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Li isotopes in calcite grown in cave-analogue conditions – speleothem Li as a proxy for localized weathering

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We report D(Li) and $\alpha^{7}_{calcite\text{-}water}$ data from carbonate growth experiments in cave-analogue conditions, in the laboratory, with the goal of characterising Li-response to changes in temperature and calcite saturation index. Li isotopes respond significantly to weathering (e.g. [1]) and speleothem-Li is showing great promise for reconstructing local silicate weathering variation over short timescales, such as during glacial cycles [2]. To further advance speleothem-based weathering reconstruction, we calibrate the response of Li in speleothem calcite to temperature and saturation state changes.

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 drip-waters. This solution is dripped onto glass plates for controlled stalagmite growth [3, 4]. Here, calcite is grown at four temperatures (7, 15, 25 and 35°C) and three calcite saturation indices ($SI_{calcite}$ = 0.1, 0.2, 0.6).

We observe D(Li) decreasing with temperature and insignificant change in $\alpha^{7}_{calcite\text{-}water}$ with temperature or saturation state. This is significant in ensuring that weathering signals are recorded in speleothems. In addition we discuss multi-proxy approaches for improved constraints on the causes (e.g. temperature or rainfall) of weathering changes.

[1] Dellinger et al. 2015. Riverine Li isotopic fractionation in the Amazon River basin controlled by the weathering regimes. *Geochimica et Cosmochimica Acta*, **164**, 71–93. [2] Philip A.E. Pogge von Strandmann et al. (in review). Lithium isotopes in speleothems: Temperature-controlled variation in silicate weathering during glacial cycles. EPSL. [3] Day, C.C., & Henderson, G.M. 2011. Oxygen isotopes in calcite grown under cave-analogue conditions. *Geochimica et Cosmochimica Acta*, **75**, 3956–3972. [4] Day, C.C., & Henderson, G.M. 2013. Controls on trace-element partitioning in cave-analogue calcite. *Geochimica et Cosmochimica Acta*, **120**, 612–627.