



Invited review

Organic proxies in speleothems – New developments, advantages and limitations

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ABSTRACT

Research into organic matter in speleothems has progressed recently to encompass new analytical approaches and applications, which offer increased potential in areas such as palaeo-temperature reconstruction and high-resolution palaeo-environmental records from the Quaternary. Here we review three major areas of relevance for future work in the field – the origin, transport and transformation of the organic matter which is ultimately preserved in speleothems; the types of proxies currently available for use or in development, and their advantages and issues; and the recently developed prospect of high-resolution organic matter records derived from the analysis of organic/trace elements complexes. The continuing extension of work in these research areas offers excellent potential for organic speleothem proxies to grow as a valuable tool in palaeoenvironmental research.

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1. Introduction

Our ability to understand and reconstruct past environments and climates depends on the availability of appropriate “archives” of information in the form of biological, chemical, and physical records preserved in the natural environment (e.g. McKay et al., 2016; Douglas et al., 2016). In a terrestrial context, possible archives include lake sediments (e.g. Morris et al., 2015; Zolitschka et al., 2015), peat cores (e.g. Swindles et al., 2012), loess/palaeosol sequences (e.g. Maxbauer et al., 2016), and speleothems (e.g. Fairchild and Baker, 2012; Wong and Breecker, 2015).

Speleothems are chemically precipitated deposits, usually formed of calcium carbonate, that grow within a cave environment as the result of degassing of cave waters (Fairchild and Baker, 2012). A wide variety of forms can develop, depending on the location of the deposit within the cave, the rate of water flow, and microbial involvement. However, the most commonly used in palaeoenvironmental studies are stalagmites and flowstones (Fig. 1.) Stalagmites grow upwards from a surface beneath drip-points, while flowstones develop under more rapidly flowing water films. Both types form in incremental layers which can be used to

constrain any environmental proxy records that they contain (Baker et al., 2008a). Stalactites and soda straws which grow downwards in tubular form from the drip points are sometimes used in palaeoenvironmental work, but less commonly, as blockages in their drip-pathways can result in a less coherent laminated structure.

Speleothems are particularly useful as palaeoclimatic archives as they are highly amenable to chemical dating, potentially back to several million years (Dorale et al., 2004; Woodhead et al., 2006; Hellstrom, 2006; Hellstrom and Pickering, 2015). At the other end of the scale, manual or automated counting of growth laminations can allow an annual or subannual resolution (Meyer et al., 2006; Baker et al., 2008a; Smith et al., 2009). Their connection to the surrounding environment via their feed dripwater allows multiple chemical signals to be preserved, including organic material (OM) which can be derived from the overlying vegetation, soil, or vadose zone, or from within the cave environment. In this paper we follow the broadly defined concept of OM applied by Blyth et al. (2008) in a previous review of the field, including molecular and detrital material transported as dissolved or suspended components in dripwaters, or generated within the cave environment, but excluding identifiable fossil material such as pollen.

The study of OM in speleothems has expanded over the last twenty years, due to the potential for development of new types of

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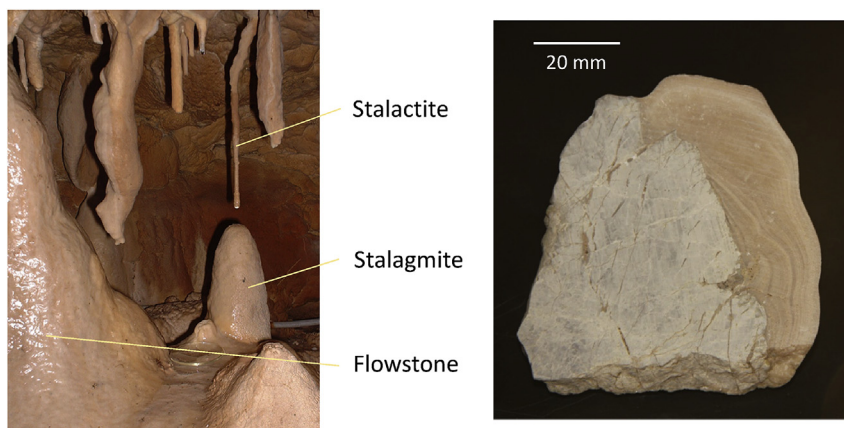


Fig. 1. These photographs show (left) the growth modes of different speleothem types within the cave, and (right) incremental growth lamination in a sectioned stalagmite that has grown vertically on the side of a block of limestone.

palaeoenvironmental record. The majority of speleothem records centre on inorganic proxies such as oxygen isotopes, which have led to a significant body of work, and particular utility in palaeohydrological and palaeoclimatic research (see McDermott (2004), Lachniet (2009), Fairchild and Baker (2012), and Wong and Breecker (2015) for reviews). Carefully targeted analysis of OM offers the opportunity to expand the range of chemical proxy records recovered, including those deriving directly from plant and microbial communities. This holds out the tantalising possibility of creating fully integrated multi-proxy records comprising of both climatic and ecological signals in a single well-dated sample. The amount of organic carbon preserved in speleothems is low, being estimated at 0.01–0.3% of total carbon (Blyth et al., 2013a; Li et al., 2014; Quiers et al., 2015). However, with increasing numbers of researchers working in this field across a range of scientific approaches, viable analytical techniques are becoming established. This review updates the Quaternary community on the current state of knowledge with respect to OM in speleothems, with particular consideration given to the potential sources of the organic signals; the range of techniques currently available for the analysis of preserved biomarker signatures; the potential use of trace element analysis as a high resolution proxy for OM input to a cave; and suggestions for the most necessary avenues of further research.

2. Sources of OM in caves

The two main sources of OM preserved in speleothems are the overlying environment (vegetation, soil, and possibly atmosphere) and microbial communities living within the cave (Yang et al., 2011; Perrette et al., 2013; Blyth et al., 2014). In most karst environments, the soil is likely to be the biggest store of organic carbon, but the contribution of this carbon in speleothems will depend on leaching from the soil, and chemical and biological alteration during transport (Fig. 2.). It is important to understand the relative contribution of surface, karst and in-cave sources of OM in any particular speleothem sample, as this may be central to achieving the best calibration of palaeoenvironmental proxies (Yang et al., 2011; Blyth et al., 2014).

2.1. Transport and alteration of surface derived OM

Soil-derived OM derives from the degradation of material such as plant litter and soil fauna. This OM can be transported in dissolved (DOM), colloidal or particulate form, with the different

fractions operationally defined by their separation on filtration. DOM is rapidly adsorbed to mineral surfaces (Jardine et al., 1989; Qualls and Haynes, 1992), with differences in the extent and rate of adsorption depending on the chemical nature of the OM and the soil properties. Hydrophilic fractions (e.g. carboxylic acids and amino acids) are most likely to be labile, in contrast to hydrophobic fractions (e.g. *n*-alkanes or lignin and its derivatives). The long-term stability of OM in the soil is discussed by Lehmann and Kleber (2015). The conventional view that soil OM comprises stable, persistent, large molecular size ‘humic substances’ (for example, see Karavanova (2013)) has been replaced by an understanding that soil OM is a continuum of degrading compounds (Lehmann and Kleber, 2015). This soil continuum model (SCM) recognises that soil OM can be stabilised if it is protected from microbial access through sorption to mineral surfaces and formation of aggregates. Desorption from mineral surfaces or the destruction of soil aggregates releases the OM into the pool of material accessible for microbial breakdown. In the SCM, soil OM is therefore a function of the characteristics of the surface litter input characteristics and the soil mineralogy, as well as the temperature, moisture and the biota present. For speleothem scientists, the SCM suggests that whenever OM is being transported, microbial breakdown of it is likely to occur. This can occur beyond the soil zone, when the OM is being transported from soil to cave.

Soil OM may be leached into the vadose zone (here defined as excluding the soil zone). Experimental quantification of the amount of downward flux of OM (leached DOM) compared to other fluxes (such as biological uptake) has proven difficult (Ghani et al., 2010). Downward leaching of DOM requires the production of transportable (dissolved or colloidal) OM in the soil, and rainfall that exceeds field capacity, in order to generate infiltration to the unsaturated zone. Hydrophilic DOC fractions are more likely to be available for leaching. However, if water movement generates the detachment and transport of colloidal material, hydrophobic DOC fractions will also be leached. An example of this was observed in an Ethiopian speleothem (Blyth et al., 2007), where the *n*-alkane record showed a rapid change at the same time as anthropogenic vegetation change.

In the vadose zone, as discussed above, soil-derived OM is still available for biological and physicochemical processing. There have been relatively few studies of the processing of vadose zone and groundwater OM outside of a contaminated site context, but those that have been undertaken provide evidence of biodegradation and mineral adsorption (Shen et al., 2014). Considering rates of process, mineral adsorption is near-instantaneous (Qualls and Haynes,

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