

Isotopic evolution of cave waters with degassing of CO₂ and evaporation

The C and O stable isotope compositions of speleothems are commonly used to make inferences about evolution of spelean waters involved in the formation of those speleothems and/or inferences about past climate. Both the $\delta^{13}\text{C}$ and the $\delta^{18}\text{O}$ of spelean waters can change, and typically can increase, after the water emerges into the cave. The diagram at right provides qualitative explanations of the general trends observed in speleothems. The most likely scenarios of those shown are Cases 1 and 3. Case 1 would happen when a water enters a cave with 100% relative humidity. The water's large CO₂ content as the result of plant respiration and decay in the overlying soil degases considerably as the water enters the cave atmosphere. In Case 3, the water enters a cave with relative humidity less than 100%. In this case, degassing of CO₂ occurs but diminishes as the water approaches equilibrium with the cave atmosphere, but evaporation can continue so long as some H₂O remains. Case 2, in which degassing precedes evaporation, seems most likely when degassing reaches equilibrium quickly, as in Case 2a.

Both degassing and evaporation can drive precipitation of CaCO₃. Degassing of CO₂ raises the pH of the water and thus increases the concentration of CO₃²⁻. Evaporation increases the concentration of Ca²⁺ and/or CO₃²⁻.

This diagram attempts to enlarge on Figure 3.15 of Gonzalez and Lohmann's (1988) Controls on mineralogy and composition of spelean carbonates: Carlsbad Caverns, New Mexico, in James and Choquette's (eds.) *Paleokarst*. It benefited from the insights of Guglielmo Angelo Caddeo.

