

Annual-scale chemical cyclicality in speleothems

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Over the past decade there has been enormous progress in establishing the characteristics of speleothems that form on an annual scale. Distinct lamina types, such as seasonal couplets, or discrete infiltration laminae, are characteristic of certain geomorphic-climatic settings. Chemical laminae on this scale either map onto the physical lamination, or can be present even in the absence of a visible layering. Whereas laminae on the scale of $>250\ \mu\text{m}$ can potentially be routinely physically sub-sampled for analysis at a sub-annual scale, most speleothems grow more slowly than this, and micro-analytical techniques are required. For trace element work, laser-ablation ICP-MS, ion microprobe and synchrotron micro-X-ray fluorescence analysis have proved the most significant in demonstrating the form of annual profiles. For stable isotope work, ion microprobe analysis can resolve seasonal changes in speleothem $\delta^{18}\text{O}$ composition related to changes in composition of infiltrating dripwater.

The primary goal of the high-resolution analytical studies has been to develop speleothems as climatic proxies, but along the way some interesting discoveries are being made about CaCO_3 geochemistry. It has also been useful to consider cave environments as systems which exchange heat, water and gaseous phases. The processes of water supply to caves and their air exchange are more closely linked than is first apparent and a key challenge is to understand how climatic factors are mediated by them. The seasonal temperature cycle is usually felt only indirectly by its impact on air circulation (and hence PCO_2) and on the seasonal growth and die-back of vegetation. Seasonal rainfall patterns, variable moderated by karstic storage, can also be identified.

Where rainfall is strongly seasonal, many sites show a strong tendency for degassing and calcite precipitation to occur prior to (upflow of) the site of deposition of a speleothem. In principle this leads to seasonal covariations in Sr, Mg and $\delta^{13}\text{C}$ and where it occurs, longer-term covariations can also be ascribed to changing levels of aridity. Individual drips may also have characteristic enrichments in certain trace elements at low flow. In contrast, it is now clear that a characteristic group of elements (e.g. P, Pb, Y) are enriched at high flows, in cases where they coincide with seasonal die-back of vegetation and transport of elements in colloidal form. S has the potential to act as a marker for seasonal changes in pH, related to PCO_2 . Seasonal resolution of $\delta^{18}\text{O}$ is crucial in regions where there is a clear link to modes of atmospheric variability. Simple transfer functions for e.g. rainfall are possible in some cases, but qualitative climate proxies are more realistic in general.