

Evolution of the isotope composition of C and O in the DIC in a water film during precipitation of calcite to the surface of a stalagmite in the presence of isotope exchange with the CO₂ of the cave atmosphere and evaporation of the water

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In a thin water layer, super saturated with respect to calcite with pH of about 8, where the aqueous CO₂ is in equilibrium with the pCO₂ of the cave atmosphere, the following processes determine the temporal evolution of the isotope composition of carbon and oxygen in the dissolved inorganic carbon (DIC).

- a) Precipitation of calcite driven by super saturation, whereby deposition rates Between the heavy and light isotopes are slightly different.
- b) Evaporation of water reducing the depth of the water layer and changing the isotope composition of oxygen in the water by Rayleigh-distillation.
- c) Isotope exchange between the CO₂ in the cave atmosphere and the DIC for both carbon and oxygen.
- d) Isotope exchange between the oxygen in the water molecules and that in the DIC.

All these processes can be described by a differential equation, which can be solved numerically.

For small times a simple solution can be given.

$$\Delta_{\text{DIC}}(T_{\text{drip}}) = \left[\left((\lambda + \varepsilon) \frac{C_{\text{eq}}}{C_0} - \varepsilon \right) \frac{T_{\text{drip}}}{\tau} + (\delta_{\text{eq}}^{\text{atm}} - \delta_0) \frac{T_{\text{drip}}}{\tau^{\text{atm}}} + (\delta_{\text{eq}}^{\text{water}} - \delta_0 - \varepsilon_w \frac{T_{\text{drip}}}{T_{\text{ev}}}) \frac{T_{\text{drip}}}{\tau^{\text{water}}} \right]$$

$\Delta_{\text{DIC}}(T_{\text{drip}})$ is the change of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (given here as small numbers and not in the ‰ notation) after the drip time T_{drip} . λ, ε are kinetic parameters of precipitation on the order of 10^{-2} and τ is the time scale of precipitation, typically about 1000 s. $(\delta_{\text{eq}}^{\text{atm}} - \delta_0)$ and $(\delta_{\text{eq}}^{\text{water}} - \delta_0)$ are the differences between the corresponding initial δ -value and that when DIC is in isotope equilibrium with the atmosphere or in the case of oxygen with the water. τ^{atm} and τ^{water} , both on the order of 10,000 s, are the time scales of the exchange reactions to approach isotope equilibrium. For carbon the last term (exchange with water) must be deleted. C_{eq} is the concentration of DIC in chemical equilibrium with the CO₂ in the cave atmosphere and C_0 is the initial concentration, when the water drips to the stalagmite. T_{ev} is the time needed to fully evaporate the water layer and $\varepsilon_w = -0.01$ is the fractionation factor for depletion of oxygen in the water by Rayleigh- distillation. This eqn. is valid for $T_{\text{drip}} < 0.2\tau$. The influence of evaporation is negligible, less than 2% of $\Delta_{\text{DIC}}(T_{\text{drip}})$. Isotope exchange may enrich $\Delta_{\text{DIC}}(T_{\text{drip}})$ by about 0.02‰. The average increase of $\Delta_{\text{CaCO}_3}(T_{\text{drip}})$ of the calcite precipitated to the stalagmite is given by $\Delta_{\text{DIC}}(T_{\text{drip}}) = \frac{1}{2} \Delta_{\text{DIC}}(T_{\text{drip}})$. A possible depletion of the isotope composition by incorporation of carbonate into the lattice of calcite can be treated separately.

We present also the evolution of for drip times $T_{\text{drip}} > 0.2\tau$. In all cases we find a further increase in $\Delta_{\text{DIC}}(T_{\text{drip}})$ until after passing a maximum $\Delta_{\text{DIC}}(T_{\text{drip}})$ for carbon approaches equilibrium with the CO₂ of the cave atmosphere after about 10,000s. For oxygen a steady state, resulting from the

In conclusion we state that for stalagmites, which grow with short drip times compared to the precipitation time neither exchange reactions nor evaporation of the water contribute to the isotope enrichment of the calcite precipitated. This is the first work where all processes, which can effect temporal isotope composition of DIC in a calcite depositing water film are described by one comprehensive model.