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Application of novel trace analysis methods for lignin and levoglucosan in flowstone samples from New Zealand during the Holocene

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Speleothems are secondary mineral deposits found in caves. They can grow continuously over 1,000-10,000 years and the ^{230}Th/U method allows accurate dating back to 500,000 years.[1] Stable conditions in caves preserve organic matter, making speleothems highly valuable climate archives. The high interest in expanding the range of organic proxies in speleothems requires highly sensitive analytical techniques. Novel trace analysis methods for lignin and levoglucosan in speleothems were established according to principles of "Green Chemistry" [2] and applied to flowstone samples from different caves in New Zealand during the Holocene.

Lignin is the second most abundant biopolymer after cellulose. It consists of three monomers, which are included into the polymer in different ratios, depending on the type of vegetation. It is found in speleothems and quantification in timely consecutive layers allows drawing conclusions on changing types and amount of vegetations above the caves, which are influenced by climate conditions like temperature and rainfall.[3] To analyse the monomeric composition, lignin has to be degraded by an alkaline oxidation. Thereby the monomers are oxidized into lignin oxidation products which are then analysed by uHPLC-ESI-HRMS. To date, lignin degradation was conducted using Cu(II)O as a catalyst, which was replaced by $CuSO_4$, eliminating the solid, toxic Cu(II)O waste, and highly reducing the amount of artefacts and used chemicals during sample preparation. The new method was successfully applied to the flowstone samples but posed further questions on the transport of lignin through the soil into the speleothem.[4],[5]

The other proxy of interest was levoglucosan, an anhydrosugar formed by cellulose combustion. For temperature studies in speleothems carbon isotopes are used which can be influenced by e.g. fire events. Therefore, it is necessary to introduce a proxy, which prevents falsely positive or negative temperature trends. Extraction of levoglucosan was conducted using graphitized carbon black and chromatographic separation by a hydrophilic interaction liquid chromatography, using a post-column flow to increase the ionization efficiency in the ESI ion source. Levoglucosan analysis was introduced into the existing workflow, without interfering with lignin analysis, and thereby a multi-proxy approach was developed. This work showed that levoglucosan is present in speleothems in quantifiable amounts. It was detected in two of the study sites, showing no correlation to lignin. A plant-based origin of levoglucosan was ruled out, suggesting a fire-related

entry into the speleothem.

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