

Lecture Abstract:

**The “Processes determining the chemical evolution of DIC in drip water inside a cave: Degassing, equilibration to the cave atmosphere, precipitation of calcite and isotopic signals ” Lecture**

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- 1.) Water entering into the cave is close to equilibrium with respect to calcite ( $\text{pH} \approx 7.5$ ,  $[\text{Ca}] = C \approx 2\text{mmol/L}$ ). From the thin film with depth of  $d \approx 0.01\text{ cm}$  flowing towards the drip site out gassing of  $\text{CO}_2$  by molecular diffusion is completed (95%) in about 10s. (Dreybrodt, 2011). It takes about 100s until the carbonate species attain equilibrium with the low  $\text{PCO}_2$  in the cave. During this time pH increases above 8. Implications to “ slow and enhanced degassing” and to cave monitoring of drip water are discussed. (Dreybrodt, 2012a)
- 2.) Precipitation of calcite from the degassed and equilibrated solution proceeds on time scales of 1000s with deposition rates given by  $R = \alpha(C - C_{\text{eq}})$ , whereby  $(C - C_{\text{eq}})$  drops exponentially with time constant  $\tau = d/\alpha$ .  $C_{\text{eq}}$  is the equilibrium concentration with respect to calcite and  $\alpha$  a rate constant (Buhmann and Dreybrodt, 1985, Romanov et al., 2008).
- 3.) Experiments under cave analogue conditions are presented verifying topics 1 and 2 (Hansen et al., 2013).
- 4.) In a water film precipitating calcite, DIC becomes enriched in  $^{13}\text{C}$  and  $^{18}\text{O}$ . Alternative theories of the isotope evolution of DIC are presented. (Dreybrodt and Scholz, 2011).  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  increase linear in time by  $\delta(t) - \delta_0 = [(\lambda + \epsilon)(C_{\text{eq}}/C_0) - \epsilon] \cdot t/\tau$  is for both alternatives for times  $t < 0.15\tau$ . For Rayleigh-distillation close to equilibrium  $\epsilon$  is the equilibrium fractionation constant and  $\lambda$  is zero. For kinetic fractionation  $\epsilon^{13} = 1 - 13\alpha/12\alpha$  and  $\epsilon^{18} = 1 - 18\alpha/16\alpha$ , respectively.  $\lambda \ll 1$  results from different values of  $C_{\text{eq}}$  for the light and heavy isotopes. Experiments to verify this are in preparation.
- 5.) At high drip rates water flows in laminar films away from the apex of the stalagmite and the DIC from which calcite is deposited at the apex is in isotopic equilibrium. For long drip times  $T_d$  calcite precipitates from a stagnant water film covering the apex where DIC in average is enriched (Dreybrodt and Scholz, 2011) by  $\delta_{\text{av}} - \delta_0 = 0.5 \cdot [(\lambda + \epsilon)(C_{\text{eq}}/C_0) - \epsilon] \cdot T_d/\tau = 0.5 \cdot [(\lambda + \epsilon)(C_{\text{eq}}/C_0) - \epsilon] \cdot T_d \cdot \alpha/d$ . In this latter case, since  $\alpha$  changes from  $0.5 \cdot 10^{-5}\text{ cm/s}$  at  $0^\circ\text{C}$  to  $4 \cdot 10^{-5}\text{ cm/s}$  at  $25^\circ\text{C}$ , enrichment

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increases with temperature beyond its temperature dependence on  $\lambda$  and  $\epsilon$  and also depends on drip time.

- 6.) Buffering of  $\delta^{18}\text{O}$  does not play a role because the exchange time of the oxygen isotopes between carbonate and water is about two orders of magnitude longer than the time of precipitation (Dreybrodt and Scholz, 2011, Dreybrodt, 2012b).

Buhmann D. and Dreybrodt W. (1985) The kinetics of calcite dissolution and precipitation in geologically relevant situations of karst areas: 1. Open system. *Chem. Geol.* 48, 189–211.

Dreybrodt W.,(2012a) Caveat: Pitfalls in the measurement of pH of drip waters in caves. *Acta Carsologica* 41,157-160

Dreybrodt W. (2012b) Comment on “Oxygen isotopes in calcite grown under cave-analogue conditions” by C.C. Day and G.M. Henderson. *Geochim. Cosmochim. Acta* 85, 383-387

Dreybrodt W. (2011) Comments on processes contributing to the isotope composition of  $^{13}\text{C}$  and  $^{18}\text{O}$  of calcite deposited in the calcite of speleothems. *Acta Carsologica* 40, 233-238

Dreybrodt W. and Scholz D. (2011) Climate dependence of stable carbon and oxygen isotope signals recorded in speleothems: from soil water to speleothem calcite. *Geochim. Cosmochim. Acta* 75, 734–752.

Hansen M., Dreybrodt W., and Scholz D.(2013).Chemical evolution of dissolved inorganic carbon species flowing in thin water films and its implications for (rapid) degassing of  $\text{CO}_2$  during speleothem growth. . *Geochim. Cosmochim. Acta* ,in press

Romanov, D., Kaufmann, G. and Dreybrodt, W. (2008)  $\delta^{13}\text{C}$  profiles along growth layers of stalagmites: comparing theoretical and experimental results. *Geochimica et Cosmochimica Acta*, 72, 438-448