Calcite dissolution kinetics in the system CaCO$_3$–H$_2$O–CO$_2$ at high undersaturation

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Received 18 August 2005; accepted in revised form 31 October 2006; available online 19 December 2006

Abstract

Dissolution rates of limestone covered by a water film open to a CO$_2$-containing atmosphere are controlled by the chemical composition of the CaCO$_3$–H$_2$O–CO$_2$ solution at the water-mineral interface. This composition is determined by the Ca$^{2+}$-concentration at this boundary, conversion of CO$_2$ into H$^+$ and HCO$_3^-$ in the solution, and by diffusional mass transport of the dissolved species from and towards the water–limestone interface. A system of coupled diffusion–reaction equations for Ca$^{2+}$, HCO$_3^-$, and CO$_2$ is derived. The Ca$^{2+}$ flux rates at the surface of the mineral are defined by the PWP-empirical rate law. These flux rates by the rules of stoichiometry must be equal to the flux rates of CO$_2$ across the air–water interface. In the solution, CO$_2$ is converted into H$^+$ and HCO$_3^-$. At low water-film thickness this reaction becomes rate limiting. The time dependent diffusion–reaction equations are solved for free drift dissolution by a finite-difference scheme, to obtain the dissolution rate of calcite as a function of the average calcium concentration in the water film. Dissolution rates are obtained for high undersaturation. The results reveal two regimes of linear dissolution kinetics, which can be described by a rate law $F = a_i(c_{eq} - c)$, where $c$ is the calcium concentration in the water film, $c_{eq}$ the equilibrium concentration with respect to calcite. For index $i = 0$, a fast rate law, which here is reported for the first time, is found with $a_0 = 3 \cdot 10^{-6}$ ms$^{-1}$ and $m_0 = 0.3$. For $c > m_0c_{eq}$, a slow rate law is valid with $a_1 = 3 \cdot 10^{-7}$ ms$^{-1}$ and $m_1 = 1$, which confirms earlier work. The numbers given above are valid for film thickness of several tenths of a millimetre and at 20°C. These rates are proven experimentally, using a flat inclined limestone plate covered by a laminar flowing water film injected at an input point with known flow rate $Q$ and calcium concentration. From the concentration measured after flow distance $x$ the dissolution rates are determined. These experiments have been performed at a carbon-dioxide pressure of 0.00035 atm and also of 0.01 atm. The results are in good agreement to the theoretical predictions.

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1. INTRODUCTION

The dissolution rates of calcite (limestone) in CO$_2$-containing aqueous solutions are determined by three rate-controlling processes: (1) the kinetics of dissolution at the mineral surface, which depends on the chemical composition of the solution at the liquid–rock boundary. (2) Mass transport by diffusion away from this boundary for the dissolved material Ca$^{2+}$, HCO$_3^-$, and CO$_3^{2-}$ and towards this boundary for the reactant CO$_2$. (3) Conversion of CO$_2$ into H$^+$ and HCO$_3^-$. Depending on geometrical conditions, i.e. the ratio $V/A$ with $V$ the volume of the solution and $A$ the reactive surface of the mineral, or flow conditions, laminar or turbulent, and the carbon dioxide pressure $p$ in equilibrium, each of these processes can be rate limiting.

Buhmann and Dreybrodt (1985) have derived a numerical model of calcite dissolution in the ternary system CaCO$_3$–H$_2$O–CO$_2$ and have shown that for thin
water films as they occur on rock surfaces exposed to rain fall, the dissolution rates depend linearly on the thickness $\delta$ of the water film for $\delta < 0.005$ cm. Due to computational restrictions at that time, however, the model yielded results only for concentrations $c$ of dissolved Ca higher than 0.2$c_{eq}$, the equilibrium concentration with respect to calcite. The results of this model have been verified experimentally (Buhmann and Dreybrodt, 1985; Dreybrodt et al., 1996). However, attempts to extrapolate the rates to zero by a linear relationship are dubious, and have failed to explain denudation rates of about 15 $\mu$m/year on bare rock surfaces, exposed to meteoric precipitation of about 1300 mm/year (Cucchi et al., 1995). We have performed preliminary fieldwork and have measured the calcium concentration of rainwater during heavy rain, after flow of about 1 m along an inclined limestone surface. Concentrations of Ca remained below 0.25 mol m$^{-3}$, which shows that for such cases most of the dissolution occurs at high undersaturation. Since dissolution of limestone by rainwater on bare rock surfaces is of interest in surface denudation in karst terraines, but also in corrosion of limestone surfaces on historical and modern buildings, more knowledge about dissolution rates at high undersaturation is required. These are also of interest in the construction of reactors where CO$_2$ containing solutions flow through columns of broken rock.

This paper revisits the model of Buhmann and Dreybrodt (1985) for thin water films in laminar flow. A new numerical approach to solve its diffusion–reaction equations is employed. It avoids some approximations, which have caused numerical problems at low Ca concentrations. By this way the dissolution rates can be calculated at concentrations as low as 0.01$c_{eq}$ for film thickness $\delta$ between 0.001 and 0.1 cm and partial pressures $p$ of CO$_2$ in equilibrium with the solution from 0.00035 to 0.01 atm. The new results show a strong increase in rates, which can be described by a linear approximation to the rate $F_{Ca}^{2+} = z_0 \cdot (m_0$c_{eq} – $c$), with $m_0 = 0.3$ and $z_0 = 3 \times 10^{-6}$ m s$^{-1}$, about one order of magnitude higher than the value of $z_1$ found by Buhmann and Dreybrodt (1985) for $c > 0.2$c_{eq}. These results motivated us to conduct experiments to measure the rate laws of CO$_2$-containing water films of several tenths of a millimeter in thickness, flowing down inclined limestone surfaces in laminar flow. The experiments and their results are reported in the last section.

2. DISSOLUTION CHEMISTRY

Limestone dissolution and precipitation is mainly controlled by the reactions occurring within the ternary system water (H$_2$O), carbon dioxide (CO$_2$), and calcite (CaCO$_3$). We follow the derivation of Buhmann and Dreybrodt (1985), and only briefly review the principles needed to describe the dissolution chemistry.

The chemical reactions and processes responsible for the removal or deposition of calcite, for the case of open-system conditions with respect to CO$_2$, are:

\[
\begin{align*}
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- \quad (1a) \\
\text{CO}_2,\text{atm} & \rightleftharpoons \text{CO}_2 \quad (1b) \\
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 \quad (1c) \\
\text{CO}_2 + \text{OH}^- & \rightleftharpoons \text{HCO}_3^- \quad (1d) \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad (1e) \\
\text{CaCO}_3 + \text{H}^+ & \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^- \quad (1f) \\
\text{CaCO}_3 + \text{H}_2\text{CO}_3 & \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (1g) \\
\text{CaCO}_3 + \text{H}_2\text{O} & \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (1h)
\end{align*}
\]

The first reaction describes the dissociation of water into hydrogen- and hydroxyl-ions, the second one the physical dissolution of carbon dioxide in water, the third and fourth reactions the conversion of carbon dioxide into hydrogen and bicarbonate, depending on the pH-value of the solution, the fifth reaction the dissociation of bicarbonate into hydrogen- and carbonate-ions, and the sixth to eight reactions the dissolution of calcite, also depending on the pH-value. The equilibrium constants of the fast reactions indicated by capitals, and the reaction-rate constants for slow reactions are listed in Table 1. All coefficients are derived from laboratory experiments (Harned and Hamer, 1933; Plummer et al., 1978; Plummer and Busenberg, 1982; Usdowski, 1982).

2.1. Stoichiometry

The steps mentioned above can be summarized into:

\[
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (2)
\]

From the above summation equation, the important stoichiometric condition can be seen: for one Ca$^{2+}$-ion dissolved one CO$_2$-molecule is consumed from the solution. In the open system, it is replaced from the CO$_2$ in the atmosphere.

\[
\text{H}_2\text{CO}_3^0 \text{can be rewritten in terms of the total amount of CO}_2 \text{ available:}
\]

\[
\text{H}_2\text{CO}_3^0 = \text{CO}_2 + \text{H}_2\text{CO}_3^0 \quad (3)
\]

2.2. Electro-neutrality

The equation of electro-neutrality, neglecting ion pairing, is

\[
2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (4)
\]

with $[X]$ (in mol m$^{-3}$) the concentration of species $X$. In natural karst water, with $6 < \text{pH} < 8$ and the concentration of $\text{H}^+$, $\text{OH}^-$, and $\text{CO}_2^{2-}$ can be neglected (Buhmann and Dreybrodt, 1985; Dreybrodt, 1988).
Table 1
Parameters used for the numerical experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log K_W$</td>
<td>mol$^{-1}$</td>
<td>22.801 - 4787.3 $T^{-1}$ - 0.010365 $T - 7.1321 \log T$</td>
</tr>
<tr>
<td>$\log K_{H}$</td>
<td>mol$^{-1}$ atm$^{-1}$</td>
<td>108.3865 - 6919.53 $T^{-1}$ + 0.01985076 $T - 40.45154 \log T + 669365 T^{-2}$</td>
</tr>
<tr>
<td>$\log K_C$</td>
<td>mol$^{2}$</td>
<td>1.7 - 171.9065 - 0.0779937 + 28.39319 $T^{-1}$ + 71.595 $\log T$</td>
</tr>
<tr>
<td>$K_0$</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>$\log K_i$</td>
<td>mol$^{-1}$</td>
<td>-356.3094 - 0.06091964 $T$ + 21834.37 $T^{-1}$ + 126.8339 $\log T - 1684915 T^{-2}$</td>
</tr>
<tr>
<td>$\log K_2$</td>
<td>mol$^{-1}$</td>
<td>-107.8871 + 5151.79 $T^{-1}$ - 0.03252849 $T + 38.92561 \log T - 563713.9 T^{-2}$</td>
</tr>
<tr>
<td>$\log K_1$</td>
<td>l mol$^{-1}$</td>
<td>1209.120 - 34765.05 $T^{-1}$ + 0.31294 $T - 478.782 \log T$</td>
</tr>
<tr>
<td>$\log K_4$</td>
<td>l mol$^{-1}$</td>
<td>-1228.732 + 35512.75 $T^{-1}$ - 0.299444 $T + 485.818 \log T$</td>
</tr>
<tr>
<td>$\log K_5$</td>
<td>l mol$^{-1}$</td>
<td>1.707 $\times 10^{-4}$</td>
</tr>
<tr>
<td>$\log k_1$</td>
<td>cm s$^{-1}$</td>
<td>0.198 - 444 $T^{-1}$</td>
</tr>
<tr>
<td>$\log k_2$</td>
<td>cm s$^{-1}$</td>
<td>2.84 - 2177 $T^{-1}$</td>
</tr>
<tr>
<td>$\log k_3$</td>
<td>mmol cm$^{-2}$ s$^{-1}$</td>
<td>-5.86 - 3177 $T^{-1}$, $T_C &lt; 25 - 1.10 - 1737 T^{-1}$, $25 &lt; T_C &lt; 48$</td>
</tr>
<tr>
<td>$\log k_4$</td>
<td>cm$^2$ mmol$^{-1}$ s$^{-1}$</td>
<td>-2.375 + 0.025 $T_C &lt; 0.05 \text{ atm} - 2.375 + 0.025 T_C + 0.56 (- \log p_{CO_2} - 1.3)$, $p_{CO_2} &lt; 0.05 \text{ atm}$</td>
</tr>
<tr>
<td>$\log k_5$</td>
<td>s$^{-1}$</td>
<td>3</td>
</tr>
<tr>
<td>$\log k_6$</td>
<td>s$^{-1}$</td>
<td>3</td>
</tr>
<tr>
<td>$\log k_7$</td>
<td>s$^{-1}$</td>
<td>13.588 - 3617 $T^{-1}$</td>
</tr>
<tr>
<td>$\log k_8$</td>
<td>l mol$^{-1}$ s$^{-1}$</td>
<td>13.635 - 2895 $T$</td>
</tr>
<tr>
<td>$\log k_9$</td>
<td>s$^{-1}$</td>
<td>14.09 - 5308 $T$</td>
</tr>
<tr>
<td>$k_a$</td>
<td>l (mol s)$^{-1}$</td>
<td>$k_a = k_i (\gamma_{H^+}/\gamma_{HCO_3^-})/K_S$</td>
</tr>
<tr>
<td>$D_{CO_2}$</td>
<td>cm$^2$ s$^{-1}$</td>
<td>$10^{-5} (0.56 + 0.058 T_C$</td>
</tr>
<tr>
<td>$D_{CO_3^-}$</td>
<td>cm$^2$ s$^{-1}$</td>
<td>$0.7 \times D_{CO_2}$</td>
</tr>
<tr>
<td>$D_{HCO_3^-}$</td>
<td>cm$^2$ s$^{-1}$</td>
<td>$0.7 \times D_{CO_2}$</td>
</tr>
<tr>
<td>$D_{CO_2^-}$</td>
<td>cm$^2$ s$^{-1}$</td>
<td>$0.7 \times D_{CO_2}$</td>
</tr>
<tr>
<td>$T_C$</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>K</td>
<td>$T_C + 273.16$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>atm</td>
<td></td>
</tr>
</tbody>
</table>

The data are taken directly from the original publication, conversion to SI-units is done in the program.

1 Plummer and Busenberg (1982).
2 Plummer et al. (1978).
3 Usdowski (1982).
4 Buhmann and Dreybrodt (1985).
5 Harden and Hamer (1933).
6 This study.

As both the activity ($X_i$) and the concentration [$X_i$] have the dimension mol m$^{-3}$, the ion activity coefficient is dimensionless. In this work we still use activities in mol m$^{-3}$ and dimensionless activity coefficients, which implies that the equilibrium constants as shown in Table 1 have dimensions. We do this to comply with the dimensions used in the cited publications.

We apply the extended Debye–Hückel theory to derive ion activity coefficients, a theory only valid for very dilute solutions, $I < 10$ mol m$^{-3}$, which is true for karst water. Following Robinson and Stokes (1955), the extended Debye–Hückel equation is given by

$$\log \gamma_i = - \frac{A \alpha_i \sqrt{I}}{1 + B \alpha_i \sqrt{I}} + b_i I$$

where $\alpha_i$ (in m) and $b_i$ (in m$^3$ mol$^{-1}$) are ion-specific parameters, and $A$ (in m$^{-1}$ mol$^{-1}$) and $B$ (in m$^{-1}$ m$^{-1}$) temperature-dependent coefficients (Truesdell and Jellinek, 1974, see Table 2). For uncharged species, e.g. CO$_2$ or H$_2$CO$_3$, the ion activity is given by

$$\gamma_i = 10^{A \alpha_i / I}$$

Activity coefficients decrease from $\gamma \approx 1$ for very dilute solutions to values between 0.6 and 0.9 for calcium concentrations close to saturation.
Table 2
Coefficients for the Debye–Hückel equation (from Dreybrodt (1988))

<table>
<thead>
<tr>
<th>Ion</th>
<th>$a_i$ [10^{-10} m]</th>
<th>$b_i$ [mol^{-1}]</th>
<th>$z_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca^{2+}</td>
<td>5.0</td>
<td>0.165</td>
<td>+2</td>
</tr>
<tr>
<td>H^{+}</td>
<td>9.0</td>
<td>—</td>
<td>+1</td>
</tr>
<tr>
<td>CO_{3}^{2-}</td>
<td>5.4</td>
<td>—</td>
<td>-1</td>
</tr>
<tr>
<td>OH^{-}</td>
<td>3.5</td>
<td>—</td>
<td>-1</td>
</tr>
</tbody>
</table>

$A = 0.4883 + 8.074 \times 10^{-4} T_C$, $B = 10^{10} \times 0.3241 + 1.600 \times 10^{-4} T_C$.

Table 3
Calcium equilibrium concentration (12) in the open system (in mol m^{-2}) for different temperatures T (in °C) and partial carbon-dioxide pressures $p$ (in atm)

<table>
<thead>
<tr>
<th>$T/p$</th>
<th>0.00035</th>
<th>0.001</th>
<th>0.005</th>
<th>0.01</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.64</td>
<td>0.92</td>
<td>1.62</td>
<td>2.07</td>
<td>4.71</td>
</tr>
<tr>
<td>20</td>
<td>0.54</td>
<td>0.77</td>
<td>1.37</td>
<td>1.75</td>
<td>3.12</td>
</tr>
</tbody>
</table>

For the calculation, the coefficients from Table 1 are used.

2.4. Equilibrium chemistry

For solutions, which are saturated with respect to Ca^{2+}, one obtains an analytical expression for the calcium equilibrium concentration $[Ca^{2+}]_{eq}$ as a function of carbon-dioxide partial pressure $p$ (in atm) in equilibrium with the solution (Dreybrodt, 1988):

$$[Ca^{2+}]_{eq} = \frac{K_K K_C K_H}{4K_{Ca^{2+}} K_{HCO_3^-}} p$$

where $\gamma_{Ca^{2+}}$ and $\gamma_{HCO_3^-}$ are the activity coefficients of Ca^{2+} and HCO_3^- (Table 3).

2.5. Rate-limiting reactions

Several slow processes control calcite dissolution. We consider the open-system case, in which a thin layer of water is in contact with the atmosphere. The atmosphere–solution interface is located at $z = 0$, the solution–rock interface at $z = \delta$.

2.5.1. Mass flux of calcium from the solid interface

At the calcite surface, three reactions (1f–h) characterise the dissolution process. In all reactions, calcite is dissolved and therefore a flux of Ca^{2+} is directed away from the interface solution–rock. The calcium flux rate $F_{Ca^{2+}}$ (in mol m^{-2} s^{-1}) has been determined experimentally by Plummer et al. (1978). From their experimental results, Plummer et al. (1978) derived a rate equation, known as PWP-equation, which is given as

$$F_{Ca^{2+}} = \kappa_1 [H^+] + \kappa_2 [H_2CO_3^{-}] + \kappa_3 - \kappa_4 [Ca^{2+}] [HCO_3^-]$$

with $z = \delta$ indicating the location of the surface of the rock. The forward reactions are controlled by the temperature-dependent rate constants $\kappa_1$, $\kappa_2$, and $\kappa_3$. The three back reactions characterised by the rate constants $\kappa_4$, $\kappa_5$, and $\kappa_6$ can be summarized into one, as they all contain the product (Ca^{2+}) (HCO_3^{-}). A common back-reaction constant is defined as $\kappa_4 = \kappa_4' + \kappa_4'' (HCO_3^-) + \kappa_4''' (OH^-)$. Note that $\kappa_4$ is both temperature- and CO_2-dependent. The expressions for $\kappa_1$, $\kappa_2$, and $\kappa_3$ listed in Table 1 are taken from Plummer et al. (1978), the empirical relation for $\kappa_4$ in this study is valid for temperatures up to 35 °C and fits well the experimental data derived by Plummer et al. (1978).

2.5.2. Conversion of carbon dioxide in the solution

The physically dissolved CO_2 in the solution is converted into H^{+} and HCO_3^{-} (1c and d). The two reactions can be summarized into a carbon dioxide conversion rate $R_{CO_2}$ (in mol m^{-3} s^{-1}) (Kern, 1960):

$$R_{CO_2} = -k_1 [CO_2] + k_3 [H^+] [HCO_3^-] - k_2 [CO_2] [OH^-] + k_4 [CO_2] [H^+] [HCO_3^-]$$

Here, a new kinetic constant $k_a$ has been introduced (Table 1), accounting for the fast dissociation of carbonic acid.

2.5.3. Mass transport by diffusion

The dissolved species (CO_2, H^+, HCO_3^{-}, CO_3^{2-}, Ca^{2+}) are transported by molecular diffusion from regions of high concentrations to lower concentrations. Depending on the thickness of the water film, the diffusion processes can be rate-limiting for calcite dissolution.

We assume a water film flowing with a velocity $v_y$, which is constant across the water film (assuming plug flow). The concentration of species $i$ is $[X_i]$, and the diffusion coefficient of species $i$ is $D_i$ (in m^2 s^{-1}). Transport of all dissolved species can then be described by a diffusion–advection equation:

$$\frac{\partial [X_i]}{\partial t} + v_y \frac{\partial [X_i]}{\partial y} - D_i \frac{\partial^2 [X_i]}{\partial z^2} = R_i$$

with $t$ the time (in s) and $y$ and $z$ the horizontal and vertical coordinates (in m), respectively. The first term of the left-hand side is the temporal change in concentration, the second term the advection of the species, and the third term the diffusion of the species. On the right-hand side, $R_i$ (in mol m^{-3} s^{-1}) is a source term of species $i$. With the assumption of plug flow, a water column moves over the rock with a constant velocity. As we consider vertical variations in concentration only, the vertical column is simply advected with the flow, and thus we can safely set $v_y = 0$ and reduce (15) to:

$$\frac{\partial [X_i]}{\partial t} - D_i \frac{\partial^2 [X_i]}{\partial z^2} = R_i$$

(16)

Based on (16), we discuss transport for the different dissolved species in the next sections.

2.5.3.1. Carbon dioxide (CO_2). Inserting the kinetic Eqs. (14) into (16) yields a diffusion–reaction equation for CO_2:

$$- \frac{\partial [CO_2]}{\partial t} + D_{CO_2} \frac{\partial^2 [CO_2]}{\partial z^2} = +k_1 [CO_2] - k_2 [H^+] [HCO_3^-] + k_3 [CO_2] [OH^-] - k_4 [CO_2] [HCO_3^-]$$

(17)
Here, $D_{CO_2}$ is the diffusion coefficient of CO$_2$-molecules, and $k_i^+$ and $k_i^-$ are the temperature-dependent carbon dioxide flux constants (see Table 1). The boundary conditions for CO$_2$ are given as:

$$\frac{\partial [CO_2]}{\partial z} \bigg|_{z=0} = 0$$

$$[CO_2]_{z=0} = K_H p_{CO_2}$$

(18)

They state that CO$_2$ does not react at the solution–rock interface, hence there is no flow, and that CO$_2$ at the atmosphere–solution interface is related to the carbon-dioxide partial pressure $p$ of the atmosphere.

2.5.3.2. Bicarbonate ($HCO_3^-$). For HCO$_3^-$ we find:

$$-\frac{\partial [HCO_3^-]}{\partial t} + D_{eff} \frac{\partial^2 [HCO_3^-]}{\partial z^2} = -k_i^+[CO_2] + k_i^+[H^+][HCO_3^-] - k_i^+[CO_2][OH^-] + k_i^+[HCO_3^-]$$

(19)

The boundary conditions for HCO$_3^-$ are:

$$[HCO_3^-]_{z=0} = [HCO_3^-]_i$$

$$\left[\frac{\partial [HCO_3^-]}{\partial z}\right]_{z=0} = 0$$

(20)

At the solution–rock interface, an initial HCO$_3^-$-concentration needs to be assigned. A realistic value is (Buhmann and Dreybrodt, 1985) $[HCO_3^-]_i \approx 2[Ca^{2+}]_i$. At the atmosphere–solution interface, no bicarbonate can leave the solution, and thus the flux must be zero.

2.5.3.3. Calcium ($Ca^{2+}$). Since we neglect ion-pairing, $[Ca^{2+}]$ does not react with other species. Then the source term within the solution is zero, $R_{Ca^{2+}} = 0$, and the diffusion equation for calcium reads:

$$-\frac{\partial [Ca^{2+}]}{\partial t} + D_{eff} \frac{\partial^2 [Ca^{2+}]}{\partial z^2} = 0$$

(21)

As $[Ca^{2+}]$ is decoupled from the other species, (21) can be solved independently. The boundary conditions for $[Ca^{2+}]$ are given as:

$$\left[\frac{\partial [Ca^{2+}]}{\partial z}\right]_{z=0} = \frac{F_{Ca^{2+}}}{D_{Ca^{2+}}}$$

$$\left[\frac{\partial [Ca^{2+}]}{\partial z}\right]_{z=0} = 0$$

(22)

Here, the flux of $[Ca^{2+}]$ from the solid crystal into the solution is described by the PWP-Eq. (13), and no $[Ca^{2+}]$ can leave the solution.

Since the dominant ionic species are $Ca^{2+}$ and $HCO_3^-$, an effective multi-component diffusion coefficient can be used for both species, which is given by the Nerst–Hartley relation (Lasaga, 1998):

$$D_{eff} = \frac{3D_{HCO_3^-}D_{Ca^{2+}}}{2D_{Ca^{2+}} + D_{HCO_3^-}} \approx 0.7D_{CO_2}$$

(23)

2.5.4. Concentration profiles

Following Buhmann and Dreybrodt (1985), we derive the concentration profiles for the dissolved species, $[Ca^{2+}]$, $[H^+]$, $[CO_3^{2-}]$, $[H_2CO_3]$ and $[OH^-]$ for a given flux $F_{Ca^{2+}}$ of $Ca^{2+}$:

$$[Ca^{2+}] (z, t) = \frac{F_{Ca^{2+}}}{\delta} \left\{ \frac{z}{\delta} - \frac{z^2}{\delta^2} \right\} + [Ca^{2+}]_{z=0}$$

$$[H^+] (z) = \frac{1}{2} \left\{ 2[Ca^{2+}] (z) - [HCO_3^-] (z) \right\}$$

$$+ \frac{1}{4} \left\{ 2[Ca^{2+}] (z) - [HCO_3^-] (z) \right\}^2$$

$$+ \frac{K_W}{\gamma_{H^+}\gamma_{OH^-}} \left\{ 2K_2[HCO_3^-(z)] \right\}$$

$$[CO_3^{2-}] (z) = \frac{K_2[HCO_3^-][HCO_3^-] (z)}{\gamma_{H^+}\gamma_{OH^-}}$$

$$[H_2CO_3] (z) = \frac{\gamma_{H^+}\gamma_{OH^-}}{K_3} [H^+] (z) [HCO_3^-] (z)$$

$$[OH^-] (z) = \frac{K_W}{\gamma_{H^+}\gamma_{OH^-}} \frac{1}{K_3}$$

(24)

For $[CO_2]$ and $[HCO_3^-]$, we solve the two coupled diffusion Eqs. (17) and (19).

To facilitate the comparison with experimental results, we plot the flux rate $F_{Ca^{2+}}$ against the average calcium concentration in the water film according to the relation:

$$[Ca^{2+}]_{av} = [Ca^{2+}]_i - \frac{F_{Ca^{2+}}}{3D_{Ca^{2+}}}$$

(25)

3. NUMERICAL METHOD AND RESULTS

We first discuss the calcium flux rates obtained from a numerical procedure.

3.1. Solution procedure

The numerical procedure to solve for the flux rates is as follows:

1. Discrète the water film of thickness $\delta$ (in m) into $N$ segments of equal thickness, thus the spatial increment is $dz = \delta/N$.

2. Assign temperature $T$, carbon-dioxide pressure $p$, and initial calcium concentration along the calcite surface: $[Ca^{2+}]_{i} \approx 0.1 \text{ mol m}^{-3}$.

3. Assign a realistic initial value for the bicarbonate concentration: $[HCO_3^-]_{i} \approx 2[Ca^{2+}]_{i}$.

4. Calculate ionic activity $a_i$, activity coefficients $\gamma_i$, and both equilibrium and rate constants, $k_i, k_i^+$, $k_i^-$ (Table 1).

5. Calculate the concentrations for $[Ca^{2+}]$, $[H^+]$, $[CO_3^{2-}]$, $[H_2CO_3]$ and $[OH^-]$ at the calcite–water interface from (24).

6. Calculate calcium flux rate $F_{Ca^{2+}}$ from (13).

7. Assign an initial approximation of the concentration profile for bicarbonate and carbon dioxide:

$$[HCO_3^-] (z) = [HCO_3^-]_{i}$$

$$[CO_2] (z) = [CO_2]_{i} + \frac{\delta}{\delta} \left\{ [CO_2]_0 - [CO_2]_{i} \right\}$$
8. Calculate concentration profiles from (24).
9. Solve diffusion Eqs. (17) and (19) with an explicit finite-difference scheme, using a time step of \( dt \leq \frac{d^2}{2D_{Ca^2+}} \).

10. Calculate carbon-dioxide flux rate \( F_{CO2} \) from numerical integration of (14) along \( z: F_{CO2} = \int_0^z R_{CO2}dz \).

11. Compare the calcium and carbon dioxide flux rates: If \( \frac{|F_{CO2} - F_{Ca^2+}|}{F_{Ca^2+}} > \varepsilon \), change \([HCO_3^-]/C_0\) and go to 5, otherwise the solution is found. The accuracy \( \varepsilon \) is taken as 0.01.

### 3.2. Flux rates

The parameter values chosen cover a wide range of situations encountered in natural karst environments, from cold \((T=10\, ^{\circ}C)\) to warm climates \((T=20\, ^{\circ}C)\), from pure rain water \((p=3.5 \times 10^{-4}\) atm\) to seepage water strongly enriched with soil carbon dioxide \((p=10^{-2}\) atm\), and from film thicknesses in the micron range \((d=2 \times 10^{-5}\) m\) to the millimetre scale \((d=10^{-3}\) m\).

Results for the calcium flux rate as a function of \([Ca^{2+}]_{av}\) are shown in Fig. 1. All flux rate curves show a typical behaviour: If the solution is strongly undersaturated with respect to calcite \(([[Ca^{2+}] < 0.3\, mol\, m^{-3}\)) \), flux rates drop steeply over one order of magnitude from large values close to \(10^{-6}\, mol\, m^{-2}\, s^{-1}\) to values around \(10^{-7}\, mol\, m^{-2}\, s^{-1}\) over a relatively short range. From then on, changes in flux rate as a function of \([Ca^{2+}]\) are much smaller. We identify the fast rate law at high undersaturation. For higher \([Ca^{2+}]\) a slow rate law takes over. While the latter slow rate law has been approximated by a linear relation, for which

![Fig. 1. Calcium flux rate as a function of average calcium concentration for different carbon dioxide pressures, temperatures, and film thicknesses (see legend). Fluxrates are given for 10 °C (left panels) and 20 °C (right panels).](image-url)
slope parameter values are tabulated in Buhmann and Dreybrodt (1985), the fast rate law has not been described before.

Looking closer into the effect of film thickness, we find the three regimes proposed by Dreybrodt (1988) and Buhmann and Dreybrodt (1985):

Regime 1: For small film thicknesses ($\delta < 0.005$ cm), flux rates increase linearly with film thickness. In this regime the conversion of $\text{CO}_2$ into $\text{H}^+$ and $\text{HCO}_3^-$ is the rate-limiting step. Due to the small film thickness, diffusion is not limiting.

Regime 2: For intermediate film thicknesses ($\delta \approx 0.01$ cm), both $\text{CO}_2$-conversion and molecular diffusion are rate limiting. Here, flux rates are fairly similar for different film thicknesses.

Regime 3: For large film thicknesses ($\delta > 0.05$ cm), diffusion becomes the dominant rate limiting process. Flux rates for larger film thicknesses start to drop again, as it can be seen for $\delta = 0.1$ cm.

Comparing the left and the right panels in Fig. 1, the temperature dependence can be seen. A rise in temperature from 10 to 20 °C increases the flux rates for all film thicknesses and partial carbon-dioxide pressures.

To elucidate a bit further the very high flux rates for strong undersaturation, we have plotted the individual contributions of the PWP-Eq. (13) in Fig. 2 for one selected scenario ($T = 10^\circ C$, $p = 0.005$ atm, $\delta = 0.01$ cm). It is obvious that the two first terms in the PWP-equation, $k_1$ ($\text{H}^+$) and $k_2$ ($\text{H}_2\text{CO}_3^-$), provide no significant contribution to the dissolution process. The dissolution due to the reaction with water, characterised by the third term $k_3$, is by far the most important forward reaction. The large dissolution rate controlled by $k_3$ is balanced by the back-reaction $k_4$ ($\text{Ca}^{2+}$) ($\text{HCO}_3^-$), which precipitates calcite from the solution. For large undersaturation, the contribution of the back-reaction is significantly smaller than the dominant forward reaction, hence one finds large calcium flux rates for $[\text{Ca}^{2+}] < 0.3$ mol m$^{-3}$.

We can compare the calculation for the parameter set $T = 10^\circ C$, $p = 0.005$ atm, and $\delta = 0.1$ cm with experimental results published in Buhmann and Dreybrodt (1985), see their Fig. 9. The calcium concentration achieved after around 150 min is around 0.7 mol m$^{-3}$ in their experiment, and our inference reaches a value of around 0.6 mol m$^{-3}$ after the same time.

3.3. Time dependence

We now derive the time dependence of the dissolution process for different temperatures and film thicknesses, and a partial carbon-dioxide pressure of $p = 0.005$ atm. Therefore, an integration is performed for the calcium concentration, starting with an initial calcium concentration of $[\text{Ca}^{2+}]_{\text{initial}} = 0$:

$$[\text{Ca}^{2+}](t) = [\text{Ca}^{2+}]_{\text{initial}} + \int_0^t \frac{F_c}{\delta} \frac{([\text{Ca}^{2+}](t))}{\text{d}t}$$  \hspace{1cm} (26)

The integration is performed, until the calcium concentration reaches the equilibrium value for the specific temperature and $\text{CO}_2$-pressure. Results for the calcium concentration as a function of time are shown in Fig. 3.

Initially, concentration increases rapidly, as the high initial flux rate controls the dissolution process, then the increase in concentration levels off. The time needed to reach calcium saturation depends strongly on the film thickness. For small film thicknesses ($\delta < 0.01$ cm), the solution is saturated after 50 min. For larger film thicknesses, the time increases significantly to values of 150 min and larger, as now mass transport by diffusion becomes rate limiting.

3.4. Simplified dissolution rate equations

So far we have discussed calcium flux rates for the ternary system $\text{CaCO}_3$–$\text{H}_2\text{O}$–$\text{CO}_2$ in contact with the atmosphere, based on the finite-difference numerical model of the dissolution process. The flux rates found are similar to earlier inferences obtained by Buhmann and Dreybrodt (1985), whose theoretical predictions have been verified in experiments on calcite dissolution (Dreybrodt et al., 1996). While Buhmann and Dreybrodt (1985) have derived a single linear approximation for their numerical flux rates, we now can add a new linear relation for very low calcium concentrations, termed the fast rate law.
Fig. 2. (a) pH-value averaged over the film thickness as a function of the average calcium concentration. (b) Individual contributions of the PWP-Eq. (13) to the calcium flux rate, shown as lines. The thick grey line is the sum of all four individual terms. (c) Individual contributions to the carbon-dioxide flux rate, obtained from the numerical integration of (14) along $z$. The thick grey line is the sum of all four individual terms. Temperature, CO$_2$-pressure, and film thickness are given in the figure.

Fig. 3. Calcium concentration as a function of time for the temperatures $10^\circ$C (gray lines) and $20^\circ$C (black lines) and for different film thicknesses.
We now abbreviate calcium concentrations, using $c = [Ca^{2+}]$, $c_{eq} = [Ca^{2+}]_{eq}$, and $c_{in} = [Ca^{2+}]_{inital}$. We approximate of the calcium flux rates by a stepwise function of the form

$$ F_{Ca^{2+}} = a_i (m_i c_{eq} - c)^{n_i}, i = 0, 1, 2 $$

with $a_i$ (in m s$^{-1}$) the rate coefficient, $m_i$ the dimensionless concentration threshold, and $n_i$ a power-law exponent.

We then fit two straight lines through all flux rates of a specific temperature by means of least-squares minimisation for the two different kinetic regimes. We choose film thicknesses between $\delta = 0.01$ and 0.1 cm, and carbon dioxide pressures between $p = 0.0035$ and 0.01 atm to facilitate the comparison with the experimental data. We then obtain two sets of $a_i$, from which we derive an average value and its standard deviation.

### 3.4.1. Fast rate law

For $i = 0$, (27) describes the linear fast rate law, characterised by a high rate coefficient $a_0$ (see Table 4). The fast rate law is valid for calcium concentrations below the threshold $c < c_0$ for which $c_0 \approx 0.3 c_{eq}$ holds.

### 3.4.2. Slow rate law

For $i = 1$, the linear slow rate law is given, with a rate coefficient $a_1$ about one order of magnitude smaller than the value for the fast rate law (see Table 4). This rate law is valid up to a second threshold, $c < c_1$, with $c_1 \approx 0.9 c_{eq}$.

### 3.4.3. High-order rate law

The case $i = 2$ only appears for natural limestone, which is not covered in this paper. In this case, impurities in the material such as clay minerals inhibit dissolution, and the dissolution rates drop by several orders of magnitude close to calcium saturation. The reason for the drop in flux rates is the accumulation of the impurities on the surface of the crystal, thus inhibiting further dissolution. This was first measured by Plummer et al. (1978), and subsequently verified for the open system (Svensson and Dreybrodt, 1992) and for the closed system (Eisenlohr et al., 1999). Hence, a non-linear high-order rate law describes the experimental data on natural limestone close to saturation, with the rate coefficient given by (Palmer, 1991; Eisenlohr et al., 1999):

$$ n_2 \approx 4 $$

$$ x_2 = x_1 (c_{eq} - c_1)^{(n_1 - n_2)} $$

The rate coefficient $x_2$ is several orders of magnitude larger than $x_1$.

Calcium flux rates based on the approximation (27) and the rate coefficients given in Table 4 are sketched in Fig. 4 for various parameter settings. We observe a twofold linear decrease in flux rates for calcium concentrations below 90% of the equilibrium value, controlled by the fast rate law for large calcium undersaturation, then by the slow linear rate law. From then on, dissolution rates drop sharply and a fourth-order rate law controls the flux rates (Svensson and Dreybrodt, 1992). Temperature and carbon dioxide partial pressure control the equilibrium concentration reached, as discussed earlier.

### 4. EXPERIMENTAL METHOD AND RESULTS

We now discuss the calcium flux rates obtained from laboratory measurements on an inclined block of limestone.

#### 4.1. Experimental method

For the dissolution experiments, we have used a plate of limestone, which has been inclined to allow water flowing down its slope. The plate has not been polished, thus the surface was slightly rough due to the commercial sawing of the limestone. We have constructed a channel of 5 cm width and a length of $L = 110$ cm by employing acryl rims fixed to the plate of limestone. A calcium solution with concentration $c_{in}$ and with defined $p$ is pumped into the inlet compartment by use of a peristaltic pump. The inlet compartment consists of a piece of acryl glass blocking the channel, but leaving a narrow space of a few 10th of a millimetre between the limestone plate and its lower surface. This inlet gate can be moved to any desired position. To avoid dissolution of limestone prior to entrance at $x = 0$, the limestone surface upstream is covered by a thin plastic or aluminium foil. At the end of the channel a funnel of acryl glass guides the solution to a glass tube through the limestone plate from where it is collected in a glass bottle. The experimental set up is shown in Fig. 5.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Coefficients for the calcium flux rate approximation</th>
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<tbody>
<tr>
<td>$T$</td>
<td>Fast</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
</tr>
<tr>
<td>$n_i$</td>
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<td>$m_i$</td>
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<tr>
<td>$x_i^0$</td>
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<tr>
<td>$x_i^1$</td>
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<tr>
<td>$x_i^2$</td>
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$T$ is temperature in °C, $i$ is an index, $n_i$ the dimensionless power-law exponent, $m_i$ a dimensionless concentration threshold, $x_i^0$ and $x_i^1$ the rate coefficients in m s$^{-1}$ from the theory and the experiments, respectively.
The water film is established by drawing the water down into a film of width $W = 2.5 \text{ cm}$ by use of a wet paper strip. This film does not touch the acryl walls, but is kept in its width by surface tension. The surface of the film is absolutely plane as can be seen by the mirror-like reflection of light. The flow rate $Q$ (in $\text{m}^3 \text{s}^{-1}$) is measured by collecting a volume of 10 ml at the outflow and measuring the time needed. The calcium concentration of the out-flowing solution is determined by measuring its conductivity, which is related linearly to the calcium concentration (Dreybrodt, 1996). Conductivity was calibrated to calcium concentration by diluting a saturated solution of CaCO$_3$ at defined $p$ and $T$ as used in the experiment.

For solutions with elevated $p$, a lid was constructed that covers the entire water film. A nitrogen–carbon dioxide mixture of defined CO$_2$-content and of high purity, 4.5
and 5, respectively, was blown through this compartment using a pressure about 10 mbar above atmospheric pressure, measured by a manometer fixed to the lid. This assured correct CO₂-pressure during the experiment.

Input solutions with \( c_{\text{in}} = 0 \) were prepared by bubbling air or an N₂–CO₂-mixture with known \( p \) through distilled water, stirred by a magnetic stirrer. Equilibration with respect to CO₂ was attained after several hours and was monitored by measuring conductivity and pH until no further change occurred. Solutions with input concentrations of about \( c_{\text{in}} \approx 0.5 \text{ cm}^{-1} \) were obtained by mixing a saturated CaCO₃-solution with identical \( p \) as the corresponding solution of distilled water. Saturated solutions were obtained by dissolving analytic grade calcite (Baker) in distilled water through which an N₂–CO₂ mixture was bubbled. During this process, the conductivity of the solution was measured. The solution was defined as saturated with respect to calcite and \( p \) when no further change of conductivity within 1 h was observed. All experiments were performed at ambient temperature of 25 °C.

The thickness of the water film for a hydrodynamical smooth surface is given by Myers (2002):

\[
\delta = \left( \frac{3\eta Q}{pg \sin \gamma} \right)^{1/3}
\]

with \( \eta \approx 10^{-3} \text{ Pa s} \) and \( p = 1000 \text{ kg m}^{-3} \) the viscosity and density of water, and \( g = 9.81 \text{ m s}^{-2} \) the gravitational acceleration. Depending on \( Q, W \) and the inclination angle \( \gamma \) used in the experiment, the film thickness ranges between 0.02 and 0.1 cm.

When a thin film of water with width \( W \) flows down a smooth, plane surface of limestone with inclination angle \( \gamma \), it dissolves calcite and the calcium concentration \( c(x) \) increases along the flow distance \( x \). For a linear rate law of dissolution, the amount of calcite dissolved per unit time between the positions \( x \) and \( x + dx \) is given by \( z_i \left( m_i, c_{\text{eq}} - c(x) \right) W \, dx \). Because of mass conservation this must be equal to \( Q \, dc \), where \( Q \) is the flow rate (in m³ s⁻¹) and \( dc \) the change in concentration between \( x \) and \( x + dx \). This leads to the differential equation

\[
\frac{dc}{dx} = \frac{W z_i}{Q} \left[ m_i c_{\text{eq}} - c(x) \right]
\]

Its solution is

\[
c(x) = m_i c_{\text{eq}} + \left( c_{\text{in}} - m_i c_{\text{eq}} \right) \exp \left( -\frac{W z_i}{Q} x \right)
\]

where \( c_{\text{in}} \) is the concentration of the solution at the inflow \( x = 0 \). This equation can be rearranged into

\[
-\ln \left( 1 - \frac{c_{\text{in}} - c(x)}{c_{\text{in}} - m_i c_{\text{eq}}} \right) = \frac{W z_i}{Q} x
\]

There are two ways to determine \( z_i \) and \( m_i \) from (33). In a first set of experiments, we fix the inlet compartment at distance \( x \) and measure output concentrations as a function of \( x \) and input concentration, keeping the flow rate \( Q \) constant for all values of \( x \). This way the thickness \( \delta \) of the film is constant for all measured points. If one plots the LHS of (33) against flow distance \( x \), one obtains a straight line with slope \( W z_i/Q \) from which \( z_i \) can be determined. The value of \( m_i \) is not known for the fast rate law and must be determined by adjusting it, such that a straight line is obtained.

In a second set of experiments, the inlet compartment is fixed at \( x = 110 \text{ cm} \). Now, the input flow rate is varied and one plots the LHS of Eq. (33) versus \( 1/Q \) to obtain a straight line with slope \( W z_i \), from which \( z_i \) can be obtained.

### 4.2. Experimental results

Both sets of experiments have been repeated for a given \( c_{\text{in}} \) and \( p \) for at least five times, with good reproducibility of the results. The determined \( z_i \) for both methods are also in good agreement, thus we only describe to results for the second method. Additionally, the experiments were carried out with two inclinations of the limestone plate: In the first case, the height difference between input and output point was \( H = 6.5 \text{ cm} \), thus \( \sin \gamma = 0.060 \), with length \( L = 110 \text{ cm} \). In the second case, \( H = 0.8 \text{ cm} \) was chosen, thus \( \sin \gamma = 0.007 \).

Film thicknesses for the first set of experiments are based on a water film of \( W = 2.5 \text{ cm} \) width and a flow rate of 0.05 cm³ s⁻¹. From (30) we then find film thicknesses of \( \delta = 0.02 \text{ cm} \) for the high inclination and \( \delta = 0.045 \text{ cm} \) for the low inclination. In the second set of experiments, the flow rate \( Q \) varied by a factor of 10, thus the film thickness changed by a factor of 2, from \( \delta \) between 0.02 to 0.043 cm for the high inclination, and \( \delta \) between 0.04 and 0.09 cm for the low inclination.

Fig. 6 shows the raw data of specific conductivity of the out-flowing solution \( \sigma \) (in S m⁻¹) versus flow rate \( Q \), for \( p = 0.00035 \text{ atm} \), \( H = 0.8 \text{ cm} \) and \( c_{\text{in}} = 0 \) and \( c_{\text{in}} = 0.6 \text{ cm} \) respectively. These data are used in the plots of Fig. 7 for \( H = 0.8 \text{ cm} \).

Fig. 7 shows the results for the experiments with variable \( Q \). For \( p = 0.00035 \text{ atm} \) and \( c_{\text{in}} = 0 \), Fig. 7a shows the result for the two inclinations. The measured points fit well to a straight line, and from its slope the rate coefficient for the fast rate law, \( z_0 \), can be determined by introducing
$Q$ and $W$ into Eq. (30). One obtains $a_0 = (1.9 \pm 0.1) \times 10^{-6}$ m s$^{-1}$ and $m_0 = 0.36 \pm 0.03$. This shows that $a_0$ is independent of the film thickness between $d = 0.02$ and 0.04 cm.

For $p = 0.00035$ atm and $c_{in} = 0.6 c_{eq}$, Fig. 7b provides measured data, which again fit two straight lines. The resulting rate coefficient for the slow kinetics, $a_1$, is $a_1 = (3.1 \pm 0.3) \times 10^{-7}$ m s$^{-1}$, which is one order of magnitude lower than $a_0$.

In Figs. 7c and d, results are shown for elevated $p$ of 0.01 atm and input concentrations of $c_{in} = 0$ and $c_{in} = 0.5 c_{eq}$, respectively. Again, the data can be fitted to straight lines and the resulting values for the rate coefficients are $a_0 = (2.0 \pm 0.2) \times 10^{-6}$ and $a_1 = (3.85 \pm 0.35) \times 10^{-7}$ m s$^{-1}$, respectively.

We have used the experimentally determined rate coefficient to derive average values and their variation for the two regimes: For the fast rate law, we find $a_0 = (2.0 \pm 0.2) \times 10^{-6}$ m s$^{-1}$, and for the slow rate law, we find $a_1 = (3.5 \pm 0.6) \times 10^{-7}$ m s$^{-1}$.

In summary, both the rate coefficients for the experiments and for the numerical predictions agree satisfactorily.

5. CONCLUSIONS

We have revisited the dissolution rates of calcite in the system CaCO$_3$–H$_2$O–CO$_2$, open with respect to CO$_2$, for a plane limestone surface covered by a thin film of solution with thickness $d$. We have employed a new numerical approach by solving the diffusion–reaction equations for the species involved as functions of time and space. This avoids approximations used by Buhmann and Dreybrodt (1985) and yields dissolution rates at high undersaturation, typically $c < 0.2 c_{eq}$, which could not be obtained so far. These new results reveal two regions of linear rate laws. For high undersaturation, a fast rate law is operative with a kinetic constant $a_0$. This is followed by a transition region with decreasing values of slope, until a second region of slow rate law with $a_1$ one order of magnitude smaller takes over. This is shown schematically in Fig. 4.

The fast rate law is predicted for the first time. Therefore, we have performed experiments to prove this theoretical finding. In these experiments, we use an inclined limestone plate with a smooth plane surface and measured the change in calcium concentration of water between an input and an output point. The solution with known $T$
and a $p$ of $3.5 \times 10^{-4}$ and 0.01 atm, respectively, flows down the plate in a well defined laminar water film. From these data, the kinetic constants $z_0$ and $z_1$ for the two linear rate laws have been determined. They agree satisfactorily with the theoretical predictions.

The new fast rate law is of utmost importance to explain dissolutional features, when rainwater flows down on limestone surfaces in short times on the order of several 10 s. The time constant to dissolve about 64% of the apparent equilibrium concentration of about $0.3C_{eq}$, valid in the last regime, is given by $\tau = \delta/z$. This is about 60 s for a film thickness of 0.02 cm. Therefore in most relevant cases the water runs off the rock with a concentration of 0.2 mol m$^{-1}$. This is confirmed by a simple experiment on a karren formation on a block of Lipica-limestone, exposed at the entrance to Postojna cave, Slovenia. During a rain of medium intensity, we have collected water from this rock with an average flow distance of 1 m. Calcium concentration of the rainwater was well below 0.01 mol m$^{-1}$, which is in good agreement with our theoretical and experimental results. This corresponds to surface denudation rates of $4 \times 10^{-5}P$ cm year$^{-1}$, with $P$ the annual precipitation in mm/year. This is close to observations by Cucchi et al. (1995), who observed rates of $1.5 \pm 1.0$ cm kyr$^{-1}$ in the karst of Triest at an average rainfall of 1350 mm/year. Such numbers should be also valid for buildings and constructions of limestone.

ACKNOWLEDGMENTS

We thank H. Rohbeck for technical support of the experiments. Two anonymous referees and the associate editor have greatly helped to improve the manuscript. The figures in this paper are drawn using the GMT graphics package (Wessel and Smith, 1991, 1998).

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Associate editor: Eric H. Oelkers