



Evaluation of the climate significance of chemical signals in Tropical speleothems by using fabrics criteria: a case study from the Cook Islands

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Crystallization pathways are at the core of incorporation of chemical species by calcium carbonate minerals. This is particularly important in speleothems where the classical equilibrium precipitation approach and the theoretical partition coefficient are not always applicable. In fact, in several speleothems non classical nucleation plays an active role and an empiric “speleothem enrichment factor” better describes the incorporation of different chemical species.

Here we present the first attempt to calibrate chemical parameters on the base of speleothem fabrics for active and Late Holocene stalagmites taken from two caves in Atiu, Cook Islands. Our multi-proxy analysis integrates high-resolution petrography, trace element and stable isotope analysis of stalagmites characterised by growth rates ranging from 20 up to 1000 $\mu\text{m}/\text{yr}$, which have been dated by U-Th series and lamina counting.

In-situ calcite farming experiments yielded calcite crystals of the order of ten nanometer from the slow drips, whereas colloidal calcite particulate (2-3 nm crystals) associated to organic and inorganic colloids formed from the fast drips. Fast/variable and slow/constant drip rate end members generate active forming stalagmite fabrics with fast growing opaque open/porous calcite and translucent compact columnar calcite respectively. In the compact fabric soluble species are incorporated within the calcite lattice, whilst OM colloids are expelled or isolated in the crystal defects. This allows using a partition coefficient for soluble elements, but not for elements adsorbed on colloids. In the open/porous fabric calcite crystals seem to grow by attachment of particles and there is a large number of sites where colloids, particulate and even solute elements can be adsorbed and incorporate outside the calcite lattice. This results in an enhanced incorporation of trace elements and thus, the theoretical partition coefficient cannot be utilized to reconstruct the original chemistry of the dripwater.

In two Late Holocene stalagmites LA-ICP-MS analyses reveal specific patterns in the elemental distribution. Most of the solute elements (Mg, Sr, Ba, Na) show a positive covariance and can be potentially be utilized as palaeo-hydrological proxy. This is corroborated by the negative correlation with colloiddally transported elements such as Y and P, and the general trend of $\delta^{13}\text{C}$ that is consistent with Mg and Sr. During wet condition (low Mg and Sr), $\delta^{13}\text{C}$ shifts toward more negative values (down to -11‰). In contrast, dry conditions are characterised by less negative $\delta^{13}\text{C}$ and higher concentration of Mg and Sr suggesting the influence of kinetic effects and/or evapotranspiration. However, the higher incorporation of solute elements during dry phases is further enhanced in the open/porous fabric and a fabric-specific elemental enrichment factor has to be taken into account.