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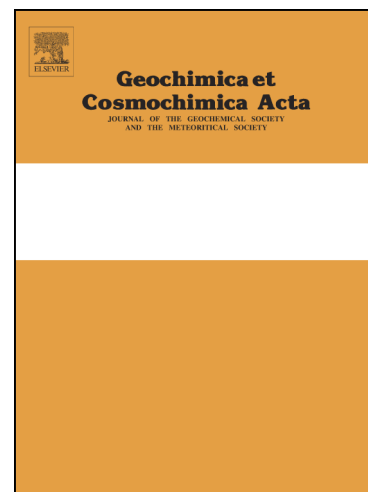
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Controls on trace-element partitioning in cave-analogue calcite

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Abstract

We report trace-element data from a series of carbonate growth experiments in cave-analogue conditions in the laboratory with the goal of better understanding environmental controls on trace-element incorporation in stalagmites. 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 (coated with seed-calcite) in a lower pCO_2 environment at 7, 15, 25 and 35°C and drip rates of 2, 6 and 10 drips per minute. $D(Sr)$ was shown to be statistically invariant over the full range of temperature and growth rate studied. No relationship between Sr/Ca and growth rate is therefore expected in stalagmite samples over comparable growth rates. $D(Mg)$ has a relationship with temperature defined by $D(Mg) = 0.01e^{0.02[\pm 0.006]T}$, but temperature is not expected to be the dominant control on Mg/Ca in cave calcite due to the larger impact of calcite precipitation on Mg/Ca . Over short timescales, in conditions where temperature is well buffered, the fraction of calcium remaining in solution (f) is likely to be the dominant control on Mg/Ca and other trace-element ratios. But differences in the response of trace-elements to f and T may allow their combined use to assess past cave conditions. High $Cd/Ca_{stalagmite}$ is particularly indicative of low amounts of prior calcite precipitation and Cd/Ca would be a useful addition to trace-element studies of natural stalagmites. Significant scatter is observed in trace-element ratios during the laboratory experiments, which cannot be explained by simple Rayleigh distillation. This scatter is well explained by solution mixing and by the mixing of calcite with different fractions of calcite growth. Accounting for the effects of mixing on trace-element concentrations or ratios may help to achieve more robust interpretations of stalagmite chemistry as part of a multi-proxy approach to assessment of past environments.

Keywords: trace-element partitioning, stalagmite, speleothem, palaeoclimate proxy, palaeoclimate

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