Quaternary Geochronology 39 (2017) 92–98

Contents lists available at ScienceDirect

Quaternary Geochronology

journal homepage: www.elsevier.com/locate/quageo

Research paper

Exploring the dating of "dirty" speleothems and cave sinters using radiocarbon dating of preserved organic matter

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ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form
10 October 2016
Accepted 6 February 2017
Available online 8 February 2017

Keywords:
Speleothems
Carbonate sinter
Dating
Radiocarbon
Organic matter

ABSTRACT

Speleothems and other carbonate deposits such as tufa containing high proportions of detrital material can be difficult to chemically date due to detrital thorium levels causing a high level of error in conventional U-Th disequilibrium dating. Here we investigate the use of an alternative technique centring on radiocarbon dating of organic matter preserved within the detrital fraction. Non-acid soluble humic, particulate and detritally absorbed organic matter was recovered from eight samples from a flowstone sinter formed within a roman aqueduct at Trento in Italy with a maximum age of 100 CE (1850 cal yr BP), and two repeat samples from a dripstone formed within the 20th Century on a wire fence at Lilly-Pilly Cave, Buchan Caves Reserve in Victoria, Australia. In the aqueduct samples the median calibrated ^{14}C ages ranged from 2232 to 2889 cal yr BP, with 95.4% probability age range in the youngest and oldest samples of 2153–2337 and 2342–3449 cal yr BP respectively. The median age of the more modern dripstone was 336 cal yr BP, with a 95.4% probability age range of 148–486 cal yr BP. These results provide very approximate ball-park estimates of the age of the sample, but are consistently too old when compared to the known maximum ages of formation. It is hypothesised that this offset is due to a combination of the nature of the organic carbon transported from the source organic matter pools, and reworking of both modern and old organic carbon by in situ microbial communities.

1. Introduction

One of the strengths in the use of carbonates such as speleothems as palaeoclimatic archives lies in their amenability to precise dating. The carbonate in speleothems is most frequently dated by uranium - thorium disequilibrium series (U-Th), which works well back to 500 ka (Richards and Dorale, 2003; Dorale et al., 2004; Hellstrom, 2006; Hellstrom and Pickering, 2015). Uranium – lead dating (U-Pb) extended our capability of obtaining ages from terrestrial carbonates well beyond this, from 1 Ma to at least 8 Ma (Woodhead et al., 2006). Radiocarbon has been relatively underused as a dating technique in speleothems, principally because radiocarbon dating of the calcite requires corrections for issues such as the dead carbon proportion (dcp), meaning that most of the studies to date have focused on younger material where detection of the bomb spike allows for more accurate modelling (Genty and Massault, 1997; Blyth et al., 2007; Hodge et al., 2011; Hua et al., 2012). Radiocarbon analysis in older speleothems has been focused on samples where the analyses could be paired with high precision U-Th dating for radiocarbon calibration (e.g. Beck et al., 2001; Hoffman et al., 2010; Southon et al., 2012) and investigation of temporal dcp variations (e.g., Rudzka et al., 2011; Griffiths et al., 2012; Noronha et al., 2014). These analyses of radiocarbon in speleothems have focused on the carbonate component derived from dissolved carbon dioxide from the breakdown of soil and vadose zone organic matter, and/or from dissolved calcium carbonate bedrock (Genty and Massault, 1999; Genty et al., 2001; Hua et al., 2012).

"Dirty" carbonates, those with significant detrital components incorporated in the matrix, are problematic from a dating point of

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http://dx.doi.org/10.1016/j.quageo.2017.02.002
1871-1014/

view, as the detrital content has a tendency to lead to high detrital thorium levels which affects conventional chemical dating (Labonne et al., 2002; Hellstrom, 2006; Hua et al., 2012; Meyer et al., 2012). Although many samples are amenable to correction (e.g. Hellstrom, 2006), and others allow for radiocarbon dating of the carbonate (e.g. Labonne et al., 2002), for some, it can become impossible to secure a usable dating frame-work. This effectively renders these samples defunct for many forms of palaeoenvironmental work, leading to the collected material being under-studied (Meyer et al., 2012). However, “dirty” material often also contains a relatively high organic content (Blyth et al., 2008, 2015), thus opening up the possibility of using radiocarbon dating of the preserved organic matter as a partial solution to this problem. To date, we are aware of only limited radiocarbon studies that utilised the organic matter preserved in speleothems, probably because the proportion of TOC has been historically hard to measure in this context and is generally very low (0.01–0.3% of total carbon; Blyth et al., 2013; Li et al., 2014; Quiers et al., 2015; Blyth et al., 2016). However, radiocarbon dating of organic compounds in moonmilk flowstones from high alpine settings, consisting of fibrous calcite crystals and with a large organic matter component (Borsato et al., 2000; Blyth and Frisia, 2008), have yielded ages consistent with those of crystalline speleothems at lower altitudes in the same area, which allowed reconstruction of long-term Holocene climate (Frisia and Borsato, 2010). Radiocarbon dating on calcareous tufa flowstones from the same alpine region, which consist of a mixture of biomediated calcite crystals, detrital components and organic matter, yielded similar ages, although inversions were common (Borsato et al., 2007). Separately, dates from Lascaux cave in France have been published, based on calcite gours, which were observed to have a mineral structure reminiscent of moonmilk (Genty et al., 2011). Four organic matter dates were obtained from this material, based on organic residue that was observed to have a filamentous structure similar to that from fungal and algal remains found in carbonate tufas (Genty et al., 2011). These dates were found to be older by approximately 500 years than those from charcoal from comparable layers, and to have a disturbed chronology (Genty et al., 2011). These results suggest that “dirty” conventional speleothems (such as stalagmites and flowstones) known to contain organic matter could potentially be dated with the radiocarbon method, but that sources and chronological disturbances need careful consideration. In this study we consider two different speleothem types from very different contexts to assess whether the issue of radiocarbon dating of organic matter returning older than expected ages is likely to be a widespread problem, or site-specific.

2. Materials and methods

2.1. Samples

The principal sample in this study is a flowstone sinter formed inside a roman aqueduct at Trento in the Italian Dolomites (henceforth referred to by the sample code T-AQ). The use of a sample from a man-made structure allows us to place a maximum date of formation independent of any chemical techniques, in this case of circa 100 CE, or 1850 cal yr BP, the aqueduct being believed to have been built during the last quarter of the 1st century (75–100 CE) and utilised until the fall of the Roman Empire and the Early Middle Ages, around 500 CE (Bassi, 2004, 2007). The sample is taken from a section of the aqueduct that was unearthed in the late 1990s, with studies suggesting the water was sourced from groundwater draining Permian to Mesozoic carbonate-evaporite-siliciclastic rocks (Bassi, 2004). That the waters feeding the aqueduct were captured from karst springs, rather than surface waters, is supported by the mineral fabrics of the flowstone and $\delta^{13}C$ data, which are typical for stalagmites/flowstones grown in caves at mid-altitudes, below the conifer vegetation belt in the region (Frisia and Borsato, 2010; Borsato et al., 2015).

The flowstone, or sinter, which has grown upon a cement mortar layer, is about 400 mm wide and up to 105 mm thick. The most common facies is characterized by lamina couplets marked by differences in porosity and fabric, with variations in the percentage of sparite and micrite. The columnar fabric (Frisia, 2015) consists of fans of sparry calcite crystals, commonly showing rounded crystal terminations capped by micrite laminae. Spar crystals may be partially truncated by micrite, show fine impurity-rich lines, and split into crystals arranged in fans (Fig. 1). Crystal tips can be corroded, as documented also in stalagmitic flowstones. Micrite is arranged in laminae capping the spar crystals, and is commonly aggregated in peloids (Frisia, 2015) associated with Fe-oxides, silt and small bivalves (Fig. 1). Both micrite and sparite consist of low-Mg calcite with variable amounts of detrital fraction, mostly associated with the micrite, including quartz, feldspar, dolomite,

Fig. 1. T-AQ thin section showing sparry columnar calcite crystals capped by micrite peloids. The micrite layer incorporates small bivalves. Note that crystal splitting occurs toward the top of columnar crystals, most probably coinciding with the input of organic compounds. These likely facilitated the occurrence of micrite. The bottom edge of the photo is 7 mm across.

Fig. 2. Subsection of the T-AQ flowstone sample showing the eight groups of layers sampled. Note the clear detrital layers associated with level 7.