Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.16709

Insights into the variability of speleothem organic carbon isotopic composition

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Speleothems are a valuable paleoenvironmental archive, and have provided several iconic reconstructions of past climate conditions. Here we explore the potential of organic carbon incorporated in trace amounts in speleothems to act as a sensitive tracer for surface ecosystem conditions. We present first applications of a method developed for the extraction and isotopic characterisation (d13C and 14C) of speleothem organic carbon.

The development and application of proxies based on organic compounds in speleothems have been hampered in the past by the low concentrations of speleothem organic matter and the high potential for contamination during handling and sample processing. Here we use a method based on wet chemical oxidation, which allows us to work with small sample amounts (80-150 mg CaCO3) and results in demonstrably low blank contaminations. Carbonate sample chips are pre-cleaned and digested in acid, after which the samples are decarbonated by flushing with He. In a second step, the non-purgeable organic carbon (NPOC) fraction of the sample is released as CO2 through wet chemical oxidation and can be analysed via mass spectrometry.

Previous iterations of the method have shown that the acid digestion step preceding the wet chemical oxidation often results in incomplete decarbonation of the samples, which impacts the final isotopic value. Moreover, significant challenges remain concerning the contamination potential. Here we present results from a series of quality assessments and following improvements to our laboratory protocols that have significantly improved the reproducibility and accuracy of our results.

Moreover, we show preliminary results from a set of globally distributed, modern speleothem samples, and compare their NPOC 14C values to surface ecosystem types, soil age and other climatic and environmental factors. This gives us a first glimpse into the potential of this tracer to act as a proxy for surface ecosystem conditions.