



Speleothem crystallization mechanisms and implications for the incorporation of climate proxies

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Pathways of calcite crystallization in speleothems are still poorly understood, despite their importance in the incorporation of climate-sensitive proxies.

Precipitation experiments carried out in caves from the South Pacific to the Italian Alps investigated by high resolution Transmission Electron Microscopy (HR-TEM) and high-resolution Synchrotron-Radiation based micro X-ray fluorescence revealed that many possible pathways of crystallization comprising classical ion-mediated, particle-mediated and formation of unstable phases (such as vaterite) are operating. These diverse pathways influence crystal morphology, micro and nano-porosity, and incorporation of trace elements into the final speleothem fabric. Micrometer-sized aggregates incorporate colloids with their bound trace elements in between the nano-crystals that constitute each aggregate. The consequence is that the thermodynamics partition coefficient concept cannot be applied to colloidally bound trace metals. Having intrinsic nano-porosity, or intrinsic thermodynamics instability, the products of the initial growth stages have potential to drive post-depositional transformations with consequences on the preservation of the original chemical and physical signals. Therefore, fabrics visible under the microscope may already be an early diagenetic product, whilst the original fabric may still be detectable by microstructural investigations.