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

Andy Baker

Department of Geography, University of Exeter, Amory Building, Rennes Drive, Exeter EX4 4R J, United Kingdom

Dominique Genty CNRS, Laboratoire d'Hydrologie et de Geochimie Isotopique, Universite de Paris-Sud, 91405 Orsay Cedex, France

Peter U Smart

Department of Geography, University of Bristol, University Road, Bristol BS8 1 SS, United Kingdom

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

Speteothem 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 (103 to 106 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, t974; 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 break- down are reflected in changes in the composition (molecular weight or degree of aroinp, ticity) 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 14C 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.