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Holocene temperature and hydrological changes reconstructed by bacterial 3-hydroxy fatty acids in a stalagmite from central China

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ABSTRACT

To achieve a sufficient understanding of the spatial dynamics of terrestrial climate variability, new proxies and networks of data that cover thousands of years and run up to the present day are needed. Here we show the first Gram-negative bacterial 3-hydroxy fatty acid (3-OH-FA) based temperature and hydrological records from any paleoclimate archive globally. The data, covering the last 9 ka before present (BP), are generated from an individual stalagmite, collected from Heshang Cave, located on a tributary of the Yangtze River, central China (30°27′N, 110°25′E; 294 m). Our results indicate a clear early-to-middle Holocene Climatic Optimum (8.0–6.0 ka BP) followed by a long-term monotonic cooling and increasing variability over the last 0.9 ka BP. The hydrological record shows two relatively long wet periods (8.8–5.9 ka BP and 3.0–0 ka BP) and one relatively dry period (5.9–3.0 ka BP) in central China. We show that 3-OH-FA biomarkers hold promise as independent tools for paleoclimate reconstruction, with the potential to deconvolve temperature and hydrological signals from an individual stalagmite.

1. Introduction

Nearly half of the Earth's population live within the influence of the modern monsoon and its importance to terrestrial eco-systems, societal wellbeing and the global economy can not be overstated (Webster et al., 1998). Records of past Holocene rainfall and temperature, which extend the relatively short instrumental record, can constrain natural monsoon variability and are particularly important for the Asian monsoon region where prediction of future changes in rainfall using climate models has proven challenging (IPCC, 2014). Such records can also illustrate the influence of the monsoon on prehistoric cultures and settlements (Xie et al., 2013).

Stalagmites have become a key archive in Quaternary paleoclimatic reconstruction due to their ability to yield continuous and undisturbed records, precise and absolute chronologies, and their global terrestrial distribution (Blyth et al., 2016; Fairchild et al., 2006; Fairchild and Baker, 2012; McDermott, 2004; Wong and Breecker, 2015). Oxygen isotopes are effectively the 'master' or standard approach for speleothem analysis, but inherently encode a mix of climatic signals (Lachniet, 2009; McDermott, 2004), including, at the regional scale, temperature changes, the isotopic composition of source waters and precipitation amount. In addition, complex site-specific factors must be taken into account, such as drip rate (Dreybrodt and Scholz, 2011) and $CaCO_3$ precipitation (Fairchild and Baker, 2012). Many previous studies have focused on the interpretation of oxygen isotopes in speleothems, but deconvolving independent temperature and precipitation signals from speleothem $CaCO_3$ remains highly challenging, as evidenced by the paucity of such deconvolved records (Hu et al., 2008b; Yuan et al., 2004).

Biomarker based proxies are now firmly established in the fields of paleoceanography and paleolimnology (Castañeda and Schouten, 2011; Eglinton and Eglinton, 2008; Schouten et al., 2013). Recently attention has turned to the potential of organic matter and biomarker techniques for speleothem research (Blyth et al., 2008, 2016). A number of biomarkers with known paleoclimatic utility have been discovered and measured in speleothems, including glycerol dialkyl glycerol tetraethers (GDGTs) (Blyth et al.,

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2014; Blyth and Schouten, 2013; Yang et al., 2011), plant derived biomarkers (Blyth et al., 2007, 2010, 2011; Bosle et al., 2014; Xie et al., 2003), branched fatty acids and hydroxy fatty acids (Blyth et al., 2006; Huang et al., 2008; Wang et al., 2012). Furthermore, Blyth and Schouten (2013) recently proposed a novel GDGT calibration, based on samples derived from 33 globally distributed speleothems from caves with a range of average air temperatures.

Biomarkers in stalagmites may originate from the overlying vegetation, overlying soil ecosystem, limestone aquifer and cave fauna (Blyth et al., 2008). Moreover, different biomarker classes may have different sources. For example, Yang et al. (2011) found that the majority of the archaeal isoprenoid and bacterial branched GDGTs measured in stalagmite samples from Heshang Cave were likely produced *in situ*. Most recently, Blyth et al. (2014) found that GDGTs preserved in stalagmites in the UK and Australia likely originated from the *in situ* microbial communities within cave systems. An artificial irrigation experiment conducted in Cathedral Cave, Australia, found different GDGT distributions among speleothem, soil and drip water samples (Baker et al., 2016). In contrast, a 2-year monitoring experiment of drip waters in Heshang Cave found that fatty acids in drip waters were most likely derived from the overlying soil and/or groundwater system via particulate entrainment and deposition (Li et al., 2011). It is noteworthy that the fatty acid ratios (ratios of $nC_{16:1}/nC_{16:0}$ and $nC_{18:1}/nC_{18:0}$; the prefix *n* indicates normal, the number before the colon specifies the number of C atoms, and the number after the colon gives the number of double bonds) showed a strong negative relationship with the external temperature recorded in Yichang meteoric station (located ca.100 km east of Heshang Cave), whereas the two ratios displayed no relationship with internal cave temperatures recorded at the HS4 site, which suggests that *in situ* cave microbes are probably not the predominant source for C_{16} and C_{18} acids in drip water collected in Heshang Cave. Li et al. (2011) concluded that, based on the distributional patterns of the fatty acids, microbes living in the overlying soils and/or groundwater system are the dominant source of fatty acids to the Heshang Cave drip waters. We note that Vaughan et al. (2011) discovered microbes living on speleothem surfaces in Kartchner Caverns, USA. Such consortia of microbes are an inevitable source of *in situ* fatty acids. Thus fatty acids measured in stalagmites may be derived from mixed sources, including overlying soils/sediments (Li et al., 2011), the ramifying network of conduits and reservoirs in the limestone and *in situ* microbes (Vaughan et al., 2011). However, even though the origin and pathways of inclusion into speleothems of biomarkers may be complex (Blyth et al., 2008, 2016), it doesn't hinder the utilization of biomarkers in paleaoclimate reconstruction. Site specific interpretation and ground truthing are required, but this is also true for established paleoclimate techniques, as outlined above. In summary, lipid biomarkers preserved in speleothems show clear potential for paleoclimate reconstruction. However, very few such biomarker based paleoclimatic reconstructions have been published (Blyth et al., 2011; Huguet et al., 2018; Li et al., 2014; Xie et al., 2003).

Gram-negative bacterial 3-hydroxy fatty acids (3-OH-FAs) are abundant in stalagmites (Blyth et al., 2006; Huang et al., 2008; Wang et al., 2012, 2016) and are characteristic compounds of Lipid A, the lipid component of the lipopolysaccharides (LPS) located in the outer membrane of Gram-negative bacteria (Szponar et al., 2002, 2003; Wollenweber and Rietschel, 1990). Based on the strong relationships with environmental pH and temperature from an altitudinal transect of soils on Shennongjia Mountain, central China, a number of novel 3-OH-FA based proxies have been proposed (Wang et al., 2016). For example, the ratio of *anteiso* to *normal* C_{15} 3-hydroxy fatty acid (RAN_{15}) was propounded to be a novel temperature proxy, and the ratio of the total sum of *iso* (*i*-) and *anteiso* (*a*-) 3-OH-FAs to the total amount of *normal* (*n*-) 3-OH-FAs (Branching Ratio) and the negative logarithm of Branching Ratio (RIAN) were propounded to be novel pH proxies (Wang et al., 2016).

In this study we present inferred temperature and hydrological records, spanning the last 9 ka BP, based on 3-OH-FA derived proxies from a single stalagmite collected from Heshang Cave, central China (Fig. 1). This work is the first demonstration of the application of 3-OH-FA based proxies for paleoclimatic reconstruction and suggests that such approaches may be used to derive independent quantitative temperature and qualitative hydrological signals from an individual stalagmite.

2. Materials and methods

2.1. Sampling site and sample information

Heshang Cave is located at 294 m above sea level (a.s.l.), on the Qing River, a tributary in the middle reaches of the Yangtze River, central China (30°27′N, 110°25′E) (Fig. 1A). Heshang Cave is one of several caves which characterize the regional karst landscape. The overlying dolomite is ca. 400 m thick and is capped with a mature layer of soil (20-40 cm-thick) and reasonably dense vegetation (Fig. 1B). The regional climate is strongly impacted by the East Asian Monsoon, with a hot and moist summer, but relatively cold and dry winter (An, 2000). Regional average annual precipitation is 1161 mm, based on the recent 64 years (1951–2014) of meteorological data from Yichang station. The seasonal temperature ranges, inside and immediately outside the cave, were constrained by 2-h resolution logging between 2004 and 2007 using HOBO H8 Pro T loggers (Hu et al., 2008a). The modern temperature immediately outside the cave varies seasonally from 3 °C to 30 °C, with an annual average of 18 °C and is statistically identical to that of the nearest government meteorological station in Changyang county (Hu et al., 2008a). The annual mean temperature inside the cave is identical to the outside measurements. However, the amplitude of the internal temperature range is about one fifth of the external cycle and lags the external temperatures by about 10 days (Hu et al., 2008a). Heshang Cave extends a distance of ≈250 m, roughly horizontally from it's entrance (see Fig. 1C) and is well decorated with stalagmites, rimstone pools, and less frequent stalactites (including an exquisite 'Lotus Flower' stalactite).

The HS4 stalagmite is 2.5 m long, and was actively growing when collected from ca. 150 m within Heshang Cave in 2001 (Fig. 1C). It shows clear annual banding throughout its growth axis, generated by the strong seasonal cycle at this site (Johnson et al., 2006). Highlights of previous work on this stalagmite include a quantitative Holocene Asian monsoon rainfall record (Hu et al., 2008b) and high resolution 8.2 ka event record (Liu et al., 2013; Owen et al., 2016). The HS4 stalagmite was divided longitudinally into 4 sections. Each section was dedicated to a different branch of analyses (e.g. $\delta^{18}O$, trace elements, organic geochemistry etc.). 206 subsamples were taken from the organic geochemistry section along the stalagmite growth axis and 73 subsamples were selected at intervals for biomarker analysis. All the outer layers of the subsample were removed during sampling to avoid any potential contamination. Based on annual layering each sample has a resolution of several decades to >100 years.

In 2013 seventeen cave sediment samples were collected within Heshang Cave from the entrance to the deepest accessible part of the cave (Fig. 1C) and nine overlying soil samples were collected from the land-surface immediately above the cave (which slopes upwards from an altitude of 457 m–489 m) (Fig. 1B). The sediment inside the cave is oligotrophic with <6 g/kg total organic carbon (Gong et al., 2015).