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Cave speleothem growth response to external weather from continuous cave atmosphere (CO2) and drip-water chemistry (DIC) isotopic measurement

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Long records of past climate are possible to interpret from isotopic and trace element abundances in speleothems. Whilst there are many good qualitative speleothem palaeo-climate records a universal quantitative transfer function from external weather / climate to speleothem record is elusive. Studies of cave environments and speleothem growth are an important step towards quantitative speleothem palaeo-climate interpretation. Net accumulation of $CaCO_3$ (speleothem growth) requires a perturbation to Gas-Aqueous-Solid equilibrium conditions in the cave environment (Aq. chem., T, P, pCO_2). The largest equilibrium change in a ventilated cave environment causing speleothem growth is fluctuating pCO_2 as a response to the cave air exchange, driven by external temperature.

Continuous CO_2 monitoring records from different caves at Jenolan (NSW, Australia) show different ventilation patterns ranging from slow drainage at week-month long time scales (Temple of Baal) to large diurnal fluctuations (Katie's Bower) dependent upon the configuration of cave openings. Seasonal differences are also apparent at Katie's Bower with summer peak CO_2 reaching 5,000 ppm compared to a winter range from 400 ppm up to 1,000 ppm.

An intense 3-week field campaign in May 2008 (winter) using an FTIR spectrometer continuously measured (5 min) trace gases (CO_2, CH_4, N_2O) H_2O and $\delta^{13}C_{CO2}$. Simultaneous drip-water pH, air flow, temperature, pressure, and relative humidity was logged by sensors in the cave together with external rainfall, temperature, pressure, and relative humidity. Drip water was sampled twice daily, coinciding with CO_2 maxima and minima, for dissolved inorganic carbonate DIC, $d^{13}C_{DIC}$, dissolved organic carbonate DOC, $\delta^{13}C_{DOC}$, alkalinity, anions, and cations. Further spot samples were taken for drip-water stable isotopes, $^{14}C_{DIC}$, and ^{3}H.

At Katie's Bower with a strong ventilation pattern speleothem growth rate varies through the diurnal cycle (coupled pH – airflow – CO_2) and between seasons. Low pCO_2 in the morning cave air causes rapid speleothem growth with CO_2 exsolved to the cave atmosphere lowering drip-water pH. pCO_2 increases to an evening maxima and slows speleothem growth before early morning T induced ventilation decreases pCO_2. $\delta^{13}C_{CO2}$ has an antithetic relationship with CO_2, with low pCO_2 morning air the highest $d^{13}C_{CO2}$ at -8 ‰ PDB. A Keeling analysis of end-member component mixing reveals the proportion of external air drawn into the cave and CO_2 produced from speleothem formation through the diurnal cycle. Drip-water $\delta^{13}C_{DIC}$ remains constant at -5 to -6 ‰ PDB throughout the winter experiment suggesting CO_2 is not re-dissolving into drip-water to dissolve speleothems nor complicate interpretation of speleothem $\delta^{13}C$ palaeo-climate records. Summer speleothem growth may have a different $\delta^{13}C$ incorporation pattern from a higher diurnal peak CO_2 (up to 5000 ppm).