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Carbon isotope exchange as a possible process to explain decreasing d13C values along stalagmite growth layers

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Hendy tests, i.e. C and O isotope measurements performed on $CaCO_3$ drilled along individual growth layers of speleothems, are an often used approach to check for non-equilibrium isotope fractionation processes during CO_2 degassing and $CaCO_3$ precipitation when water is running down the stalagmite flank. Published data of Hendy tests and laboratory and cave experiments, where the evolution of the C and O isotopic composition of $CaCO_3$ was investigated on glass plates or along glass channels showed that $\delta^{13}C$ and $\delta^{18}O$ values remained either constant or increased. An increase in the C and O isotope composition along the growth layer is usually regarded as evidence of disequilibrium isotope fractionation. Constant C and O isotope values are interpreted to reflect carbonate precipitation near isotopic equilibrium.

Here, we investigated the stable C and O isotope composition along individual growth layers of a Holocene stalagmite from the Swiss Alps. Unexpectedly, individual Hendy tests reveal decreasing $\delta^{13}C$ values from the center to the edge of the stalagmite. This decrease in $\delta^{13}C$ along growth layers is opposite to what is expected from Rayleigh fractionation processes. To our knowledge, such a decrease was never reported. Given that the $\delta^{18}O$ measurements do not show this pattern - all Hendy tests show constant or slightly increasing $\delta^{18}O$ values along growth layers - we suggest that the decrease in $\delta^{13}C$ is caused by carbon isotope exchange processes between the dissolved inorganic carbon and the CO_2 of the cave atmosphere.