



Application of lignin analysis to flowstone, stalagmite and drip water samples – potentials of a new proxy

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Lignin oxidation products (LOPs) are widely used as vegetation proxies in lake sediment cores and natural waters and can be found in speleothems and cave drip water, too. They provide not only a quantitative vegetation signal, but also allow to differentiate between angiosperm and gymnosperm as well as woody and herbaceous plant sources.[1] Lignin is one of the main constituents of wood and woody plants. It is a biopolymer that mainly consists of three monomers, p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The proportion of these three monomers varies with the type of vegetation. To analyse the composition of lignin particles in speleothems, it is necessary to extract the speleothem samples, to digest the lignin polymer to split it into its monomeric oxidation products, and to enrich and quantify these LOPs.

In the method we are presenting here, speleothem samples are dissolved in hydrochloric acid and the acidic solution is extracted by solid phase extraction (SPE). Cave drip water samples are acidified and extracted by SPE, too. The resulting organic fraction is submitted to an alkaline cupric oxide oxidation using a microwave digestion system.[2] The LOPs are enriched by SPE and analysed by ultra-high performance liquid chromatography coupled to electrospray high resolution mass spectrometry (UHPLC-ESI-HRMS).

We applied this method to a 120 kiloyears old flowstone from Victoria Cave in Spain[3] to compare the vegetation signal of different interglacial periods, to a 200 years old stalagmite from Zoolithencave in Germany[4] to distinguish between periods of grassland and forest vegetation, and to cave drip water samples from a monthly monitoring project of Herbstlabyrinth-Advent Cave in Germany[5] to understand seasonal changes in the lignin input. The results were compared with $\delta^{13}\text{C}$ analysis. These different applications show the potentials and limitations of lignin analysis in speleothems for paleovegetation reconstruction.

References:

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