Monitoring of Cave Air CO_2 Using High Temporal Resolution Isotope Ratio Infrared Spectroscopy

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The formation of speleothems in the cave is a complex geochemical process dependent on various hydrological and environmental conditions. Using stable isotopes as a paleoclimate proxy is a challenge due to the multitude of fractionation processes. It is of utmost importance to understand and possibly quantify mechanisms in the cave that are influencing speleothem precipitation. The environmental process that is considered to be crucial for the equilibrium carbonate precipitation is the spatial and temporal variability of CO_2.

To better characterize cave ventilation patterns, monitoring of pCO_2 , $\delta^{13}C$ and $\delta^{18}O$ in cave air at high temporal resolution (up to 1 s) was performed in Spannagel Cave, a high-alpine cave system in the Zillertal Alps, Austria. A Thermo Scientific Delta Ray Isotope Ratio Infrared Spectrometer was installed in a chamber ca. 100 m behind the cave entrance. The air temperature was independently monitored inside and outside the cave.

The data show two distinct patterns in terms of CO_2 concentration and its isotopic composition, which are closely coupled with the temperature difference between the cave interior and the outside atmosphere. This gradient controls the direction of air flow in the cave on a seasonal to synoptic timescale (chimney-type ventilation). The summer circulation is characterized by CO_2 closely resembling atmospheric values (pCO_2 = 399 ± 12 ppm, $\delta^{13}C$ = -8.5 ± 0.7‰, $\delta^{18}O$ = 8.1 ± 2.5 ‰). The winter circulation mode features generally higher CO_2 concentrations and lower isotopic compositions (pCO_2 = 409 ± 14 ppm, $\delta^{13}C$ = -10.1 ± 0.7 ‰, $\delta^{18}O$ = 2.3 ± 1.5 ‰).

The high temporal resolution of stable isotope data allows tracking cave air ventilation changes, including transient and short-lived ones. Specifically, periods impacted by respiration from cave visitors were filtered based on a linear mixing model.