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Stable carbon and oxygen isotope fractionation processes during speleothem growth: systematic investigation in novel laboratory experiments

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The most widely applied climate proxies in speleothems are stable carbon and oxygen isotopes (δ^{13}C and δ^{18}O). The interpretation of the stable isotope signals in terms of past temperature and/or precipitation variability is complex because both δ^{18}O and δ^{13}C depend on a complex interplay of various processes occurring in the atmosphere, the soil and karst above the cave and inside the cave. Quantitative reconstruction of climate parameters such as temperature and precipitation has, thus, remained impossible so far.

Here we present several novel laboratory experiments aiming to understand the basic physical and chemical processes affecting the δ^{18}O and δ^{13}C signals during precipitation of calcium carbonate on the stalagmite surface. In particular, we aim to quantify the influence of kinetic isotope fractionation and verify recently published modelling studies (Dreybrodt, 2008; Scholz et al., 2009, Dreybrodt and Scholz, 2011).

Several experiments are conducted:

1. Degassing of CO_2 from a thin film of water sparged with CO_2 flowing down an inclined glass plate. pH and electric conductivity are systematically documented in order to monitor degassing of CO_2. The results show that degassing of CO_2 is fast, and the pCO_2 of the solution is in equilibrium with the atmosphere after a short distance of flow.

2. Carbon isotope exchange between atmospheric CO_2 and dissolved bicarbonate. The results show that carbon isotope exchange may have a significant effect on the δ^{13}C value of the dissolved bicarbonate and, thus, speleothem calcite, in particular for slow drip rates.

3. Degassing of CO_2 and calcite precipitation from a thin film of water supersaturated with respect to calcite flowing down an inclined calcium carbonate plate. Drip water is sampled after different lengths of flow path and, thus, different residence times on the plate, and pH, electrical conductivity and the stable isotope composition of the water are determined. Decreasing conductivity with increasing distance of flow path documents precipitation of calcium carbonate. We observe progressively increasing δ^{13}C and δ^{18}O values with increasing distance of flow in agreement with the model predictions.

4. Calcite precipitation from a thin film of water supersaturated with respect to calcite flowing down an inclined glass plate. The precipitated calcite shows a clear enrichment in both δ^{13}C and δ^{18}O, and the absolute values are in good agreement with the stable isotope values of the dissolved bicarbonate (see experiment 3).

References

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