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Partitioning of trace metals in cave (and cave-analogue) carbonate precipitates – towards a quantitative hydrological proxy in stalagmites

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Speleothems (secondary cave carbonate deposits) are particularly valuable for studying past climates over a range of temporal and spatial scales, owing to their continuous growth and exceptional viability for radiometric dating. However, the interpretation of many speleothem-based palaeoenvironmental proxies (e.g., stable isotope ratios $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) in terms of particular environmental or climatic controls remains challenging, and is typically limited to qualitative reconstructions of past environmental conditions and dynamics.

In this study, we develop a novel class of quantitative hydrological proxies by exploring the kinetic behaviour of a suite of first-row transition metals (e.g., Ni, Cu, Co) found in stalagmites. The transport of these elements from the surface to the cave is strongly controlled by the binding to natural organic matter (NOM) present in infiltrating waters. The rate of dissociation of such metal-NOM complexes at the dripwater-stalagmite interface has recently been suggested to determine the availability of these elements for the incorporation into precipitates (Hartland & Zitoun, 2018). The link between NOM-complex dissociation and metal availability for deposition presents an opportunity to quantitatively relate respective carbonate metal concentrations to the time available for complexes to disintegrate and release metals within the thin water films on stalagmite surfaces.

We present preliminary analyses assessing trace metal kinetics and partitioning in monitored natural cave settings, as well as cave-analogue experimental setups. Our findings demonstrate the contrasting controls on the concentrations of different elements in speleothems, and highlight the potential for kinetically-limited elements in stalagmites to enable quantitative estimations of past hydrological variability.

References:

Hartland, A., Zitoun, R. (2018) Transition metal availability to speleothems controlled by organic binding ligands. *Geochem. Persp. Let.* 8, 22–25.