

LETTER:

PROBLEMS IN USING THE APPROACH OF RAYLEIGH DISTILLATION TO INTERPRET THE ^{13}C AND ^{18}O ISOTOPE COMPOSITIONS IN STALAGMITE CALCITE

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Wolfgang DREYBRODT^{1,2}

INTRODUCTION

When calcite is precipitated from a water film on top of a stalagmite to its surface, the carbonate in the solution and consequently also the carbonate in the calcite deposited becomes enriched in the heavy isotopes ^{18}O and ^{13}C (Hansen *et al.* 2016; Dreybrodt & Scholz 2011; Romanov *et al.* 2008). This isotope signal is added to the isotope imprint resulting from climate variability. Therefore a physical model of the evolution of the isotope composition of carbonate in a water film, either flowing down the surface of the stalagmite at high drip rates or stagnant, when the drip rate is low, is necessary to discriminate the climate signal from the signal resulting from physical processes in the cave.

Currently two models are proposed. In the first one (Scholz *et al.* 2009) one assumes that the isotope evolution can be described by a Rayleigh distillation process (Mook 2000) where during the entire process of pre-

cipitation the fractionation factor for carbon or oxygen, respectively remains constant. In another model one assumes that precipitation is a uni-directional non-equilibrium process, where the constants in the rate equations are slightly different for the light and the heavy isotope (Dreybrodt 2008; Dreybrodt & Scholz 2011). Results from these models have been compared for various scenarios by Scholz *et al.* (2009), Dreybrodt and Scholz (2011), Dreybrodt and Deininger (2014) and Dreybrodt and Romanov (2016).

Differences of opinion clearly exist in the research community regarding which of these models best represents reality. In this letter I discuss the meaning of the Rayleigh equation for precipitation of calcite under equilibrium conditions and for precipitation of calcite governed by uni-directional rate equations.

RAYLEIGH DISTILLATION

We consider a reservoir containing N molecules with both rare and abundant isotopes. The number of the rare isotopes is N_A , that of the abundant ones N_B and $N_A \ll N_B$. Now by some physical or chemical process, such as evaporation or precipitation to a solid, a small number dN_A of rare isotopes and dN_B of abundant isotopes are removed

irreversibly from the reservoir step by step. We now ask for the evolution of the isotope composition in the reservoir. The isotope ratio of the molecules remaining in the reservoir is $R = N_A/N_B$, the isotope ratio of the removed isotopes dN_A and dN_B is $R_{\text{rem}} = dN_A/dN_B$. Now in isotope equilibrium, $R_{\text{rem}} = \alpha_{\text{iso}} \cdot R$ where α_{iso} is the isotope

¹ Faculty of Physics and Electrical Engineering, University of Bremen, Germany

² Karst Research Institute ZRC SAZU, Postojna, Slovenia e-mail: dreybrodt@t-online.de

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fractionation factor, which is a constant during the entire process. Then

$$\frac{dN_A}{dN_B} = \alpha_{\text{iso}} \frac{N_A}{N_B} \quad \text{or} \quad \frac{dN_A}{N_A} = \alpha_{\text{iso}} \frac{dN_B}{N_B} \quad (1)$$

Integration yields

$$\ln(N_A / N_{A_0}) = \alpha_{\text{iso}} \ln(N_B / N_{B_0}) \quad (2)$$

N_{A_0} and N_{B_0} are the initial numbers, when removal of the molecules starts. From this one finds

$$(N_A / N_{A_0}) = (N_B / N_{B_0})^{\alpha_{\text{iso}}} \cong (N / N_0)^{\alpha_{\text{iso}}} \quad (3)$$

Dividing by N_B / N_{B_0} and observing $N_B \cong N$ and $N_{B_0} \cong N_0$, because $N_B \cong N_A$, one gets the Rayleigh equation

$$R = R_0 \left(\frac{N}{N_0} \right)^{\alpha_{\text{iso}} - 1} = R_0 \left(\frac{N}{N_0} \right)^{\varepsilon} \quad \text{or by using concentrations}$$

$$R = R_0 \left(\frac{C}{C_0} \right)^{\varepsilon} \quad (4)$$

because concentrations C are proportional to the number of the molecules N in the reservoir.

Note that R does not depend on time, but only on the fraction $f = N/N_0$ of molecules remaining in the reservoir, independent on the pathway of removal. **The reason for this is the condition that α_{iso} is a constant during the entire process.** Therefore the concept of Rayleigh distillation must be used with care, always regarding the processes in the background.

An example is evaporation of water. If evaporation proceeds in isotope equilibrium with a vapor atmosphere, from which vapor is removed slowly, then, $\alpha_{\text{iso}} = \alpha_{\text{eq}}$ where α_{eq} is the equilibrium fractionation coefficient between liquid water and vapor. On the other hand if water evaporates irreversibly into a dry atmosphere with humidity of zero, the conditions of evaporation are constant, no matter, how much water has been already removed. Therefore also in this unidirectional non-equilibrium process the Rayleigh equation is valid. Here the different diffusion coefficients of the isotopes determine the value of α . For equilibrium evaporation $\alpha_{\text{eq}} - 1 = \varepsilon_{\text{eq}} = -0.01$ whereas for evaporation into dry air $\varepsilon = -0.035$ (Horita *et al.* 2008).

CLASSICAL RAYLEIGH EQUATION: EQUILIBRIUM REACTION

The isotope evolution of carbonate during precipitation of calcite proceeding slowly under conditions of chemical and isotope equilibrium of all species involved has been described by Mook (2000) using mass conservation between the species in the solution and the environment (calcite and the cave atmosphere). Such conditions exist when calcite precipitates from stagnant water layers with depths of more than 1 cm, as they exist in cave pools. In this case out gassing of CO_2 is slow with time constant $\tau_D = 4d^2/\pi^2 D$, where d is the water depth and D is the constant of molecular diffusion of CO_2 in water (Dreybrodt & Scholz 2011). The equilibrium concentration C_{eq} of HCO_3^- then changes slowly and precipitation proceeds close to equilibrium. Under equilibrium conditions the isotope ratio $R = N_A/N_B = A/B$ for the heavy and the light isotope in the HCO_3^- ions is described by the Rayleigh

equation. A, B stand for the concentration of the corresponding isotope.

$$R = R_0 (C / C_0)^{\varepsilon_{\text{eq}}} \quad (5)$$

$R_0 = A_0/B_0$ is the isotope ratio at the onset of precipitation, C_0 is the initial hydrogen carbonate concentration and C is the actual one. $\varepsilon_{\text{eq}} = \alpha_{\text{eq}} - 1$ is the equilibrium fractionation factor for carbon or oxygen, respectively, determined solely by the corresponding mass action constants (Mickler *et al.* 2004, 2006). Eqn. 5 is valid only, if for all times t the solution is in thermodynamic and isotope equilibrium or at least very close to it. Then α_{eq} remains constant during the entire process. For equilibrium fractionation, α_{eq} is derived by thermodynamics and does not depend on the details of the reaction mechanisms.

EXTENDED RAYLEIGH EQUATION: UNI-DIRECTIONAL REACTION

If out gassing, however, is fast, C_{eq} which depends on the p_{CO_2} in the surrounding atmosphere, within several 10 s,

rapidly reaches its final value (Dreybrodt 2011; Hansen *et al.* 2013) and precipitation of calcite proceeds under

disequilibrium until finally equilibrium with respect to calcite is reached and precipitation stops. Precipitation in this case is ruled by the rate laws (Dreybrodt 2008; Dreybrodt & Scholz 2011)

$$\frac{dA}{dt} = -\frac{\alpha_p^A}{d}(A - A_{eq}); \quad \frac{dB}{dt} = -\frac{\alpha_p^B}{d}(B - B_{eq}) \quad \text{and} \quad \frac{A_{eq}}{A_0} = \gamma \frac{B_{eq}}{B_0}; \quad \gamma \cong 1 \quad (6)$$

where A and B are the concentrations of the heavy (rare) and light (abundant) isotope in the HCO_3^- respectively, A_{eq} and B_{eq} are the equilibrium concentrations when precipitation stops, d is the depth of the water film on top of the stalagmite, and α_p^A , α_p^B , are rate constants, slightly different for the heavy and the light isotope.

A_{eq} and B_{eq} are related by $A_{eq}/A_0 = \gamma \cdot B_{eq}/B_0$, $\gamma \cong 1$. This relation needs some explanation: Let us present the rare isotopes in the carbonate of the solution by red nuclei with concentration A, and the abundant ones by white nuclei with concentration B. First we assume identical properties of both. Then the chance of some nucleus to be incorporated into the calcite deposited is equal for a red and a white nucleus. If the initial concentrations in the aqueous solution are A_0 and B_0 , the ratio N_A^c/N_B^c of the number of rare (red) and abundant (white) isotopes in the calcite deposited must be equal to the ratio A_0/B_0 at all times. Therefore at equilibrium we have $N_A^{c,eq}/N_B^{c,eq} = A_0/B_0$. In reality the chance of the rare isotope to be incorporated into the crystal is slightly different from that of the abundant one and may differ from the chance of the abundant one by a factor $\beta \cong 1$. Then one has $N_A^{c,eq}/N_B^{c,eq} = \beta A_0/B_0$ at all times. On the other hand, in equilibrium with respect to calcite one has fractionation for the isotope ratios $R_{eq}^c = \alpha R_{eq}$. With $R_{eq}^c = N_A^{c,eq}/N_B^{c,eq} = \alpha \cdot A_{eq}/B_{eq} = \beta \cdot A_0/B_0$ one finally gets $A_{eq}/A_0 = \beta \cdot B_{eq}/\alpha \cdot B_0 = \gamma \cdot B_{eq}/B_0$ with $\gamma \cong 1$.

The isotope evolution can now be derived from equation (6). By division one gets

$$\frac{dA}{A - A_{eq}} = \frac{\tau_B}{\tau_A} \frac{dB}{B - B_{eq}} = \alpha_{kin} \frac{dB}{B - B_{eq}} \quad \text{with} \quad \tau_A = d / \alpha_p^A; \quad \tau_B = d / \alpha_p^B \quad (7)$$

τ_A and τ_B are the exponential decay times of precipitation.

Eqn. 7 can be rewritten as

$$\frac{dA}{dB} = \frac{\tau_B}{\tau_A} \frac{A - A_{eq}}{B - B_{eq}} = \alpha_{kin} \frac{A - A_{eq}}{B - B_{eq}} = \alpha_{kin} \left(\frac{1 - \frac{A_{eq}}{A}}{1 - \frac{B_{eq}}{B}} \right) \frac{A}{B} = \alpha_{iso} \frac{A}{B} \quad (7a)$$

Here α_{iso} clearly is a function of A and B and the condition that α_{iso} must be a constant during the entire process is violated.

Integration of equation (7) and some algebraic manipulations yields

$$\frac{R}{R_0} = \left[\left(\frac{B(t) - B_{eq}}{B_0 - B_{eq}} \right)^{\alpha_{kin}} \cdot \left(1 - \frac{A_{eq}}{A_0} \right) + \frac{A_{eq}}{A_0} \right] \cdot \frac{B_0}{B(t)} \quad \text{with } \alpha_{kin} = \tau_B / \tau_A \quad (8)$$

Using $B(t) \cong C(t)$, $B_0 \cong C_0$, and $A_{eq}/A_0 = \gamma \cdot B_{eq}/B_0 = \gamma \cdot C_{eq}/C_0$ one finds

$$\frac{R}{R_0} = \left[\left(\frac{C(t) - C_{eq}}{C_0 - C_{eq}} \right)^{\alpha_{kin}} \cdot \left(1 - \frac{\gamma C_{eq}}{C_0} \right) + \frac{\gamma C_{eq}}{C_0} \right] \cdot \frac{C_0}{C} \quad (9)$$

which is further on called the extended Rayleigh equation. This extended Rayleigh equation has been derived already from the time evolution of $R(t)$ by Dreybrodt (2008). It must be stressed here that $C(t)$ is the solution of the differential equation

$$\frac{dC}{dt} = -\frac{\alpha_p^B}{\delta}(C - C_{eq}) = -\frac{C - C_{eq}}{\tau_B} \quad (10)$$

which is

$$C(t) = (C_0 - C_{eq}) \exp\left(-\frac{t}{\tau_B}\right) + C_{eq} \quad (11)$$

If any other function is introduced instead of $C(t)$, eqn. 9 is no longer valid.

If C_{eq} is zero, not possible for calcite precipitation, eqn. 9, reads

$$\frac{R}{R_0} = \left[\left(\frac{C(t)}{C_0} \right)^{\alpha_{kin}} \right] \cdot \frac{C_0}{C} = \left(\frac{C(t)}{C_0} \right)^{\alpha_{kin}-1} = \left(\frac{C(t)}{C_0} \right)^{\varepsilon_{kin}} \quad (12)$$

This equation is valid only for reactions with pure linear kinetics with rate laws $dA/dt = -A/\tau_A$ and $dB/dt = -B/\tau_B$ where $C(t) = C_0 \cdot \exp(-t/\tau_A)$. One obtains a Rayleigh equation, formally identical with the classical Rayleigh equation, eqn. 4 for equilibrium. It describes, however, a quite different kinetic process and is valid only for a pure linear reaction with $C(t) = C_0 \exp(-t/\tau_A)$, (White 2007, 2013). The difference to the equilibrium reaction is hidden in $\alpha_{kin} = \tau_B/\tau_A$, which is a ratio of reaction times and in no way is related to α_{eq} .

To call α_{kin} kinetic partition coefficient for calcite precipitation is misleading for two reasons:

a) The reaction of calcite precipitation is not pure linear, because the rate law is $dA/dt = -(A - A_{eq})/\tau_A$ and $dB/dt = -(B - B_{eq})/\tau_B$,

b) α_{kin} is a constant related to rate constants and not to mass action constants.

To describe the isotope evolution for calcite precipitation the full kinetic equation

$$\frac{R}{R_0} = \left[\left(\frac{C(t) - C_{eq}}{C_0 - C_{eq}} \right)^{\alpha_{kin}} \cdot \left(1 - \frac{\gamma C_{eq}}{C_0} \right) + \frac{\gamma C_{eq}}{C_0} \right] \cdot \frac{C_0}{C} \quad (9)$$

must be used.

COMPARING THE RESULTS FROM THE CLASSICAL AND THE EXTENDED RAYLEIGH EQUATION

Now we compare the results using the classical Rayleigh (eqn. 5) and its extended version (eqn. 9) by inserting into both the time evolution $C(t)$ (eqn. 11), which has been verified experimentally by Hansen *et al.* (2013). Fig. 1 presents the result of the classical Rayleigh equation (5) by introducing (11) into it. Fig. 1a depicts the isotope evolution in time for three values of ε . The parameters determining precipitation, λ , and τ_A are also listed in the Fig. 1. For times below 200 s, one observes an increase of $R(t)$ linear in time. Then the curves bend to reach a constant value. Fig. 1b illustrates the same situation as a function of $C(t)/C_0$. Again $R(C)$ rises linearly with decreasing C/C_0 for $C/C_0 > 0.8$ and then reaches its final value at $C/C_0 = 0.2$ when precipitation stops.

In comparison to Fig. 1 we show the results for the same case when one uses the extended Rayleigh (eqn. 9) and inserts eqn. 11. Fig. 2a shows $R(t)$ as a function of time. The full lines depict $\varepsilon = -0.005$ and $\gamma = 1.003$ or $\gamma = 1.000$ respectively. The dashed ones show the combination $\varepsilon = -0.003$ and $\gamma = 1.003$ or $\gamma = 1.000$ respectively and the dotted ones illustrate $\varepsilon = -0.001$ and $\gamma = 1.003$ or $\gamma = 1.000$ respectively. In all curves for times $t < 200$ s one finds a linear increase in time. The final value reached is $R = \gamma$. Fig. 2b shows the results of Fig. 2a plotted as function of C/C_0 . For $C/C_0 > 0.8$ one observes a linear increase with decreasing C/C_0 . The linear increase in time can be explained by expanding $R(t)$ to first order in t .

For $t < 0.2 \tau_A$ one finds (Dreybrodt & Scholz 2011; Dreybrodt & Romanov 2016)

$$R(t) - 1 = \delta(t) = \left[\varepsilon \cdot \frac{C_{eq}}{C_0} - \varepsilon \right] \cdot \frac{t}{\tau_A} \quad (13)$$

for the classical Rayleigh equation and

$$R(t) - 1 = \delta(t) = \left[(\lambda + \varepsilon) \cdot \frac{C_{eq}}{C_0} - \varepsilon \right] \cdot \frac{t}{\tau_A} \quad \text{with } \lambda = \gamma - 1 \quad (14)$$

To conclude: When using the Rayleigh equation in its time dependent version $R = R_0 \cdot (C/C_0)^{\varepsilon_{eq}}$, one has to be sure that the underlying process supports its application.

for the extended one. δ is the delta-notation used in small numbers in the order of 0.001 instead of ‰. Note that for $\gamma = 1$, $\lambda = 0$, eqns. 13 and 14 become identical.

The linear increase of R with decreasing C/C_0 for values $1 > C/C_0 > 0.8$ reads

$$R(C) - 1 = \delta(C) = \left[\varepsilon \cdot \frac{C_{eq}}{C_0} - \varepsilon \right] \cdot \left(\frac{C}{C_0} - 1 \right) \quad (15)$$

for the classical Rayleigh equation and

$$R(C) - 1 = \delta(C) = \left[(\lambda + \varepsilon) \cdot \frac{C_{eq}}{C_0} - \varepsilon \right] \cdot \left(\frac{C}{C_0} - 1 \right) \quad \text{with } \lambda = \gamma - 1 \quad (16)$$

for the extended one.

Therefore fitting experimental data from the early linear increase of $R(C)$ by the classical Rayleigh equation is always possible (Hansen *et al.* 2016) but determining the value of ε from it leads to values, which are flawed.

Figs. 3a and 3b present two examples, how data generated by the extended Rayleigh equation with $\varepsilon = -0.003$, $\gamma = 1.003$ and $\varepsilon = -0.005$, $\gamma = 1.000$, respectively, can be fitted satisfactorily for values $1 > C/C_0 > 0.6$ by the classical Rayleigh equation with $\varepsilon = -0.0046$ for the first example and $\varepsilon = -0.0038$ for the second one. To find out experimentally, which of the two approaches, the classical or the extended version of the Rayleigh equation is valid, one has to measure the dependence of the initial slope for various values of C_0/C_{eq} .

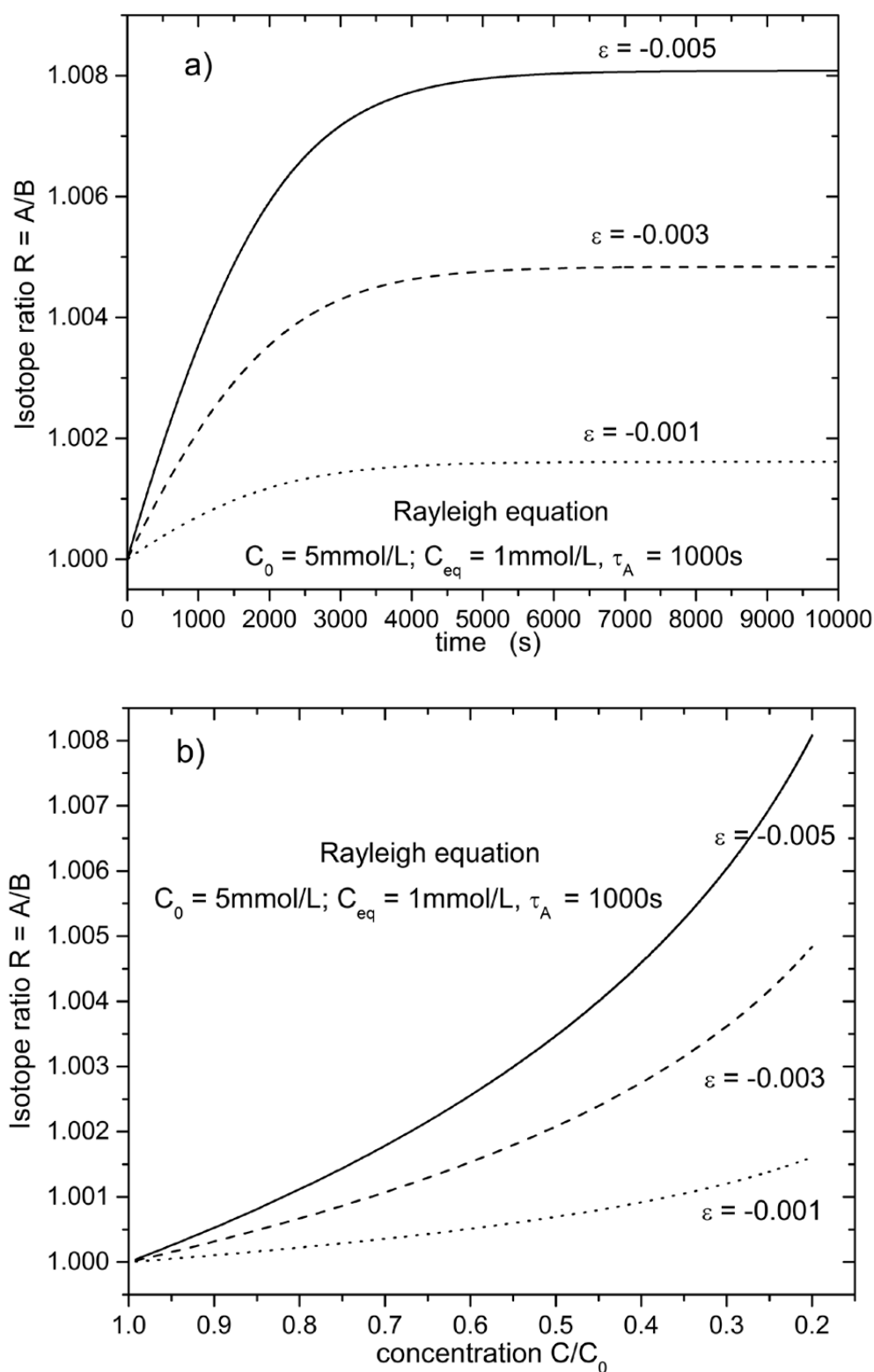


Fig. 1: Evolution of the isotope ratio R for the classical Rayleigh equation $R = R_0 (C/C_0)^\epsilon$ for various values of ϵ . a) as function of time with $C(t) = (C_0 - C_{\text{eq}}) \exp(-t/\tau_b) + C_{\text{eq}}$ and b) as function of concentration.

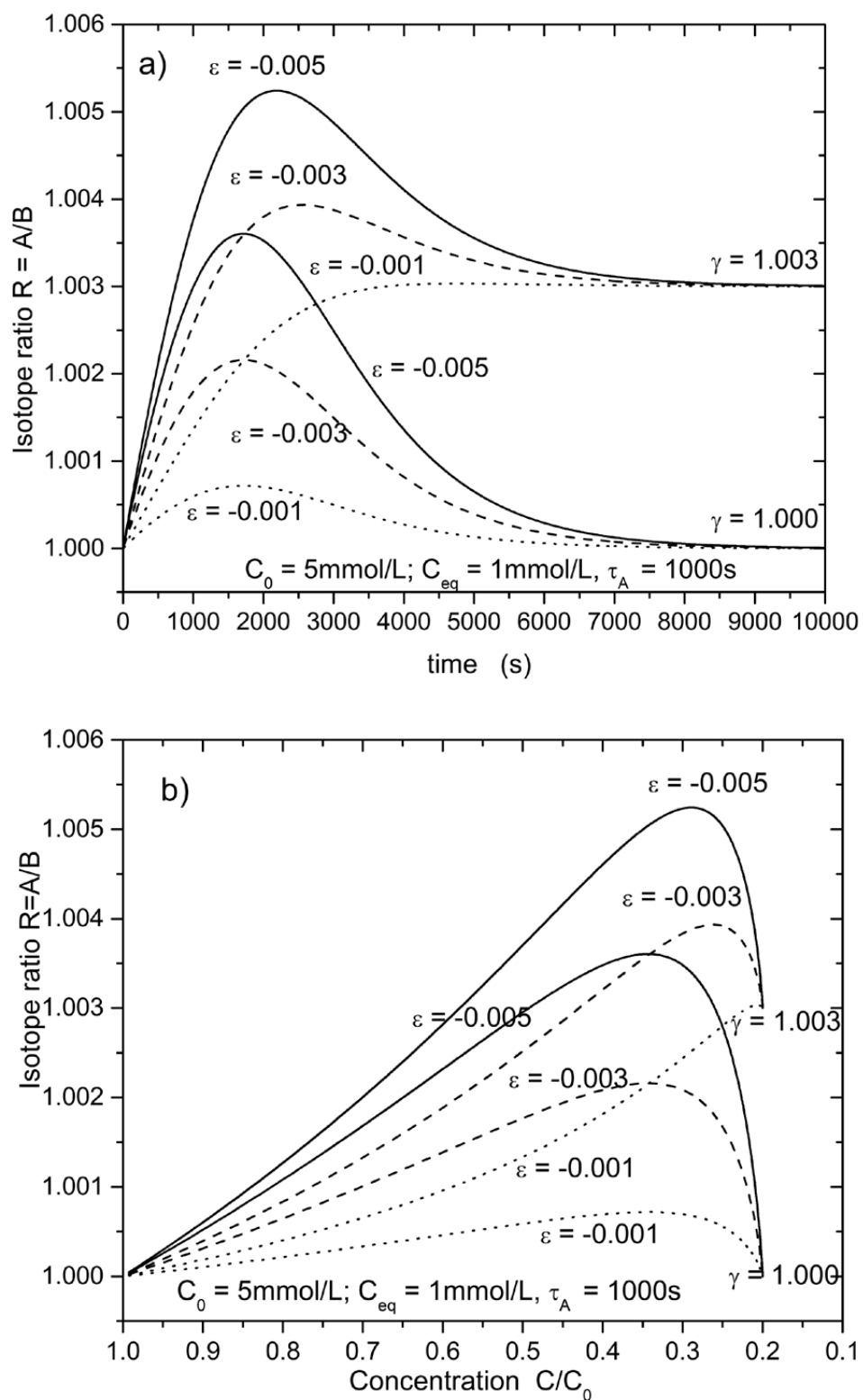


Fig. 2: Evolution of the isotope ratio R for the extended Rayleigh equation (eqn. 9) for various values of ε and γ . a) as function of time with $C(t) = (C_0 - C_{eq})\exp(-t/\tau_b) + C_{eq}$ and b) as function of concentration C .

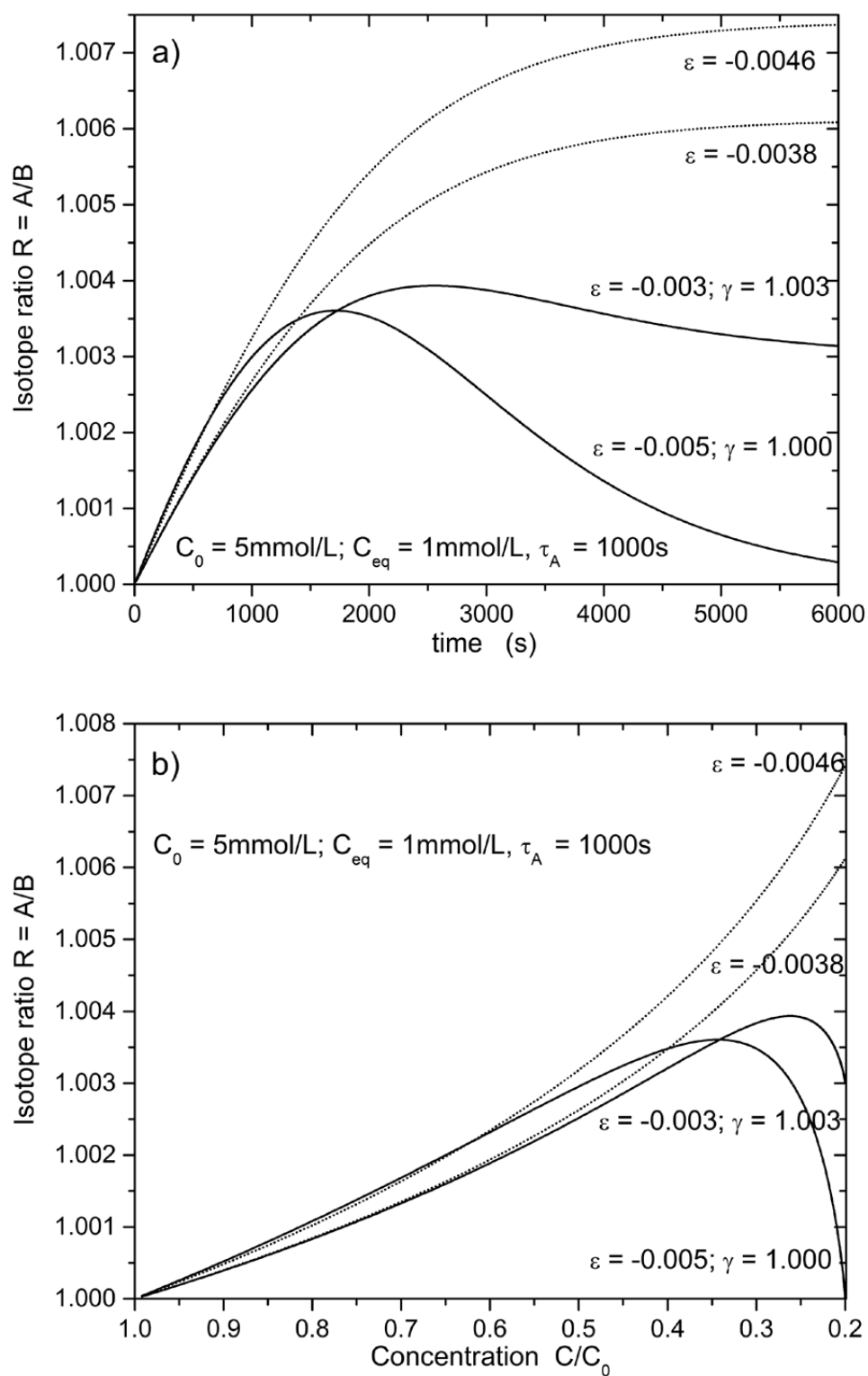


Fig. 3: Comparison of the evolution of the isotope ratio R for the extended Rayleigh equation (eqn. 9), full lines and the classical Rayleigh equation, dotted curves as function of a) time and b) concentration. The values of ϵ for the classical Rayleigh equation have been chosen to match the corresponding curves of the extended Rayleigh equation for times $t < 500$ s.

CONCLUSION

In modeling the isotope evolution of DIC during precipitation of calcite many researchers (Deininger *et al.* 2012; Polag *et al.* 2010; Mühlinghaus *et al.* 2007, 2009; Romanov *et al.* 2008; Scholz *et al.* 2009) have used a time dependent modification of the classical Rayleigh equation $R(t) = R_0 \cdot (C(t)/C_0)^{\epsilon}$ by inserting the time evolution $C(t)$ of, HCO_3^- , $C(t) = (C_0 - C_{\text{eq}}) \exp(-t/\tau_B) + C_{\text{eq}}$.

In view of the discussion above this is not a valid approach. Instead of using the classical Rayleigh equation the extended version must be used.

It is always possible to fit experimental data in their linear range for $C(t)/C_0 < 0.6$ by using the classical Rayleigh equation. The resulting fitting parameter ϵ_{fit} , however, does not have any physical meaning and cannot be used for any reasonable interpretation of the data. It is just a parameter to describe the experimental data by some equation. One might as well use a linear function in t or in C to do this.

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REFERENCES

- Deininger, M., Fohlmeister, J., Scholz, D. & A. Mangini, 2012: Isotope disequilibrium effects: The influence of evaporation and ventilation effects on the carbon and oxygen isotope composition of speleothems – A model approach.- *Geochimica et Cosmochimica Acta*, 96, 57–79. <http://dx.doi.org/10.1016/j.gca.2012.08.013>
- Dreybrodt, W., 2008: Evolution of the isotopic composition of carbon and oxygen in a calcite precipitating $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$ solution and the related isotopic composition of calcite in stalagmites.- *Geochimica et Cosmochimica Acta*, 72, 4712–4724. <http://dx.doi.org/10.1016/j.gca.2008.07.022>
- Dreybrodt, W., 2011: Letter: Comments on processes contributing to the isotope composition ^{13}C and ^{18}O to speleothems.- *Acta Carsologica*, 40, 233–238. <http://dx.doi.org/10.3986/ac.v40i2.8>
- Dreybrodt, W. & M. Deininger, 2014: The impact of evaporation to the isotope composition of DIC in calcite precipitating water films in equilibrium and kinetic fractionation models.- *Geochimica et Cosmochimica Acta*, 125, 433–439.
- Dreybrodt, W. & D. Romanov, 2016: The evolution of ^{13}C and ^{18}O isotope composition of DIC in a calcite depositing film of water with isotope exchange between the DIC and a CO_2 containing atmosphere, and simultaneous evaporation of the water. Implication to climate proxies from stalagmites: A theoretical model.- *Geochimica et Cosmochimica Acta*, In press, August 2016. <http://dx.doi.org/10.1016/j.gca.2016.07.034>
- Dreybrodt, W. & D. Scholz, 2011: Climatic dependence of stable carbon and oxygen isotope signals recorded in speleothems: from soil water to speleothem calcite.- *Geochimica et Cosmochimica Acta* 75, 734–752. <http://dx.doi.org/10.1016/j.gca.2010.11.002>
- Hansen, M., Dreybrodt, W. & D. Scholz, 2013: Chemical evolution of dissolved inorganic carbon species flowing in thin water films and its implications for (rapid) degassing of CO_2 during speleothem growth.- *Geochimica et Cosmochimica Acta*, 107, 242–251. <http://dx.doi.org/10.1016/j.gca.2013.01.006>

- Hansen, M., Schöne, B.R., Spötl, C. & D. Scholz, 2016: Simulating speleothem growth in the laboratory: Determination of stable isotope fractionation factors during precipitation of speleothem calcite. EGU General Assembly 2016.- Geophysical Research Abstracts, 18, EGU2016-13868. Available from: <http://meetingorganizer.copernicus.org/EGU2016/EGU2016-13868.pdf> [Accessed September 30th 2016].
- Horita, J., Rozanski, K. & S. Cohen, 2008: Isotope effects in the evaporation of water: a status report of the Craig-Gordon model.- *Isotopes in Environmental and Health Studies*, 44, 23–49. <http://dx.doi.org/10.1080/10256010801887174>
- Mickler P. J., Banner J. L., Stern L., Asmerom Y., Lawrence, Edwards R. & E. Ito., 2004: Stable isotope variations in modern tropical speleothems: evaluating equilibrium vs. kinetic isotope effects.- *Geochimica et Cosmochimica Acta* 68, 4381–4393. <http://dx.doi.org/10.1016/j.gca.2004.02.012>
- Mickler, P.J., Stern, L.A. & J.L. Banner, 2006: Large kinetic isotope effects in modern speleothems.- *GSA Bull.*, 118, 1–2, 65–81. <http://dx.doi.org/10.1130/B25698.1>
- Mook, W.G., 2000: *Environmental isotopes in the hydrological cycle: principles and applications*. In *Introduction, Theory, Methods, Review*.- IAH and UNESCO, pp. 185, Paris. Available from: http://www-naweb.iaea.org/napc/ih/documents/global_cycle/Environmental%20Isotopes%20in%20the%20Hydrological%20Cycle%20Vol%201.pdf [Accessed September 30th 2016].
- Mühlinghaus, C., Scholz D. & A. Mangini, 2007: Modelling stalagmite growth and $\delta^{13}\text{C}$ as a function of drip interval and temperature.- *Geochimica et Cosmochimica Acta*, 71, 2780–2790. <http://dx.doi.org/10.1016/j.gca.2007.03.018>
- Mühlinghaus, C., Scholz D. & A. Mangini, 2009: Modelling fractionation of stable isotopes in stalagmites.- *Geochimica et Cosmochimica Acta*, 73, 7275–7289. <http://dx.doi.org/10.1016/j.gca.2009.09.010>
- Polag, D., Scholz, D., Mühlinghaus, C., Spötl, C., Schröder-Ritzrau, A., Segl, M. & A. Mangini, 2010: Stable isotope fractionation in speleothems: Laboratory experiments.- *Chemical Geology*, 279, 31–39. <http://dx.doi.org/10.1016/j.chemgeo.2010.09.016>
- Romanov, D., Kaufmann G. & W. Dreybrodt, 2008: $\delta^{13}\text{C}$ profiles along growth layers of stalagmites: comparing theoretical and experimental results.- *Geochimica et Cosmochimica Acta*, 72, 438–448. <http://dx.doi.org/10.1016/j.gca.2007.09.039>
- Scholz, D., Mühlinghaus C. & A. Mangini, 2009: Modelling $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the solution layer on stalagmite surfaces.- *Geochimica et Cosmochimica Acta*, 73, 2592–2602. <http://dx.doi.org/10.1016/j.gca.2009.02.015>
- White, W.M., 2013: *Geochemistry*.- Wiley-Blackwell, pp. 668, Chichester.
- White, W.M., 2007: *Geochemistry*, Chapter 9. Stable Isotope Geochemistry an online Textbook.- [Online] Available from: <https://www.imwa.info/geochemistry/Chapters/Chapter09.pdf> [Accessed 30th September 2016].