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Organic proxies in speleothems: analytical method and first data from cave KNI-51

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Speleothems are important archives for paleo environments thanks to their high temporal resolution and potential for precise and accurate dating. Organic biomarkers in speleothems are not widely explored because of low concentrations and high sample amount required to obtain detectable levels. The potential for paleoenvironmental reconstruction from organic molecules in speleothems is high, but low contamination and high sensitivity analytical tools are required to obtain well resolved and reliable records.

We developed a method for the analysis of fire-derived polycyclic aromatic hydrocarbons (PAHs) and n-alkanes in speleothems and applied it to aragonite stalagmites from cave KNI-51 in the central Australian tropics. These stalagmites have already been precisely dated by U/Th methods, and have detailed oxygen isotopic time series that provide a detailed record of past Australian monsoon rainfall variability [1].

The characteristics of the cave make it suitable for this research, thanks to the considerably high growth rates of the stalagmites (1-2 mm yr-1), that allow analysis at an ∼annual resolution. In addition, cave KNI-51 is shallow, contained within highly permeable rillenkarren limestone, and overlain by extremely thin, carbon-poor soils. Thus, the sequestration, biodegradation, or mobilization of PAHs and n-alkanes in soils and bedrock are minimized, allowing them to be easily transported from the surface to the stalagmite. In order to check for the risk of contamination of the aragonite layers during flooding episodes, we also analyzed sediments from above and inside the cave. Results show that flood sediments do not bias our analyses of carbonate material.

With respect to the few existing methods for PAH analysis in speleothems [2, 3], some substantial modifications were made to the pre-analytical phase, all of which were aimed at increasing the analytical signal: our analytical protocol allows detection of analytes in stalagmites at the ng to sub-ng level by guaranteeing the lowest contamination. Samples are drilled from pre-cleaned stalagmite slabs, dissolved in HCl at low temperature, solvent-extracted and volume reduced in a class 10,000 organic cleanroom. 19 different 2- to 6-ring PAH compounds and 26 n-alkanes (C10-C35) were analyzed and quantified by GC-MS.

Preliminary results suggest increased fire activity in the mid-15thcentury, marked in particular by the presence of fluoranthene, pyrene, benzo(e)pyrene and indeno(1,2,3-c,d)pyrene. Only high molecular weight n-alkanes in the range C23-C32 had significant concentrations in most samples, showing no marked odd-even predominance, likely indicating the presence of another source beside plant residues in soil.

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