



Geochemical mapping of organic carbon in stalagmites using liquid-phase and solid-phase fluorescence



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ABSTRACT

The soil-derived organic matter incorporated in speleothems provides a proxy for the impacts of climate and environmental changes on the surrounding catchment. These organic proxies, combined with inorganic proxies, can be used to investigate variations in carbon fluxes. The present article describes a method for obtaining high spatial-resolution estimations of speleothem organic carbon concentrations by using the relationship between liquid phase fluorescence and the organic carbon contents of soil samples. Applying this method to soil and stalagmite samples from three locations in the French Prealps gave estimated stalagmite carbon concentrations of between 0.27 and 3.03 mg C/g of calcite, which are consistent with measured concentrations reported in the literature. We assessed the high-resolution reliability of our procedure by comparing TOC estimations with solid phase fluorescence values for samples taken every 2-mm along one of the stalagmites (TAM). Due to variations in the optical properties (e.g., optical density) of the calcite, revealed by Near Infra Red Reflectance, it was necessary to draw up a nonlinear model in order to obtain good estimates ($R^2 = 0.81$) of organic carbon concentrations from solid-phase fluorescence results. The resulting high-resolution map of organic carbon concentrations along the TAM sample was consistent with the recent history of the area's environment. Our results show that variations in carbon flux in mountain karst environments are strongly linked to changes affecting the area's soils.

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1. Introduction

Since studies first demonstrated the presence of organic matter (OM) entrapped in calcite (Baker et al., 1996; Ramseyer et al., 1997), a number of organic components of speleothems are being used as proxies for investigating changes in soils, vegetation, and climate (e.g., Baker et al., 1998; Blyth and Schouten, 2013; Blyth et al., 2011, 2013, 2014; Bosle et al., 2014; Li et al., 2014; Perrette et al., 2005, 2008; Webb et al., 2014).

Combining data obtained from organic and inorganic proxies has provided insight into variations in carbon fluxes in karst environments (e.g. Baker and Genty, 1999; McGarry and Baker, 2000); however, current organic carbon quantification procedures need to be improved before speleothems can be used as high-resolution records of carbon flux, which are a major issue in the climate change context (Ciais et al., 2013). In fact, carbon measurement procedures described in the literature are either quantitative but low-resolution destructive methods (Blyth et al., 2013; Hartland et al., 2014; Li et al., 2014;

Ramseyer et al., 1997; Smailer and White, 2013; Van Beynen et al., 2001) or semi-quantitative but high-resolution spectroscopic methods (Baker et al., 1996, 1997). Spectroscopic techniques have also been used to determine the organic carbon concentrations of karst waters (Charlier et al., 2010; Tissier et al., 2013). In the present research, we applied this approach to speleothems via a new procedure in which spectroscopic analyses are combined with a carbon extraction method that consumes only small amounts of material. Although solid-phase fluorescence has become a commonly used technique for analyzing speleothems (Crowell and White, 2012; Orland et al., 2014; Perrette et al., 2005; Webb et al., 2014), results have to be interpreted with caution (McGarry and Baker, 2000). In addition, quantifying the organic carbon content of speleothems requires a large amount of calcite for the solid/liquid extraction phase (Blyth et al., 2013; Hartland et al., 2014; Li et al., 2014; Ramseyer et al., 1997; Van Beynen et al., 2001), which is incompatible with studies of carbon fluxes over short time-scales and prevents results being combined with high-resolution solid phase fluorescence (SPF) analyses.

Although some recent works show that organic matter in speleothem can also be sourced from microbial input (e.g. Blyth et al., 2014; Yang et al., 2011), it is assumed that bulk organic matter entrapped in speleothems is provided by soils (Baker et al., 1996; White and Brennan, 1989), and highlighted in studies comparing speleothem and dripwaters fluorescence (Hartland et al., 2014; Li

Abbreviations: \hat{C} , Predicted carbon concentration; LPF, liquid phase fluorescence; NIRR, near infra-red reflectance; OM, organic matter; SPF, solid phase fluorescence; TOC, total organic carbon; QS, quinine-sulfate; QSU, quinine-sulfate units; WEOM, water extractable organic matter.

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et al., 2014). We developed in this study a procedure for determining a speleothem's Total Organic Carbon (TOC) content by combining speleothem OM Liquid-Phase Fluorescence (LPF) measurements with LPF and TOC values for a bank of local soil leachates considered to represent both the spatial and the past evolution of soils. The present article describes how we applied this new procedure to three speleothems and discusses the use of solid-phase fluorescence to estimate and map speleothem organic carbon concentrations, and thereby reconstruct local carbon fluxes in karst environments.

2. Material and method

2.1. Speleothem samples

We tested our TOC quantification procedure on three stalagmites from similar mountain environments in the northern French Prealps (Fig. 1 and Fig. A in supplementary information) – the Garde-Cavale cave system and the “Ferme” cave, both of which are in the Bauges Massif, and the Choranche cave system in the Vercors Massif. The Garde-Cavale cave system lies below the Nivolet-Revard Plateau in the western part of the Bauges Massif. It consists of 42.8 km of passages, between 1380 m and 1055 m a.s.l., developed in Urgonian and Valanginian limestones. Vegetation above the system is a mixture of beech and spruce forest, and pastured grassland. The sampled stalagmite is in a 30-m-deep chamber (“Précieux Chamber”), whose roof is made of calcite-cemented sandstone decorated with soda-straws showing slow and regular percolation. It is 60-cm long, massive, orangey-brown in color, and composed of alternating zones of porous and compact monocrystalline calcite (Fig. 1). A full paleoenvironmental study of this early Holocene stalagmite is ongoing. We extracted two samples from the edge (around –4700 yr B.P.) of the lower part of the stalagmite (GC1) and the porous calcite (GC2). Environment during the first middle part of Holocene is mainly characterized by forest and poor

developed soils (Giguet-Covex et al., 2011), assumed to be similar to those of today.

The “Ferme” cave also lies below the Nivolet-Revard Plateau. It is a 65-m linear passage that follows the dip ($\sim 10^\circ\text{E}$) of the surrounding Hauterivian marly limestone. We sampled a 10-mm-long stalagmite that is growing 25 m from the cave entrance at a depth of less than 10 m and directly below a dairy farm. This modern, active stalagmite is fed by fast flows that follow the joint network through the marly limestone. It consists of two sections of compact columnar calcite separated by a detrital layer (clay and oxides). Both sections of columnar calcite are yellow to orange in color, although the more modern calcite has a greenish hue (Fig. 1). As our goal was simply to test our carbon quantification procedure on a stalagmite from an environment modified by human activity (dairy farm), rather than carry out a detailed environmental analysis, we did not obtain U/Th ages for the samples. We extracted three samples from the stalagmite. FER1 was taken from the lowest and oldest part below the detrital layer and is assumed to be undisturbed due to the calcite coalescence and the absence of inclusion. FER2 and FER3 were taken above the detrital layer, from areas of compact and porous calcite, respectively. Regarding growth rate, dripwater mineralization and ancient cadastral documentation, FER3 can surely be associated with the dairy farm presence. The case of FER2 could be less evident; however, the comparison of TOC estimations and fluorescence spectra shows that this sample could also be associated to the presence of the dairy farm.

The “Choranche” system lies within the broad anticline of the Coulmes Plateau. It rises at the bottom of the Urgonian (Barremo-Bedoulian) scarp that forms the northern side of the Bourne Gorge. The sample we used for this study was part of a borehole core taken in 1996 from a stalagmite growing in the Cathedral Chamber (N $45^\circ 5'$, E $5^\circ 2'$, 610 m a.s.l.) of the Chevaline Cave. This stalagmite is fed by two flows: (i) a fast runoff flow that takes less than 3 h to penetrate the 300 m of limestone separating the stalagmite from the surface (unpublished salt tracing results) and (ii) a seepage flow. Vegetation in the watershed feeding the stalagmite is mostly mixed deciduous–coniferous forest and grassland. Previous studies have correlated the characteristics of the top 60 mm of the stalagmite sample with environmental changes that occurred on the plateau. Perrette et al. (2008) drew up an age model for this stalagmite based on distinctive stratigraphic layers, lamina counts, and U/Th dating. This intensively studied sample allowed us to assess the feasibility of combining TOC quantification with high spatial resolution SPF. We took 20 samples from the core's three stratigraphic units (Fig. 1). Samples TAM1 to TAM12 were taken from zone U3, which formed before $1701 \text{ AD} \pm 26 \text{ yr}$. This homogeneous zone is dominated by porous, opaque laminations with occasional thin layers containing clays and charcoal produced by slash and burn agriculture on the plateau. Samples TAM13 to TAM18 were taken from zone U2, which was deposited between $1701 \text{ AD} \pm 26 \text{ yr}$. and $1892 \text{ AD} \pm 8 \text{ yr}$. The calcite in this zone is more porous and contains many mineral and organic particles. The last two samples (TAM19 and TAM20) were taken from zone U1, which was deposited between $1892 \text{ AD} \pm 8 \text{ yr}$. and 1996 AD. This zone consists of compact and translucent calcite with no inclusions.

2.2. Soil samples

In order to take into account all the different types of soil-derived OM that may be entrapped in the speleothems, we took samples of the main soil types from the three study sites. Soils were sampled with a pedologic approach focusing on the soil and vegetation characteristics. The two main soil types found in mountain karst environments are Eutric Cambisol and Folic Leptosol (WRB, 2006), which develop on calcareous substrates. Podzols can form in areas where sandstones overlie karst systems (WRB, 2006), but they are much less common than Cambisols and Leptosols. One of the soils in the recharge area of the Garde Cavale stalagmite is a Podzol. The types of OM supplied by each

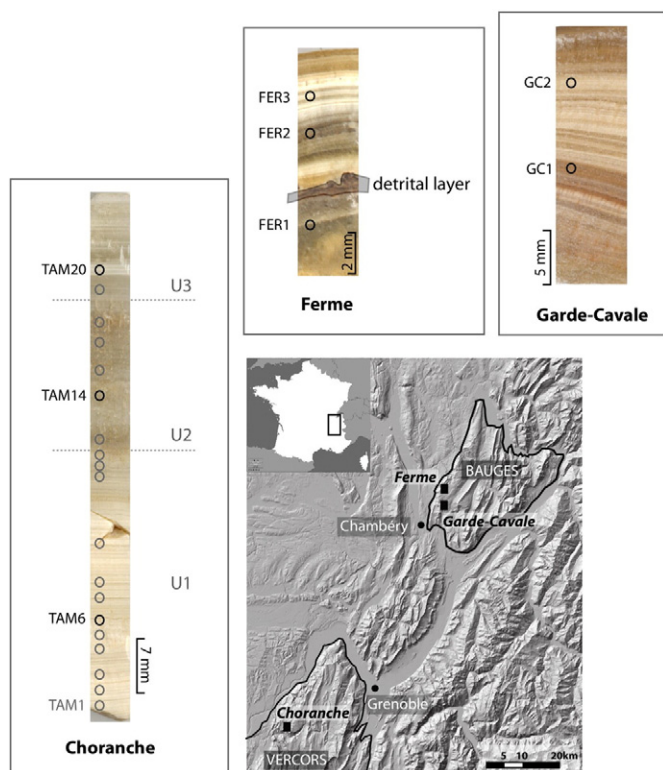


Fig. 1. Location of the karst system, sampling locations, and the corresponding stalagmite sections.

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