken using POVRay to construct an animation which can be viewed at http://www.ncl.ac.uk/ecam/stal/long.gif; Figure 2 presents a frame from this animation. Figures 1 and 2 therefore provide additional information that can be utilised in the palaeoclimatic and palaeoenvironmental interpretation of stalagmite CC3. Three periods of similar luminescence intensity and wavelength can be observed in this sample: (1) up to 10,000 BP (2) from 10,000 to 4000 BP and (3) from 4,000 BP to present.

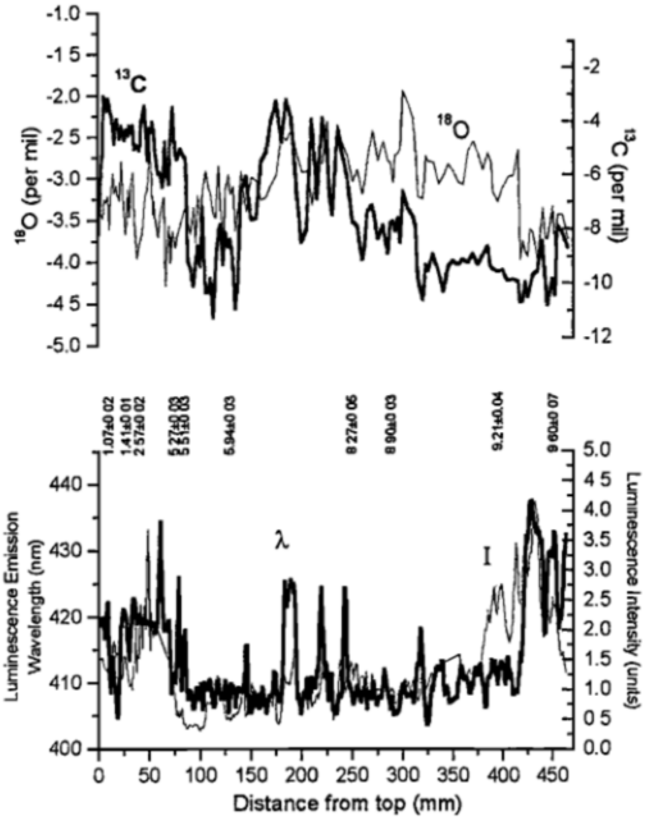

Figure 1. Graph of luminescence emission wavelength (λ), luminescence intensity (I), ^{13}C and ^{18}O variations against distance for stalagmite CC3. Age of the sample is shown by the TIMS U-Th analyses (from *McDermott et al.* [1999])

The significant change in luminescence emission wavelength visible in Figures 1 and 2 at 422 mm (9,400 ± 50 BP based on interpolation between TIMS U-Th analyses at 400 and 450 mm; McDermott et al. [1999]) is 600 years after the start of the Holocene. Luminescence excitation and emission wavelengths decrease from a mean of 429±6 nm to 410±5 nm, suggesting that the organic acids trapped within the stalagmite have a lower molecular weight or less aromatic structure. Such a decrease in molecular weight is likely to be caused by either an increase in temperature, decrease in rainfall or a vegetation change [McGarry and Baker, 2000]. The timing of the wavelength shift is slightly earlier than the 16 °C increase in mean annual temperature and change in climate from continental to maritime in the British Isles at the start of the Holocene (c. 9,300 to 8,600 BP), as reconstructed by coleopteran assemblages [Atkinson et al., 1987]. Luminescence intensity decreases c. 500 years after the luminescence wavelength decrease (Figure 1 and 2). Luminescence intensity is both a function of the concentration of organic acids trapped within the stalagmite as well as calcite porosity [Genty et al, 1997]. For stalagmite CC3, porosity changes occur with crystallographic variations, and none exist over this section of stalagmite (Figure 4, McDermott et al. [1999]); hence we hypothesise that the intensity change is due to a decrease in organic matter concentration. The lag between luminescence wavelength and intensity is interpreted as

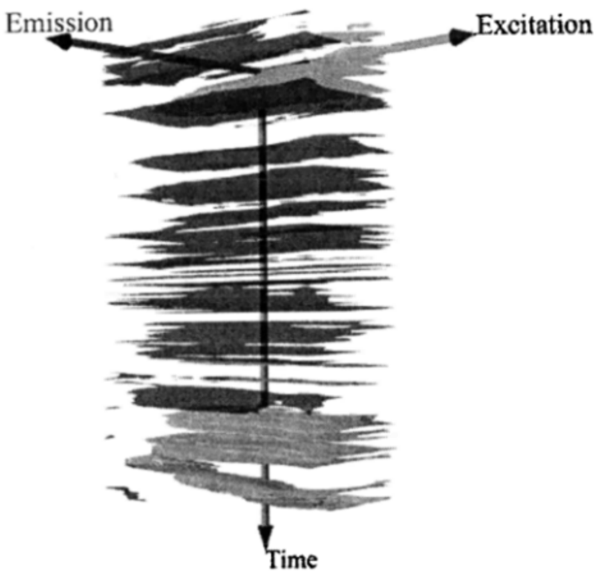

Figure 2. 3-D visualisation of stalagmite CC3 luminescence excitation, emission and intensity variations. Base of sample is at the top. Yellow contours are 150 intensity units, red contours are 60 intensity units. Note the increased luminescence intensity at top and base, as well as the general correlation between increased luminescence wavelength and intensity. A movie of this visualisation can be viewed at http://www.ncl.ac.uk/ecam/stal/long.gif

reflecting a relatively rapid response of soil organic acid molecular weight to a major climate change event, compared with the longer time period needed for soil and vegetation.

The second major change in luminescence wavelength occurs at 86 mm from the top of the stalagmite (4,000±500 BP based on TIMS U-Th analyses at 55 and 95 mm). Luminescence wavelength increases from a mean of 410±5 nm to one of 417±6 nm, suggesting an increase in molecular weight or a change to a more aromatic chemical structure. A luminescence intensity increase also occurs and with a lag, although the precise timing of this lag is not determinable due to the slow growth rate at this time. High luminescence intensity is maintained throughout the last 4,000 years of stalagmite deposition, and does not correlate with periods of changing calcite texture, suggesting that luminescence intensity is a proxy for the total concentration of organic carbon contained within the stalagmite, and that continual disturbance of the soil was occurring. Previous studies have demonstrated both a decrease in molecular weight of organic carbon due to cultivation [Martin et al, 1998], as well as an increase in molecular weight due to increased soil moisture after loss of forest cover and its associated root systems [McGarry and Baker, 2000]. Given the increase in luminescence wavelength observed here, we suggest the latter process is dominant. The luminescence emission wavelength and intensity change occurs at the same time as a significant regional land-use change in SW Ireland. Pollen and fossil tree stump evidence in the region all show a decline in woodland as settlement increased in the region and forests were cleared [Barnowsky, 1988; Dodson, 1990; Little et al., 1996]. For example, Dodson [1990] observes a loss of birch cover in the nearby Dingle Peninsula at c. 3500 BP and a replacement by peat and cereal pollen. Barnowsky [1988] observes a similar loss of pine and alder at 4,100 radiocarbon years BP in the region. Fields today overlie the cave, and we suppose that the land above the cave has been used for agricultural purposes for considerable time. Indeed, bone deposits found within near-surface fissures in the cave have a mix of cattle, sheep and rabbit, suggesting local farming since Roman period [John Gunn, pers. commun.].

Visualisation of the luminescence timeseries therefore demonstrates significant changes in both luminescence wavelength and intensity. The broad changes coincide with changes in growth rate of the stalagmite, which is fastest between 9,600 and 4,000 BP (50-70 μm yr-1) and slowest before 9,600 and after 4,000 BP [20-40 μm yr-1; McDermott et al., 1999]. Since dripwater calcium ion concentration is the main control on stalagmite growth rate [Baker et al., 1998b], which is in turn dependant on soil CO$_2$ concentrations, this correlation between soil dependant proxies is unsurprising. When compared to ^{18}O and ^{13}C isotopic data for CC3, it is apparent that no correlation is observed with ^{18}O, confirming that this is providing a climate proxy that is independent of soil and vegetation change. For ^{13}C, no correlation is observed between ^{13}C and luminescence at 9,600 BP, suggesting that the climate and vegetation change at this time period did not affect vegetation photosynthetic pathways (e.g a C3 vegetation was present). In contrast, a correlation between ^{13}C increase and luminescence increase at 4,000 BP is observed, suggesting that this change, probably from forest cover to grassland and agricultural use did involve a change in photosynthetic pathways. It is apparent that there is some correlation with luminescence fluxes and changes in ^{13}C between the period 5000 and 9000 BP, with three periods of increase luminescence wavelength and intensity, and corresponding ^{13}C. These results could be interpreted as suggesting that a vegetation change occurred at these times; figure 3 shows an enlarged visualisation of the luminescence data at this time

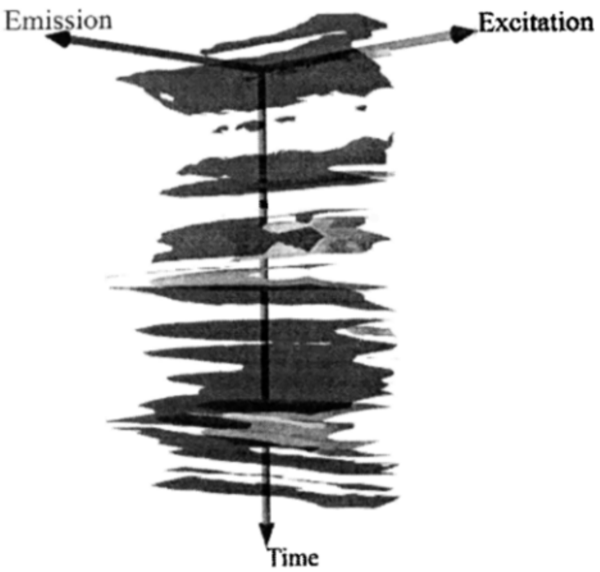

Figure 3. 3-D visualisation of stalagmite CC3 from 160-260 mm from top; 260 mm is at top of view of view. Red contours show 60 intensity, yellow 90 intensity. Note the strong correlation between increasing luminescence intensity and luminescence wavelength. A movie of this visualisation can be viewed at http://www.ncl.ac.uk/ecam/stal/movie.gif

period which can be viewed as an animation at http://www.ncl.ac.uk/ecam/stal/movie.gif. The three peaks correspond in time with oscillations observed in the particle size of ocean sediments off the British Isles (at c. 8,200, 7,400 and 7,000 BP) and interpreted as variations in ocean current strength [Bianchi and McCave, 1999]. We suggest our luminescence data (with peaks at c. 7,100±200, 7,800±200 and 8,000±200 BP) reflects soil or vegetation instability caused by regional climate changes, possibly following the short but relatively severe cooling phase at 8,200 BP [Alley et al., 1997; von Grafenstein et al., 1999].

4. Conclusions

Results presented here from stalagmite CC3 demonstrate the utility of visualisation techniques in the presentation and interpretation of luminescence intensity and wavelength timeseries. When compared to ^{13}C isotopic data for the stalagmite, we are able to construct a 10,000 years record of climate and environmental change for Crag Cave, SW Ireland. Major shifts in luminescence wavelength correlate in part with ^{13}C shifts, and show potential as a multi-proxy approach to understanding ^{13}C in stalagmites. In addition, high frequency oscillations in luminescence wavelengths are observed, which may reflect vegetation or soil instability over short (hundred to thousand year) timescales. Future researches on additional stalagmites from the region will further our understanding of soil and vegetation responses to climate change in the region. In addition, with the development of visualisation devices other than isosurfaces: for example it is possible to trace the (x,y) location of the maximum luminescence as a function of time, regardless of the value of that maximum. In this way sudden shifts in wavelengths could be more readily identified. Also needed is a more rigorous statistical modelling framework, so that error and uncertainty in the location of isosurfaces and maximum traces could be estimated and ultimately visualised. With such improvements in visualisation, increased palaeoclimate information may be gained from stalagmite luminescence EEM timeseries.

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References

Alley, R.B., Mayewski, P.A., Sowers, T., Stuiver, M., Taylor, K.C., and Clark, P U., 1997, Holocene climate instability: a prominent, widespread event 8,200 years ago. *Geology*, 25, 483-486.

Atkinson, T.C., Briffa, K.R. and Coope, G.R. , 1987, Seasonal temperatures in Britain during the past 22,000 years, reconstructed using beetle remains. *Nature*, 325, 587-592

Baker, A. and Genty, D., 1999. Fluorescence wavelength and intensity variations of cave waters. *J. Hydrology*, 217, 19-34.

Baker, A., Genty, D. and Smart, P.L.,1998a. High-resolution records of soil humification and palaeoclimate change from speleothem luminescence excitation-emission wavelength variations. *Geology*, 26, 903-906

Baker, A., Genty, D., Dreybrodt, W., Barnes, W.L., Mockler N.J. and Grapes, J., 1998b. Testing theoretically predicted stalagmite growth rate with Recent annually laminated samples: implications for past stalagmite deposition. *Geochimica et Cosmochimica Acta*, 62, 393-404

Baker, A., Caseldine, C.J., Gilmour, M.A., Charman, D., Proctor, C.J., Hawkesworth, C.J. and Phillips, N., 1999. Stalagmite luminescence and peat humification records of palaeomoisture for the last 2,500 years. *Earth and Planetary Science Letters*, 165, 157-162.

Barnosky, C.W., 1988. A late-glacial and post-glacial pollen record from the Dingle Peninsula, County Kerry. Proceedings of the Royal Irish Academy, 88, 2-37

Bianchi, G.G. and McCave, I.N., 1999, Holocene periodicity in North Atlantic climate and deep-ocean flow south of Iceland. *Nature* ,397, 515-517

Brunsdon, C., Fotheringham, A.S. and Charlton, M.E., 1998. An investigation of methods for visualising highly multivariate datasets. In Unwin, D. and Fisher, P. (Eds) Case Studies of Visualisation in the Social Sciences. ESRC/JISC Technical Report.

Caseldine , C.J., Baker, A., Charman, D. and Hendon, D., in press. A comparative study of NaOH peat extracts: implications for humification studies. The Holocene

Coble, P.C., Green, S., Blough, N.V. and Gagosian, R.B., 1990. Characterisation of dissolved organic matter in the Black Sea by fluorescence spectroscopy. *Nature*, 348, 432-435.

Coble, P.G., 1996. Characterisation of marine and terrestrial dissolved organic matter in seawater using excitation-emission matrix spectroscopy. *Marine Chemistry*, 51, 325-346.

Del Castillo, C.E., Coble, P.G., Morell, J.M., Lopez, J.M., and Corredor J.E., 1999. Analysis of the optical properties of the Orinoco River plume by absorption and fluorescence spectroscopy. *Marine Chemistry*, 1999, 66, 35-51

Dodson, J.R., 1990. Fine resolution pollen analysis of vegetation history in the Lough Adoon Valley, Co. Kerry, western Ireland. *Review of Palaeobotany and Palynology*, 64, 235-345.

Genty, D., Baker, A. and Barnes, W.L., 1997. Comparison entre les lamines luminescentes et les lamines visibles annualles de stalagmites. *Comptes Rendus de l'Academie des Sciences*, 325, 193-200.

Little, D.J., Mitchell, F.J.G., von Engelbrechten, S., Farrell, E.P., 1996, Assessment of the impact of disturbance and prehistorical *Pinus sylvestris* on vegetation dynamics and soil development in Uragh Wood, SW Ireland. *The Holocene*, 6, 90-99.

McDermott, F., Frisia, S., Huang, Y., Longinelli, A., Spiro, B., Heaton, T.H.E., Hawkesworth, C.J., Borsato, A., Keppens, E., Fairchild, I.J., van der Borg, K., Verheyden, S. and Selmo, E., 1999. Holocene climate variability in Europe: evidence from δ^{18}O, textural and extension-rate variations in three speleothems. *Quaternary Science Reviews*, 18, 1021-1038.

Martin, D., Srivastava, P.C., Ghosh, D. and Zech, W., 1998. Characteristics of humic substances in cultivated and natural forest soils of Sikkim. Geoderma, 84, 345-362.

McGarry, S.F. and Baker, A., 2000, Organic acid fluorescence: applications to speleothem palaeoclimate reconstruction. *Quaternary Science Reviews*, in press

Meisner, R.E., Bittner, M., and Dech, S.W., 1999. Computer animation of remote sensing-based time series data sets, *IEEE Transactions on Geoscience and Remote Sensing*, 37(2), 1100-1106

POVRay, 1999, *Persistence of Vision Raytracer*, http://www.povray.org

Von Grafenstein, U., Erlenkeuser, H., Brauer, A., Jouzel, J. and Johnsen, S.J., 1999. A mid-European decadal isotope-climate record from 15,500 to 5,000 years B.P. Science, 284, 1654-57.

Young, S.,1996, "Graphics and Inference" in Nonparametric Modelling", Ph.D Thesis, University of Glasgow.

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