

# LETTER:

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

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### 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  $^{18}\text{O}$  and  $^{13}\text{C}$  (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  $\alpha_{\text{iso}}$  is the isotope

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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  $\alpha_{\text{iso}}$  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  $\alpha_{\text{eq}}$  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  $\alpha$ . 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  $\text{CO}_2$  is slow with time constant  $\tau_D = 4d^2/\pi^2D$ , where  $d$  is the water depth and  $D$  is the constant of molecular diffusion of  $\text{CO}_2$  in water (Dreybrodt & Scholz 2011). The equilibrium concentration  $C_{\text{eq}}$  of  $\text{HCO}_3^-$  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  $\text{HCO}_3^-$  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  $\alpha_{\text{eq}}$  remains constant during the entire process. For equilibrium fractionation,  $\alpha_{\text{eq}}$  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  $C_{\text{eq}}$  which depends on the  $p_{\text{co}_2}$  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  $\alpha_p^A$ ,  $\alpha_p^B$  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

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

$\tau_A$  and  $\tau_B$  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  $\alpha_{iso}$  clearly is a function of A and B and the condition that  $\alpha_{iso}$  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  $\alpha_{eq}$ .

To call  $\alpha_{kin}$  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)  $\alpha_{kin}$  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  $\varepsilon$ . The parameters determining precipitation,  $\varepsilon$ , and  $\tau_A$  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.  $\delta$  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  $1 > C/C_0 > 0.8$  can be found by expanding eqn.11 linear in time as  $C(t) = (C_0 - C_{eq})(1 - t/\tau_A) + C_{eq}$ . Solving for  $t/\tau_A$  and inserting into eqns. 13 or 14 yields

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

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

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  $\varepsilon$  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  $C_0/C_{eq}$ .

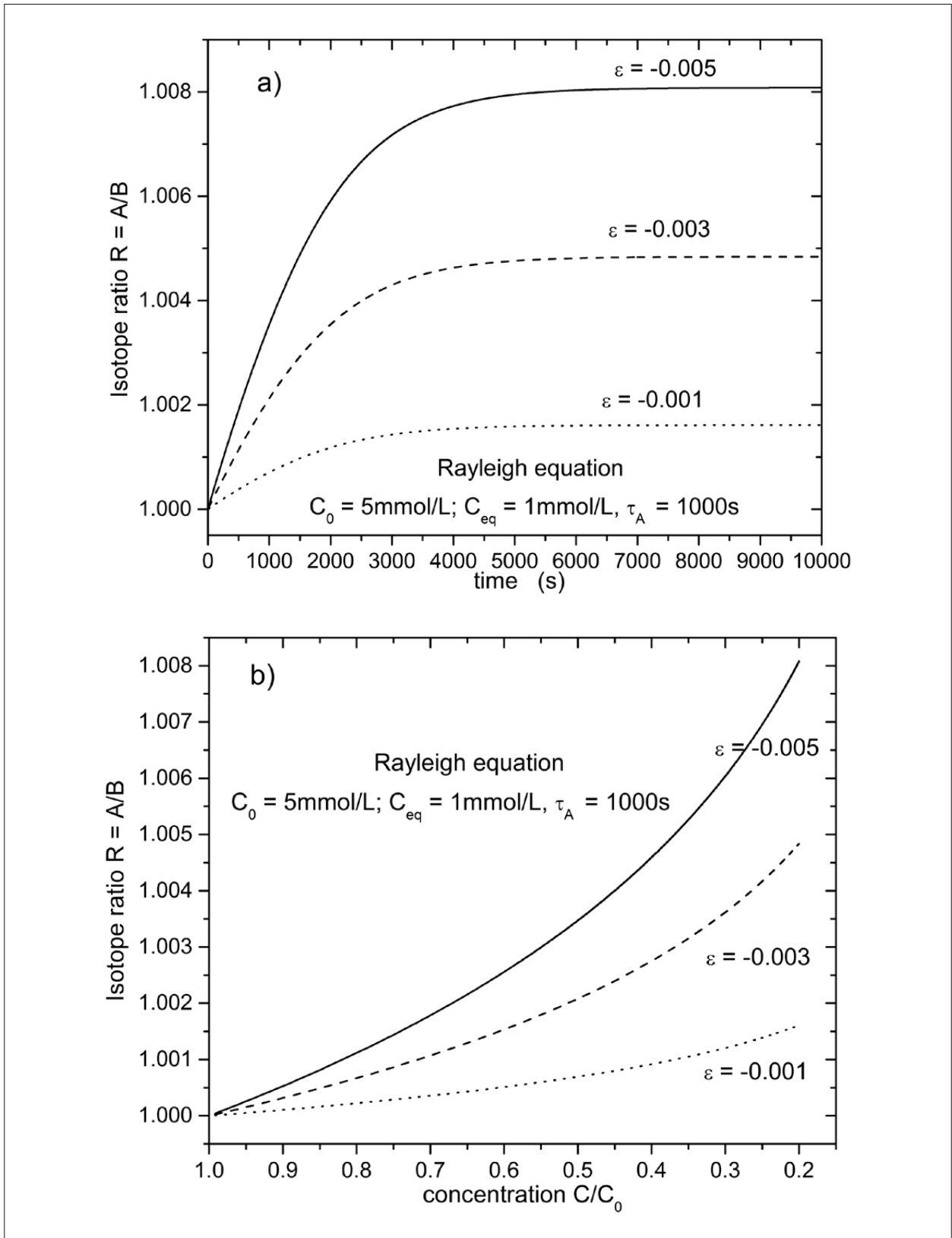


Fig. 1: Evolution of the isotope ratio  $R$  for the classical Rayleigh equation  $R=R_0(C/C_0)^\epsilon$  for various values of  $\epsilon$ . a) as function of time with  $C(t)=(C_0-C_{\text{eq}})\exp(-t/\tau_A)+C_{\text{eq}}$  and b) as function of concentration.

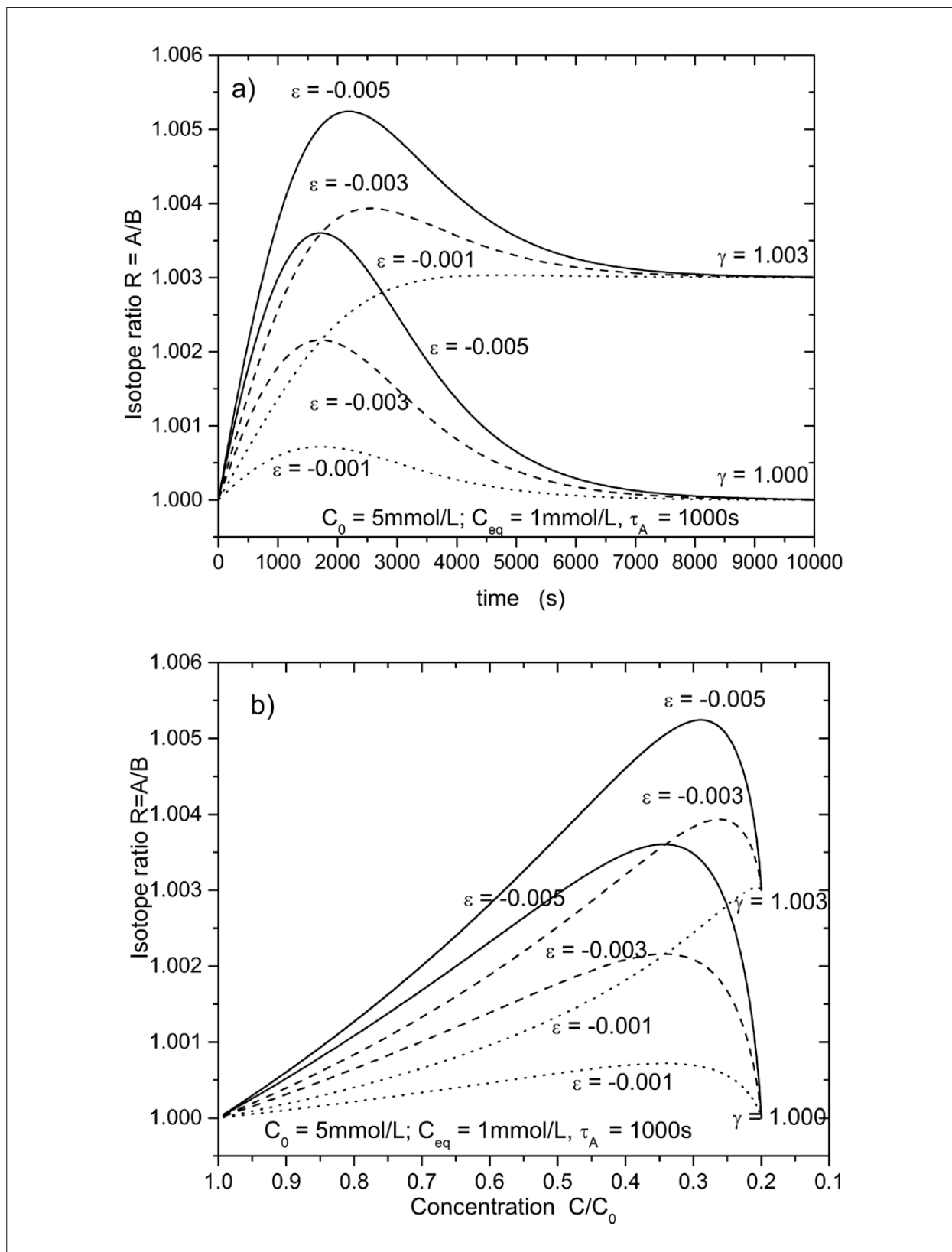


Fig. 2: Evolution of the isotope ratio  $R$  for the extended Rayleigh equation (eqn. 9) for various values of  $\epsilon$  and  $\gamma$ . a) as function of time with  $C(t)=(C_0-C_{eq})\exp(-t/\tau_A)+C_{eq}$  and b) as function of concentration  $C$ .

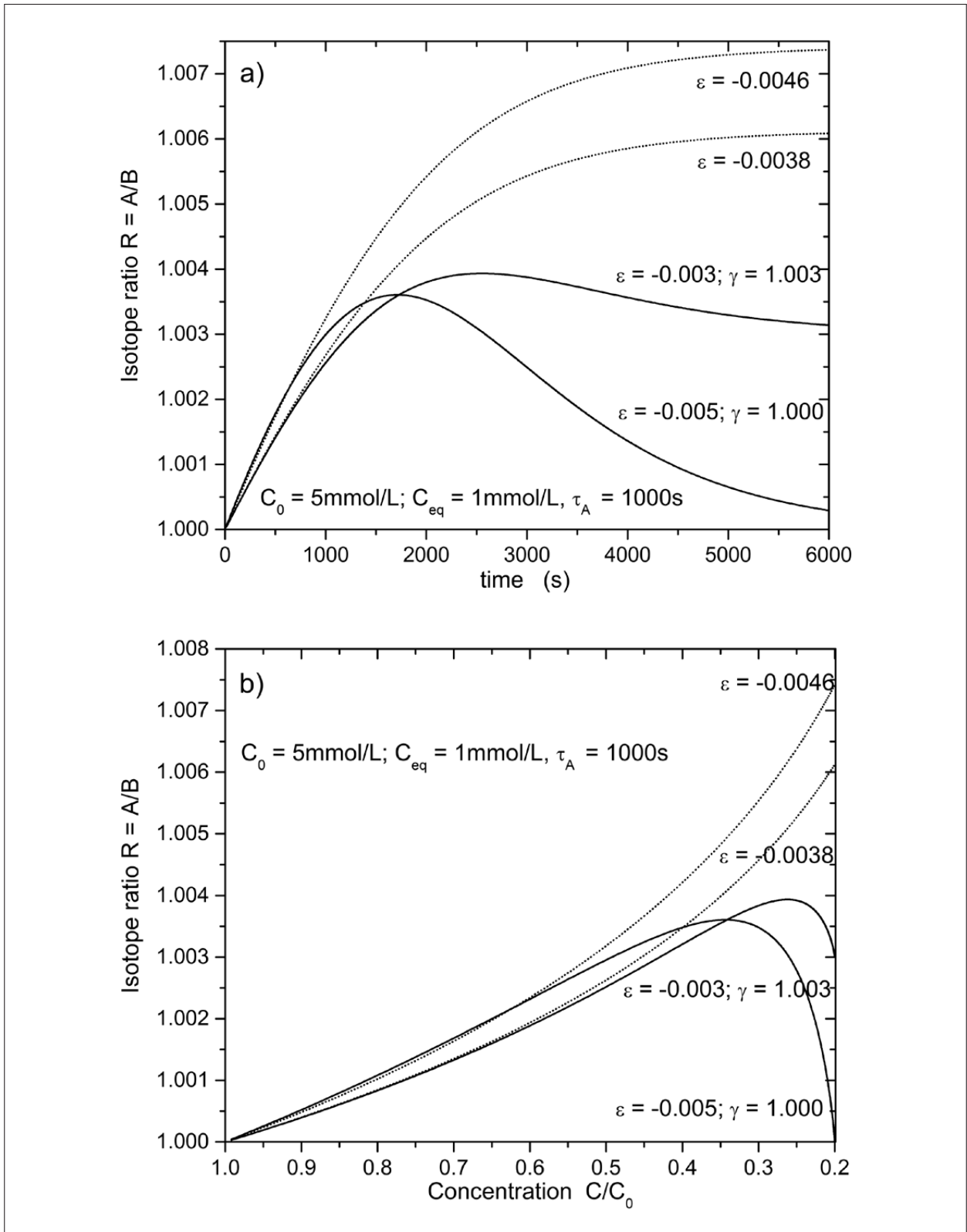


Fig. 3: Comparison of the evolution of the isotope ratio  $R$  for the extended Rayleigh equation (eqn. 9), full lines and the classical Rayleigh equation, dotted curves as function of a) time and b) concentration. The values of  $\epsilon$  for the classical Rayleigh equation have been chosen to match 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,  $\text{HCO}_3^-$ ,  $C(t) = (C_0 - C_{\text{eq}}) \exp(-t/\tau_b) + C_{\text{eq}}$ .

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  $\epsilon_{\text{fit}}$ , 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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