

O and C isotopes in calcite grown under cave-analogue conditions – response to changing saturation state

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We report oxygen and carbon isotope data from a series of carbonate growth experiments in cave-analogue conditions, in the laboratory, with the goal of better understanding these isotope systems, which are fundamental to speleothem research and for reconstructing change within the critical zone. The experimental setup closely mimics natural processes (e.g. precipitation driven by CO_2 -degassing, low ionic strength solution, thin solution film) but with a tight control on growth conditions (temperature, pCO_2 , drip rate, calcite saturation index and the composition of the initial solution). Calcite is dissolved in deionized water in a 20,000 ppmV pCO_2 environment, with trace-elements (Li, Na, Mg, Co, Sr, Cd, Ba, U) at appropriate concentrations to mimic natural cave dripwaters. This solution is dripped onto glass plates (coated with seed-calcite) for controlled stalagmite growth [1, 2].

In these experiments, cave-analogue calcite is grown at six different solution calcite saturation indices ($SI_{\text{calcite}} = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$). All other conditions are kept constant (temperature 15°C , drip rate 6 drips min^{-1} , cave $pCO_2 < 1000$ ppm).

For oxygen, we observe a significant increase in $\alpha_{\text{calcite-water}}$ with calcite saturation index, with increasing α bracketing one of the most commonly used fractionation factors [3]. These results are significant within the current debate over the range and applicability of fractionation factors (eg. [3, 4, 1]). There is no significant change in $\delta^{13}\text{C}_{\text{calcite}}$. We use the controlled conditions of this laboratory setup to discuss the significance of this response to calcite saturation state and to gain a better understanding of the underlying fractionation mechanisms.

[1] Day, C.C., & Henderson, G.M. 2011. Oxygen isotopes in calcite grown under cave-analogue conditions. *Geochimica et Cosmochimica Acta*, **75**, 3956–3972. [2] Day, C.C., & Henderson, G.M. 2013. Controls on trace-element partitioning in cave-analogue calcite. *Geochimica et Cosmochimica Acta*, **120**, 612–627. [3] Kim, S.T., & O’Neil, J.R. Equilibrium and non-equilibrium oxygen isotope effects in synthetic carbonates, *Geochimica et Cosmochimica Acta*, **61**, 3461–3475. [4] Coplen, T.B., Calibration of the calcite-water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory. *Geochimica et Cosmochimica Acta*, **71**, 3948–3957.