

¹³C-LABELLED TMAH THERMOCHEMOLYSIS OF LIGNIN MONOMERS IN SPELEOTHEMS

Alison Blyth¹, Marine Quiers², Yves Perrette², Timothy Filley³

¹Curtin University, Perth, WA, Australia

²University of Savoy, Chambéry, France

³Purdue University, West Lafayette, Indiana, USA

Organic matter preserved in speleothems has been demonstrated to record fluctuations in palaeoenvironmental parameters including land use and vegetation regime, temperature, and microbial input (Blyth et al., 2016). However, although coherent records corresponding with known vegetation changes have been observed (Blyth et al., 2007; Blyth et al., 2011), satisfactory direct proxies for vegetation have yet to be fully formulated, especially given recent research demonstrating that previous assumptions in the field about *n*-alkane chain length and plant type can no longer be considered robust (Bush & McInerney 2013).

Analysis of lignin phenols in speleothems has been undertaken to a very limited extent, with the extremely small sample size and proportion of organic matter (0.01 – 0.3% of speleothem carbon) making analysis via conventional cupric oxidation methods challenging. Two studies using tetramethylammonium hydroxide thermochemolysis as an alternative approach demonstrated that recovery of compounds was possible, even in samples of up to 3 Ma in age (Blyth & Watson 2009; Blyth et al., 2010). However, this approach has a fundamental challenge in that TMAH thermochemolysis liberates compounds not only from lignin, but also from other macromolecules such as tannin. Due to the structural rearrangement and methylation of compounds during the analytical process this can result in compounds from different sources being superficially indistinguishable via GC-MS (Filley et al., 1999; Filley et al., 2006). To resolve this, ¹³C-labelled TMAH may be used in the reaction, as GC-MS will then be able to separate compounds that have been methylated during the analysis from those with a naturally occurring methyl group. Here we report the first results applying this approach in speleothems, using a speleothem time-series from France.

GC09B is a Holocene speleothem collected from the Garde-Cavale cave system in the French Prealps, and with an age range of 1-6 ka. This speleothem grows below a 30 m thick sandstone (Quiers et al 2015). Sub-samples of speleothem calcite were digested in 3M HCl, and the phenolic component was recovered by elution over a nonendcapped C18 solid phase extraction cartridge (IST Isolute). The concentrated organic sample was mixed with ¹³C labelled TMAH in a platinum sample boat, and analysed via Pyrolysis-GC-MS at Purdue University.

Although prior TMAH studies have recovered a range of phenolic compounds in speleothems, only two monomers definitively attributable to lignin were identified in all these samples – G6 (3,4-dimethoxy benzoic acid) and S6 (3,4,5-trimethoxy benzoic acid). In both cases, the compounds were dominated by tannin derived monomers, but a clear time series was seen in the proportion of lignin derived input, with G6 changing from a 30-44% lignin input in the upper part of the speleothem to 9-15% prior to 4 ka. S6 showed a less definite, but broadly opposite trend, with an increase in lignin input earlier in speleothem formation.

This preliminary study clearly shows that ^{13}C -labelled TMAH can be applied in speleothem samples, and clearly separate lignin and tannin derived inputs. The presence of coherent time-series trends is also encouraging in suggesting that useful palaeoenvironmental information can be recovered. The limited number of compounds extracted in this study is probably a function of the organic matter content of this specific speleothem controlled by the transfer of organic matter through the poorly karstified sandstone roof. Previous studies suggest that a greater range of compounds should be available in at least some other samples. However, although the technique looks to have substantial utility as part of multi-proxy analyses of organic matter in speleothems, we do not yet have data to suggest that it will serve as a direct vegetation proxy. We therefore suggest that this research should be taken forward by refining both TMAH and cupric oxide techniques in the speleothem context to maximise the range of information recoverable.

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