



Towards a quantitative proxy of cave dripwater hydrology

Adam Hartland (1), Chaoyong Hu (2), Gabriel Enge (3), Rebecca Zitoun (4), Niklas Lehto (5), Mahdiyeh Salmanzadeh (1), Beth Fox (1), Anthony Dosseto (3), and Sebastian Breitenbach (6)

(1) School of Science, University of Waikato, New Zealand, (2) China University of Geosciences, Wuhan, China, (3) Wollongong Isotope Geochronology Laboratory, School of Earth & Environmental Sciences, University of Wollongong, (4) Chemistry Department, University of Otago, New Zealand, (5) Faculty of Agriculture and Life Sciences, Lincoln University, New Zealand, (6) Ruhr-Universität Bochum, Geology, Mineralogy & Geophysics, Sediment- and Isotope Geology, Bochum, Germany

Speleothems capture a wide range of geochemical signals related to hydroclimate variability. However, the quantification of climatic parameters (e.g. rainfall, temperature) using traditional proxies is hampered by the multitude of influencing factors.

The goal of this research is to develop new quantitative records of past rainfall by examining a novel set of geochemical processes recorded in speleothems. By applying techniques from environmental chemistry (voltammetry, diffusive gradients in thin films (DGT)) and geochemistry (stable metal isotope analysis) we aim to unravel the evolution of dripwater hydrochemistry within the soil and epikarst— a domain where percolation flow dissolves CO₂, mobilises soil organic matter and approaches equilibrium with the host rock— from processes occurring at the solution-crystal interface. With the advent of new proxies (e.g. $\delta^{44}\text{Ca}$) for bedrock dissolution and prior calcite precipitation (PCP), we can now delineate the evolution of dripwater along its aquifer flowpath, making tractable the study of more subtle processes operating at the speleothem growth surface. Here we present the results of an ongoing, interdisciplinary effort to constrain the effect of metal-ligand interactions and PCP on trace metals in dripwater and speleothems from two caves in New Zealand and China with a view to developing an independent proxy of past drip rate variability.

DGT data from Heshang drip point HS4 demonstrate that Mn and Cu form complexes with organic ligands with slow dissociation rates. We hypothesise that this process should lead to the increased availability of Cu and Mn ions to substitute into speleothem calcite at times of slower dripping. This was confirmed by analysis of Cu and Mn through the 8.2 kyr event in the HS4 stalagmite which the $\delta^{44}\text{Ca}$ data of Owen et al. EPSL (2016) has shown to be a period of notable aridity. PCP appears to be a confounding factor for the trace metals of interest, with stable Cu isotope data through this interval ($\delta^{65}\text{Cu}$) also confirming the strong influence of PCP on Cu in this system. Further experimental work aims to expand our understanding of PCP and metal-ligand interactions on the evolution of Cu and Ca isotope ratios as we seek to delineate these distinct karst aquifer hydrochemical processes.

References

Owen, R.A., Day, C.C., Hu, C.-Y., Liu, Y.-H., Pointing, M.D., Blättler, C.L., Henderson, G.M., 2016. Calcium isotopes in caves as a proxy for aridity: Modern calibration and application to the 8.2 kyr event. *Earth Planet. Sci. Lett.* 443, 129–138. doi:10.1016/j.epsl.2016.03.027