High-resolution spatiotemporal pH monitoring of coupled CO_2 degassing and $CaCO_3$ precipitation dynamics

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In situ monitoring of chemical and physical parameters of drip sites in caves (or groundwater seepage in tunnels) allows for an advanced understanding on the controls of carbonate precipitation dynamics. The pH can be used as key parameter to trace varying CO_2 degassing and saturation states with respect to $CaCO_3$ in aqueous media. Due to rapid CO_2 degassing of drip water reaching the cave or tunnel atmosphere, and slow drip rates, pH measurements using conventional (electrode based) methods, can be altered towards higher pH within seconds. Thus, a precise and immediate pH measurement is crucial to determine the prevailing $CaCO_3$-CO_2-H_2O processes, i.e. reaction kinetics, isotope fractionation, and the occurrence of intermediate carbonate phases. Furthermore, it may allow to distinguish between site-specific and more general climate related signals. In the present study novel optical pH sensors with an integrated sensing layer containing pH sensitive dyes are applied in order to quantify and visualize spatial pH distributions of simulated and real-life drip water forming speleothems with high-temporal and spatial resolution. Preliminary results in flow path simulating laboratory experiments that use multiple pH sensors show a standard deviation of only ± 0.1–0.01 for pH and a good reproducibility of the measurements under restrictive conditions with a water film thickness of < 1 mm and slow flow rates of ~1.5 cm/s. As the pH sensors are suitable for even thinner water films of ~0.1 mm, their applicability was tested in Katerloch Cave, producing pH profiles along the flow path of an active stalagmite. The data of the pH sensors reflect the prevailing CO_2 degassing dynamics, which was also supported by hydrochemical analysis using spatiotemporally resolved fluid sampling with glass capillaries containing volumes between 100 to 200 µl.