The effect of prior calcite precipitation (PCP) on the determination of the isotope fractionation factor $^{18}\alpha_{calcite/H_2O}$ based on speleothems

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During the last years, several studies have calculated the oxygen isotope fractionation factor between water and calcite ($^{18}\alpha_{calcite/H_2O}$) based on the $\delta^{18}O$ values of speleothem calcite and the corresponding drip water samples. All studies found that the widely used fractionation factor, $^{18}\alpha_{calcite/H_2O}$, of Kim and O'Neil (1997) underestimates oxygen isotope fractionation during the precipitation of calcite.

Here we present a conceptual idea to explain the observed deviation between speleothem-based fractionation factors and the experiments carried out by Kim and O'Neil (1997). In case of prior calcite precipitation (PCP) before the drip water reaches the stalagmite top (which is very likely for the majority of drip sites), the $\delta^{18}O$ value of the dissolved HCO_3- increases due to isotope fraction effects caused by progressive calcite precipitation resulting in isotopic disequilibrium with respect to the $\delta^{18}O$ value of H_2O. This isotopic disequilibrium may be balanced by oxygen isotope exchange between H_2O and HCO_3-, which results in a re-equilibration between HCO_3- and H_2O. However, the degree of re-equilibration strongly depends on the re-equilibration time.

If the oxygen isotope equilibrium between HCO_3- and H_2O has been disturbed by PCP (e.g., in karst fractures or on the surface of stalactites above the stalagmite) and oxygen isotope re-equilibration has not been completed prior to the formation of a speleothem, the $\delta^{18}O$ value of the precipitated calcite will be larger than expected for isotope equilibrium between HCO_3- and H_2O. Thus, if $^{18}\alpha_{calcite/H_2O}$ is calculated from such a calcite sample (e.g., collected from a watch glass deposited inside a cave or from the tip of a stalagmite) and the corresponding drip water, the reconstructed $^{18}\alpha_{calcite/H_2O}$ value will be larger than the true equilibrium value. This idea is supported by laboratory experiments, which show that the $\delta^{18}O$ values of both HCO_3- and calcite increase during progressive calcite precipitation, mimicking PCP. Thus, drip sites showing PCP are not appropriate for the determination of equilibrium $^{18}\alpha_{calcite/H_2O}$ values.