



Balance of $p\text{CO}_2$ in the carbonate-bearing unsaturated zone controlling mineral precipitation: Implications for geo-environmental analyses in caves

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The chemical composition of shallow groundwater reflects quickly and effectively any changes occurring in atmospheric and soil-substrate conditions in catchment area. Hydrobiogeochemical processes are highly dynamic at the seasonal and shorter temporal scales. Weathering processes in carbonate substrates involve a series of chemical reactions that implies short-term contributions to the net ecosystem carbon balance via consumption or emission of CO_2 . After rainwater infiltrates into the soil, CO_2 -enriched water reaches the underlying unsaturated porous rock (vadose zone). The imbalance of CO_2 -partial pressure ($p\text{CO}_2$) between the infiltration soil-derived water and the cave air favor the processes of mineral precipitation. Precipitation of carbonate mineral in subsurface environments implies long-term net carbon sequestration, but also short-term CO_2 release from the substrate to the atmosphere. Moreover, the variations of cave air $p\text{CO}_2$, on daily to seasonal timescales, potentially affect the timing of mineral deposition and, consequently, the Ca-mineral proxy climate records derived from stalagmites collected at the same sites.

In this study an exhaustive monitoring program of the geochemical characteristics of seepage water and mineral precipitation rates was carried out in several karstic caves from Spain. These caves represent a wide range of possible karst scenarios with different geological and environmental features as well as several management models. The changes on the oversaturation/precipitation states of carbonated mineral are controlled by the CO_2 -recharge or depletion of the cave atmospheres, which is under the direct influence of the external conditions. For each cave environment an inherent stationary range of $p\text{CO}_2$ has always been identified, within which two coeval processes are detected: 1) slight and gradual mineral oversaturation of the seepage water with low precipitation rates of calcite and aragonite, and 2) decrease of the subsaturation degree of the Mg^{2+} -carbonate phases. These thermodynamically equilibrium ranges for $p\text{CO}_2$ determine the type and rate of mineral precipitation in each cave. Overcoming this theoretical $p\text{CO}_2$ range could entail an inhibition the mineral deposition or, even provoke the beginning of corrosion process. Conversely, the intense depletion of $p\text{CO}_2$ level below this range would alter the type of calcium-carbonated phases that contributes in the current speleothems growth.

Study results demonstrate the subsurface water is an indicator to understand the geochemical processes in the local carbon cycle on short timescales, especially those related to terrestrial ecosystems located in karst terrains. The environmental conditions, related to the suitable range of CO_2 defined for each cave environment, should be considered in order to avoid any alteration of the deposition rates and mineral typology of speleothems, both to establish correct climate-proxy relationships in speleothems and channeling the management efforts into cave conservation.