

## **Influence of isotopic re-equilibration on speleothem and fluid inclusion isotope ratios after primary calcite precipitation**

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Oxygen isotope ratios in speleothems (notably stalagmites) have been used since decades to successfully infer paleotemperatures and deduce paleo-environmental information. In addition, recent technical developments allow to increasingly use fluid inclusions as an archive for drip-water and together with the surrounding calcite as paleothermometer.

A basic requirement for isotope data interpretation is the complete knowledge of the fractionation between calcite and fluid. Most laboratory and in-situ cave experiments focus on calcite growth and the isotope fractionation between calcite and feed solution. Potential isotope exchange and re-equilibration processes after the initial deposition have mostly been neglected. However, experiments of Oelkers et al. (2015) showed that the isotope exchange between minerals and fluid can proceed rapidly (within days), even at chemical equilibrium. In hydrous Mg carbonates a similar process of continuous isotope exchange between carbonate and fluid was observed after the carbonate precipitation was completed (Mavromatis et al., 2015). These observations suggest that the isotope ratios of speleothem calcite may be affected by this continuous exchange, likely driving the isotope composition continuously towards equilibrium at the respective cave conditions. In addition, fluid inclusions are suspected to be sensitive to an isotope exchange with the surrounding carbonate highlighting the need to precisely understand and quantify this effect.

We assessed the oxygen isotope exchange between calcite and solution at chemical equilibrium conditions with theoretical estimates and laboratory experiments over an intermediate time scale (hours-weeks). A large isotope gradient ( $\sim 20\text{‰}$ ) between solution and calcite was prepared in the experiment to investigate the dynamics of this re-equilibration process. We used a theoretical model based on a Rayleigh fractionation approach and the direct comparison with the experiment to determine quantitative estimates of oxygen isotope exchange rates and to infer the dimension of the actively participating molecular layer at the surface of the calcite mineral.

### References:

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Oelkers, E. H., Berning, U.-N., Rinder, T., Mavromatis, V., Perez-Fernandez, A., Pogge von Strandmann, P., 2015. Rapid isotopic fractionation among minerals and fluids during dissolution, precipitation, and at equilibrium. *Goldschmidt abstracts*, 2318.