Dissolution kinetics of calcium carbonate minerals in H$_2$O-CO$_2$ solutions in turbulent flow: The role of the diffusion boundary layer and the slow reaction H$_2$O + CO$_2$ = H$^+$ + HCO$_3^-$

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Abstract—Dissolution and precipitation of calcium carbonate minerals in aqueous solutions with turbulent flow are controlled by a diffusion boundary layer (DBL) adjacent to the surface of the mineral, across which mass transfer is effected by molecular diffusion. A rotating disk technique was used to investigate the effect of the DBL on the dissolution rates of CaCO$_3$. This technique allows an exact adjustment of the thickness of the DBL by controlling the rotation speed of a circular sample of CaCO$_3$. Measurements of the dissolution rates in H$_2$O-CO$_2$-Ca$^{2+}$-solutions in equilibrium with various partial pressures of CO$_2$ from $1 \cdot 10^{-3}$ up to 1 atm showed a dependence of the rates $R$ on the rotation frequency $\omega$, given by $R \propto \omega^n$. The exponent $n$ varies from 0.25 at low $P_{CO_2}$ to about 0.01 at a $P_{CO_2}$ of 1 atm. This reveals that the rates are not controlled by mass transport only, which would require $n = 0.5$. The experimental data can be explained employing a theoretical model, which also takes into account the slow reaction CO$_2$ + H$_2$O = H$^+$ + HCO$_3^-$ and the chemical reactions at the surface (Dreybrodt and Buchmann, 1991). Interpretation of the experimental data in view of this model reveals that conversion of CO$_2$ plays an important role in the control of the rates. At high $P_{CO_2}$ and large DBL thickness ($\varepsilon > 0.001$ cm), conversion of CO$_2$ occurs mainly in the DBL and, therefore, becomes rate limiting. This is corroborated by the observation that upon addition of the enzyme carbonic anhydrase, which catalyzes CO$_2$-conversion, the dissolution rates are enhanced by 1 order of magnitude. From our experimental observations we conclude that the theoretical model above enables one to predict dissolution rates with satisfactory precision. Since the precipitation rates from supersaturated solutions are determined by the same mechanisms as dissolution, we infer that this model is also valid to predict precipitation rates. The predicted rates for both dissolution and precipitation can be approximated by a linear rate law $R = \alpha \cdot (c_{eq} - c)$, where $c_{eq}$ is the equilibrium concentration with respect to calcite and $\alpha$ a rate constant, dependent on temperature. $P_{CO_2}$, DBL thickness ($\varepsilon$), and the thickness of the water sheet flowing on the mineral. Values of $\alpha$ are listed that can be used for a variety of geologically relevant conditions.

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NOTATION

$R$ dissolution rate mmole cm$^{-2}$ s$^{-1}$
$A$ surface area of rotating disk cm$^2$
$V$ volume of the solution cm$^3$
$D$ coefficient of diffusion cm$^2$ s$^{-1}$
$r$ radius of rotating disk cm
$F$ diffusional flux mmole cm$^{-2}$ s$^{-1}$
$c$ concentration mmole cm$^{-3}$
$c_{eq}$ equilibrium concentration mmole cm$^{-3}$
$P_{CO_2}$ partial pressure of CO$_2$ atm
$\lambda$ concentration mmole cm$^{-3}$
$\alpha$ activity mmole cm$^{-3}$
$\varepsilon$ thickness of DBL cm
$\omega$ angular velocity s$^{-1}$
$\nu$ kinematic viscosity of water cm$^2$ s$^{-1}$
$\delta$ thickness of turbulent core cm
$\alpha$ rate constant cm s$^{-1}$

1. INTRODUCTION

Dissolution and precipitation of calcite in a CO$_2$ - H$_2$O system play an important role in many geological processes, such as diagenesis of calcareous deep-sea sediments (Berner, 1980; Boudureau and Canfield, 1995), the formation of karst in limestone terranes (Dreybrodt, 1988; Ford and Williams, 1989; White, 1988), the evolution of water chemistry in calcite depositing stream systems (Hermann and Lorah, 1987; Dreybrodt et al., 1997; Liu et al., 1995), and the global cycle of CO$_2$ (Archer and Maier-Reimer, 1994; Kempe, 1977). Both the precipitation and the dissolution rates in the system H$_2$O-CO$_2$-CaCO$_3$ are controlled by three rate determining processes: (1) The kinetics at the mineral surface, which is given by the mechanistic rate equation (called PWP equation) proposed for dissolution by Plummer et al. (1978) and which has later been verified also for precipitation (Dreybrodt and Plummer, 1986; Reddy et al., 1981; Inskeep and Bloom, 1985). This PWP-equation reads

$$R = \kappa_1(H^+) + \kappa_2(\text{H}_2\text{CO}_3^\ast) + \kappa_3 - \kappa_4(\text{Ca}^{2+}) (\text{HCO}_3^-) \quad (1)$$

where the rate $R$ is given in mmol cm$^{-2}$ s$^{-1}$; and $\kappa_1$, $\kappa_2$, $\kappa_3$, and $\kappa_4$ are temperature dependent rate constants and the parentheses denote activities in mmole cm$^{-3}$ of the corresponding species at the surface of the mineral; (2) The slow
reaction $\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ exerts a significant influence on the rates because stoichiometry requires that for each calcium ion released from the solid one CO$_2$ molecule must react to form $\text{H}^+ + \text{HCO}_3^-$. At large mineral surface area and small volumes of the solution this slow reaction can be rate determining. Its kinetics has been reviewed by Kern (1960) and Usdowski (1982); (3) Mass transport of the reacting species away from and towards the mineral surface by molecular diffusion. Taking into account these three processes, Buhmann and Dreybrodt (1985a,b, 1987) put forward a model from which dissolution and precipitation rates can be calculated for a sheet of water of given thickness, covering the surface of the mineral. They have shown that due to CO$_2$ conversion the rates depend on the thickness of this water sheet. The influence of mass transport is significant when the water is stagnant or flows laminarly on the calcite. If, however, the flow becomes turbulent, molecular diffusion is enhanced by turbulent eddies, such that under otherwise unchanged conditions the rates of dissolution or precipitation, respectively, can increase by almost 1 order of magnitude.

Thus the rates are also controlled to a significant extent by the hydrodynamic conditions under which dissolution or precipitation occurs. This was first observed in the field. Deposition rates of calcite from water flowing turbulent across rimstone dams were found to be higher by a factor of up to 5 compared to those observed in the corresponding pools, with identical chemical composition, but almost stagnant water (Liu et al., 1995). Recently, it has been shown experimentally (Dreybrodt et al., 1996a,b) that the model of Buhmann and Dreybrodt (1985a,b) is also valid for solutions contained in porous media of calcite both for dissolution and precipitation, respectively, thus proving its basic assumptions. This model, however, is too crude to treat correctly the case of turbulence. Therefore, Dreybrodt and Buhmann (1991) extended it by introducing a diffusion boundary layer separating the bulk of the solution from the surface of the mineral. Mass transport through this layer proceeds by molecular diffusion, whereas in the turbulent bulk complete mixing occurs within extremely short time spans. This extended model predicts rates, which depend on the thickness of the diffusion boundary layer. An experimental means to create such diffusion boundary layers of well-defined thickness is the rotating disk technique (Levich, 1962; Pleskov and Filinovskii, 1976). In this paper we report on measurements of dissolution rates of marble and limestone for various boundary layer thicknesses under CO$_2$-pressures from $10^{-3}$ atm up to 1 atm. These experiments agree satisfactorily with the rates predicted by the diffusion boundary-layer (DBL) model and offer a deeper understanding of the dissolution and precipitation rates under turbulent flow in natural systems.

2. EXPERIMENTAL METHODS

2.1. Materials

Marble and limestone (from Guilin, China) disks, 3 cm in diameter, were cored from marble slabs of 5 mm thickness. These samples were cemented into the holder of the rotating disk apparatus. This was then mounted to the shaft of the rotating disk equipment and polished during rotation by using progressively 400 (64 μm), 800 (32 μm), 1200 (21 μm), 2400 (10 μm), and finally 4000 (4 μm) grit size waterproof silicon carbide paper. This procedure assures a continuous surface of the disk including its rim. The roughness of the surface was measured by mechanically scanning with a diamond tip. Its value was $1.2 \pm 0.3 \mu m$. This value is 1 order of magnitude lower than the thickness of the smallest boundary layer used in the experiments. The surface area of the marble sample in contact with the solution was 7 cm$^2$. The marble was white and of coarse crystalline structure. It contained less than 1% Mg. To investigate the influence of the slow reaction $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$, an enzyme catalysing this reaction was introduced into the solution to obtain concentrations of 0.1 μmole. Bovine carbonic anhydrase was purchased as lyophylized powder from Sigma and used as obtained. Some experiments were carried out with limestone from Guilin, China, and with a sample of monocrystalline Iceland spar. To obtain solutions in equilibrium with fixed CO$_2$ partial pressures ($P_{co2}$) N$_2$-CO$_2$ gas mixtures with $P_{co2} = 10^{-3}$, $5 \times 10^{-3}$, $10^{-2}$, $5 \times 10^{-2}$, $10^{-1}$, and 1 atm were bubbled through the solution.

2.2. Experimental Set-Up

A schematic of the experimental apparatus is shown in Fig. 1. Runs were performed in a 1.2 L glass beaker containing 1180 mL of a solution, which was prepared by dissolution of calcite powder in bidistilled water to the wanted concentration under a specified CO$_2$ partial pressure. The beaker was immersed in a constant temperature water bath capable of maintaining the temperature to ±0.5°C. The solution vessel was covered with Plexiglas lids with holes allowing insertion of the motorized shaft, electrodes, and a gas dispersion tube. A commercial N$_2$-CO$_2$ gas mixture with fixed $P_{co2}$ was bubbled through a metal dispersion tube into the reaction vessel. Thus the experiment was performed as a free drift experiment under the condition of an open-system with respect to CO$_2$. In this case the chemical composition of the solution is determined entirely by the partial pressure of CO$_2$ in equilibrium with the solution and the Ca concentration (Dreybrodt, 1988). The disk-shaped sample was held centred about 4 cm above the bottom of the reaction vessel on the end of a shaft. A motor drove the shaft, and gear reducers allowed the disk to rotate in the solution at speeds varying from 0 to 3500 rpm (rotations per min). The rotation speed was held constant by a controller within 6%. The rotating disk was formed by use of epoxy from a mold into which the limestone disk and a screw was fitted. This screw served as the rotation axis of the disk and was fixed to the shaft. Then using the rotating shaft as a lathe to which the cast was fixed, it was shaped into its final form, warranting that the whole set was free of asymmetric centrifugal forces leading to disturbance of well-defined hydrodynamic conditions. The rock face was polished while the rotating disk was fixed to the rotating shaft of the apparatus.
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Fig. 2. Ca\textsuperscript{2+} concentration vs. time for a typical experiment. The straight lines show a linear increase of the concentration at constant rotating speeds. The numbers on the line denote rotating speeds listed in the inset. The corresponding dissolution rates are also given.

Measurements of the dissolution rates were performed at a fixed rotation speed by measuring the increase in the electrical conductivity of the solution. The conductivity was measured by a conductivity cell, and the data were stored in a computer at intervals of one second. Then they were converted to calcium concentrations by the relation

\[ [\text{Ca}^{2+}] \text{(mmol/L)} = 6.18 \times 10^{-5} \text{cond.} (\mu \text{s/cm}) - 1.38 \times 10^{-2}; \gamma = 0.999 \]

which is valid in the dilute solutions of our experiments. This relation was found in the following way. First we calculated the chemical composition of the solution for various calcium concentrations and specified \( P_{\text{CO}_2} \) as used in the experiments, by employing the program Equilibrium (Dreybrodt, 1988). Thus we obtained pH, [HCO\textsubscript{3}\textsuperscript{-}] and [CO\textsubscript{3}\textsuperscript{2-}] as a function of [Ca\textsuperscript{2+}]. These values were then used to calculate the conductivity by WATEQ.4. These results were also verified experimentally by titrating for Ca concentration at the beginning and the end of each run. The record of a typical run with \( P_{\text{CO}_2} = 1 \times 10^{-3} \text{ atm} \) and initial [Ca\textsuperscript{2+}] = 3 \times 10^{-4} mol/L is shown by Fig. 2. The straight lines give the increase in concentration at differing rotating speeds from 100 rpm up to 3500 rpm. The rates were calculated from the slopes by

\[ R = \frac{V}{A} \frac{d[\text{Ca}^{2+}]}{dt} \]

where \( V \) is the volume of the solution and \( A \) the area of dissolving surface. The experimental error obtained by repeating typical experiments for several times was \( \pm 10\% \). The thickness of the boundary diffusion layer (DBL) is given (Levich, 1962) by

\[ \varepsilon = 1.61(D/v)^{1/3} \cdot (v/\omega)^{1/2} \]

where \( D \) is the coefficient of molecular diffusion (7.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} at 20°C) and \( v \) the kinematic viscosity of water. \( \omega \) is the angular velocity in \( \text{ s}^{-1} \). In our set-up \( \varepsilon = 5 \times 10^{-3} \text{ cm} \) at a rotating speed of 100 rpm, and at 3500 rpm \( \varepsilon = 8.5 \times 10^{-4} \text{ cm} \). In all experiments the Reynolds number \( Re = r \omega / v \) (\( r \) radius of sample) is below 7 \times 10^3, such that laminar flow can be assumed (Pleskov and Filinowskii, 1976).

To ensure the accuracy of our set up, we performed dissolution experiments on gypsum. The sample was cut from a piece of a gypsum single crystal (Marienglas, Harz, Germany). In this case dissolution rates are entirely determined by molecular diffusion across the boundary layer (Opdyke et al., 1987)

\[ R = \frac{D}{\varepsilon} ([\text{Ca}_{\text{eq}}^{2+}] - [\text{Ca}^{2+}]) \]

[Ca\textsubscript{eq}\textsuperscript{2+}] is the equilibrium concentration of gypsum (15.4 mmole/L at 20°C). Thus by measuring the dissolution rates at a given rotating speed, \( \varepsilon \) can be determined experimentally. Figure 3 shows the result for four rotating speeds. The full line represents Eqn. 3. The good agreement between experiment and theory shows that the set-up works satisfactorily.

3. EXPERIMENTAL RESULTS

The dissolution rates (cf. Eqn. 2) measured on the marble sample at 20°C for various partial pressures of CO\textsubscript{2} as a
Table 1a. Experimental dissolution rates of marble at 10°C for various rotational speeds and $P_{CO_2}$ pressures in atm. (1) The first entry gives the experimental rates, (2) the second one the rates as obtained from the DBL-model, and (3) the ratio of both. Rates are given in $10^{-9}$ mmole cm$^{-2}$ s$^{-1}$. The rates were measured at calcium concentrations of $10^{-4}$ mmole cm$^{-3}$.

<table>
<thead>
<tr>
<th>RPM</th>
<th>$P_{CO_2}$</th>
<th>Rates</th>
<th>Rates (with BCA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500</td>
<td>0.001 atm</td>
<td>14.40</td>
<td>15.20</td>
</tr>
<tr>
<td>2500</td>
<td>0.002 atm</td>
<td>8.74</td>
<td>7.15</td>
</tr>
<tr>
<td>600</td>
<td>0.005 atm</td>
<td>7.04</td>
<td>2.02</td>
</tr>
<tr>
<td>300</td>
<td>0.002 atm</td>
<td>6.74</td>
<td>7.15</td>
</tr>
<tr>
<td>150</td>
<td>0.004 atm</td>
<td>6.44</td>
<td>5.87</td>
</tr>
<tr>
<td>100</td>
<td>0.005 atm</td>
<td>5.44</td>
<td>5.87</td>
</tr>
</tbody>
</table>

* Relates to concentrations of $1 \cdot 10^{-3}$ mmole cm$^{-3}$.

Table 1b. Comparison of experimental dissolution rates of marble obtained in solutions with and without BCA at 3000 rpm and 100 rpm for various $P_{CO_2}$ at 10°C and 30°C. Rates are given in $10^{-9}$ mmole cm$^{-2}$ s$^{-1}$.

<table>
<thead>
<tr>
<th>$P_{CO_2}$</th>
<th>T</th>
<th>Rates 3000 rpm</th>
<th>Rates with BCA 3000 rpm</th>
<th>Rates 100 rpm</th>
<th>Rates with BCA 100 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0003</td>
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<td>90.0</td>
<td>89.9</td>
<td>18.8</td>
<td>18.6</td>
</tr>
<tr>
<td>0.001</td>
<td>30</td>
<td>100.0</td>
<td>99.9</td>
<td>24.6</td>
<td>24.7</td>
</tr>
<tr>
<td>0.005</td>
<td>30</td>
<td>107.0</td>
<td>120.0</td>
<td>24.7</td>
<td>47.1</td>
</tr>
<tr>
<td>0.01</td>
<td>30</td>
<td>110.0</td>
<td>192.0</td>
<td>28.6</td>
<td>78.6</td>
</tr>
<tr>
<td>0.1</td>
<td>30</td>
<td>110.0</td>
<td>715.0</td>
<td>54.9</td>
<td>330.0</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>241.0</td>
<td>2160.0</td>
<td>163.0</td>
<td>729.0</td>
</tr>
</tbody>
</table>

Figure 5 shows the dissolution rates for various $P_{CO_2}$ at Ca concentrations of about $10^{-4}$ mole/L. The open squares represent the dissolution rates at a rotating speed of 100
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T: 10°C, [Ca²⁺] < 0.5 [Ca²⁺ eq]

rpm, CA

0 3000, no

- 3000, 0.1μM

- 100, no

- 100, 0.1μM

Open system

Fig. 5. Dissolution rate vs. P_{CO₂} for rotating speeds at 100 rpm (squares) and 3000 rpm (circles). The open symbols represent the rates in the solution without BCA, the full symbols those with addition of BCA (0.1 μM).

rpm (ε = 5·10⁻³ cm) without BCA and the full squares show the corresponding rates with BCA added. Similarly the open (full) circles depict the rates for rotating speeds of 3000 rpm (ε = 9·10⁻⁴ cm) without and with BCA, respectively. At low P_{CO₂}, addition of BCA causes no significant change in the rates. For P_{CO₂} > 0.01 atm a significant enhancement of the rates occurs when BCA is added. Measurements were performed at 10°C and 30°C. Table 1b lists the rates with and without BCA under otherwise identical conditions for these two temperatures and for various P_{CO₂}. Below P_{CO₂} = 5·10⁻¹ atm BCA has no influence on the rates. But at 1 atm the rates are enhanced by a factor of 10. Enhancement at the higher temperature is lower than at 10°C. These results show that some change in the dissolution of calcite occurs at high P_{CO₂}. Therefore, one must be cautious when extrapolating from such experiments to dissolution processes in nature, which often occur at low P_{CO₂} (<5·10⁻³ atm).

Fig. 6. The geometry of the DBL-model. The DBL extends from Z = 0 to Z = ε. The well mixed core extends from Z = 0 to Z = -δ. The arrows denote fluxes of CO₂⁺, HCO⁻, and Ca²⁺ from the mineral surface. Note that F is given by the PWP-eqn. (Eqn. 1) employing the activities of the species at Z = ε.

4. INTERPRETATION OF THE EXPERIMENTAL RESULTS

The most comprehensive model of calcite dissolution and precipitation that takes into account the existence of a DBL is that of Dreybrodt and Buhmann (1991). A short description of its basic assumptions is given here, as we will use this model to interpret the experimental data. Figure 6 shows the DBL of thickness ε, separating the calcite surface from the turbulent bulk of thickness δ. In this geometry δ = V/A, where V is the volume of the solution and A the surface area of the dissolving mineral. In the region of the bulk complete mixing is assumed, such that no concentration gradients can build up. This is modelled by assuming the turbulent diffusion coefficient D, higher by a factor of 10⁶ than the coefficient of molecular diffusion, which describes mass transfer in the DBL. The flux F of Ca²⁺ at the solid surface is given by the PWP equation (Eqn. 1) using the activities of the species at the surface. For stochiometrical reasons this flux must equal to the total amount of CO₂ converted to H⁺ + HCO⁻ in a column with area of 1 cm² covering the region from -δ ≤ z ≤ ε. This is given by

\[ F_{CO₂} = \int_{-\epsilon}^{\epsilon} \frac{d[CO₂]}{dt} dz \]  

\[ d[CO₂]/dt \] is the change of the CO₂ concentration in time, resulting from two elementary reactions, occurring simultaneously.

\[ CO₂ + H₂O ⇌ H₂CO₃ ⇌ H⁺ + HCO⁻ \]

\[ CO₂ + OH⁻ ⇌ HCO⁻ \]

The rate constants of these reactions are well-known

Fig. 7. Dissolution rates vs. the DBL-thickness ε for various P_{CO₂}. The symbols represent the experimental points from Fig. 4. The full lines are obtained from the DBL-theory and are scaled by a factor of 2. The symbols denote the P_{CO₂} values used for their calculation. Concentration of Ca was 3·10⁻⁵ mmol/cm² for the open symbols and 1·10⁻³ mmole/cm² for the closed symbol.
Using these boundary conditions, the equations of mass transport can be solved numerically (Dreybrodt and Buhmann, 1991). For general information on chemical reactions in DBL, the reader is referred to the textbook of Beek and Mutzall (1975). In the following, we give results which have been obtained employing this programme. As a first step, we calculated the dissolution rates for the experiments as depicted in Fig. 4. They are listed in Table 1a. The DBL thickness was obtained from Eqn. 3. For the experimental conditions with a disk area of 7 cm$^2$ and a total volume $V$ of solution of 1180 cm$^3$ the ratio $V/A = 167$ cm. This ratio determines the value of $\delta = V/A$ of the turbulent core (cf. Fig. 6).

Table 1a also lists the experimental values for comparison. All the experimental rates are higher by a factor of about 2. This can be seen from the ratio between experimental and theoretical values. Thus if one multiplies the theoretical rates by a scaling factor of two, they are in satisfactory agreement with the experimental data. This is shown by Fig. 7, which depicts as full lines the scaled theoretical dissolution rates as a function of $c$ for the various $P_{CO_2}$ partial pressures as used in the experiment. The data points represent the experimental data from Fig. 4. The reason for this behaviour is not very clear. One reason may be that owing to the roughness of the surface in the order of 1 pm, the effective surface area for dissolution is higher than the geometrical one, which would yield correspondingly an overestimation of the experimental rates. Another reason could be the variability of the PWP-rate constants with varying natural material. An increase of K$^+$ by a factor of two raises the dissolution rates by the same factor (Dreybrodt and Buhmann, 1991). Rate constants of this magnitude have been observed by Compton and Daly (1984). Compton et al. (1985) have shown that surface roughness exerts a significant influence on the rate constant K$^+$.

At the calcite surface ($z = 5 \times 10^{-3}$ cm) due to the dissolution process there is a flux of $HCO_3^-$ and $CO_3^{2-}$ from the boundary layer to the bulk.
calcite surface towards the bulk. In order to keep the saturation index with respect to calcite sufficiently low, such that this flux can be maintained, $\text{CO}_3^{2-}$ must react with $\text{H}^+$ to form $\text{HCO}_3^-$. Due to mass transport by diffusion towards the bulk the flux of $\text{HCO}_3^-$ (given by the slope of the profile) increases slightly for two reasons: First, $\text{CO}_3^{2-}$ ions react with $\text{H}^+$ ions diffusing from the bulk into the DBL, and second, close to the solid phase boundary CO$_2$ migrating from the bulk reacts to $\text{H}^+$, which is then consumed by the reaction with $\text{CO}_3^{2-}$. Nevertheless, there is still a considerable flux of $\text{CO}_3^{2-}$ into the bulk, such that most of $\text{CO}_3^{2-}$ released from the solid reacts to $\text{HCO}_3^-$ in the bulk consuming there protons released by CO$_2$ conversion. Therefore, most of the conversion of CO$_2$ must be effective there. This situation, however, becomes different when the thickness of the boundary layer exceeds some critical value. If the DBL is sufficiently thick, the time for the species to migrate across the layer becomes so long that the chemical reactions entirely take place in the layer. To show this, we have calculated separately the total amount of CO$_2$ converted in the bulk and in the DBL for various $\varepsilon$. This is shown by Fig. 9. At a critical thickness $\varepsilon \approx 10^{-2}$ cm the conversion rate in the layer equals that in the bulk. For smaller $\varepsilon$ the rate in the bulk by far exceeds that in the DBL. This explains the variation of
The theoretical model of Buhmann and Dreybrodt (1985a,b) has been tested experimentally and found to provide reliable predictions (Baumann et al., 1985; Dreybrodt et al., 1996a,b) in the case of stagnant or laminarly flowing solutions for both dissolution and precipitation rates. In this work we show that the DBL model correctly describes the dissolution rates with decreasing ε: The rate of CO₂ conversion in the bulk is given by

\[ F_{\text{CO}_2} = \delta \cdot \frac{d[\text{CO}_2]}{dt} \]  

(8)

If δ is sufficiently large only small deviations of \([\text{CO}_2]\) from equilibrium are necessary to meet the condition \(F_{\text{CO}_2} = F_{\text{CI}}\). Therefore, CO₂-conversion is not rate limiting. Molecular diffusion across the layer, however, still plays an important role, and, therefore, the rates depend on ε. This also explains why adding carbonic anyhdrase to the solution at low \(P_{\text{CO}_2}\) and for \(\epsilon < 10^{-3}\) cm does not enhance the rates, as shown in Fig. 5.

We call dissolution under such hydro-chemical conditions bulk controlled. In contrast to bulk controlled dissolution at low \(P_{\text{CO}_2}\), the situation is quite different for high \(P_{\text{CO}_2}\). Figure 10 provides the concentration profiles for \(P_{\text{CO}_2} = 0.1\) atm for \(\epsilon = 5 \times 10^{-3}\) cm and otherwise unchanged conditions. Note there is a steep decrease of the CO₂⁻ concentration within 5 \(\times 10^{-4}\) cm, which is mirrored by a steep decrease of H⁺ due to the reaction to form HCO₃⁻. HCO₃⁻ shows a dramatic increase of its flux towards the bulk in this region. The carbonate ions migrating towards the bulk react with the H⁺ ions diffusing towards the calcite surface, and, therefore, the amounts of both fluxes must decrease. This can be seen clearly by the slopes in the narrow region of 5 \(\times 10^{-4}\) cm adjacent to the solid. Close to this region there is a steep increase in the flux of H⁻ towards the solid, which results from conversion of CO₂ diffusing from the bulk towards the surface of the calcite. The flux of H⁻ ions entering from the bulk is much lower than the flux in the region of CO₂ conversion, as can be judged from the slopes. This supply of H⁻ is caused by CO₂ conversion in this region. Outside this region, the concentration of carbonate is practically zero such that no carbonate is transferred into the bulk. HCO₃⁻ shows a constant flux towards the bulk. Figure 11 shows the CO₂-conversion rates in the bulk and in the layer for \(P_{\text{CO}_2} = 0.1\) atm as a function of ε. In contrast to Fig. 9 the critical value of \(\epsilon = 10^{-3}\) cm is lower by 1 order of magnitude. For smaller ε the reaction is bulk controlled. For \(\epsilon > 1 \times 10^{-3}\) cm the conversion of CO₂ occurs solely in the layer. Therefore, conversion of CO₂ is rate limiting and the dissolution rates become independent of ε. In this case the addition of carbonic anyhdrase is effective in catalysis of CO₂-conversion, and the calcite dissolution rates increase upon addition of this enzyme, as depicted in Fig. 5 for rotating speeds of 100 rpm (ε = 5 \(\times 10^{-3}\) cm) and also for 3000 rpm (ε ∼ 1 \(\times 10^{-3}\) cm). The decrease of the CO₂ enhancement factors from 10°C to 30°C (cf. Table 1b) can also be understood. The CO₂-conversion rate constants increase with temperature (Usdowski, 1982). Therefore, at higher temperature the effect of CA is smaller than at low temperature, and correspondingly the enhancement of calcite dissolution rates is also lower.

Summarizing, we have found that in the presence of a diffusion boundary layer two limits exist: At low \(P_{\text{CO}_2}\) (<10⁻² atm) and ε < 5 \(\times 10^{-3}\) cm most of the carbonate ions can diffuse across the DBL and react there to HCO₃⁻, whereby the H⁺ ions necessary for this are supplied by CO₂ conversion in the bulk. In this case of bulk control this reaction is not rate limiting, and a complex interplay of the surface controlled reaction (PWP rate equation) and diffusion is at work.

For high \(P_{\text{CO}_2}\) (>0.01 atm) CO₂-conversion takes place in a narrow region close to the solid. This reaction becomes rate limiting even for such low values of the thickness of the layer as 10⁻³ cm. The good agreement of the predictions of the model with the experimentally observed data gives confidence that reliable estimations can be made. Considering the scaling factor of 2 an accuracy of ±25% can be estimated.

5. APPLICATION OF THE RESULTS

The theoretical model of Buhmann and Dreybrodt (1985a,b) has been tested experimentally and found to provide reliable predictions (Baumann et al., 1985; Dreybrodt et al., 1996a,b) in the case of stagnant or laminarly flowing solutions for both dissolution and precipitation rates. In this work we show that the DBL model correctly describes the
behaviour of dissolution rates for turbulent flow. In view of these results and the fact that both dissolution and precipitation are determined by the same physical and chemical mechanism, we suggest that the predictions of this model are also valid for precipitation. Initial applications of this model for the interpretation of precipitation rates in natural stream systems (Dreybrodt et al., 1997; Liu et al., 1995) have yielded good results. For example growth rates of stalagmites in cave environments are in reasonable agreement to predictions from our models (Dreybrodt, 1988; Baker and Smart, 1995).

We, therefore, feel encouraged to list results obtained from the DBL model for dissolution and precipitation rates for various natural occurring conditions. These can be used to give at least a first estimation, when applied to geological problems. Figure 12 illustrates dissolution rates (a) and precipitation rates (b) for $P_{CO_2} = 1 \times 10^{-3}$ atm for various thickness of $\varepsilon$. The thickness $\delta$ of the turbulent bulk is $\delta = 1$ cm. For large values of $\varepsilon > 0.005$ cm rates are drastically reduced, compared to the top curve, which gives the maximal rates from the PWP equation using the bulk activities of the species ($\varepsilon = 0$). There is a significant change in the rates for $5 \times 10^{-3} \text{ cm} \leq \varepsilon \leq 1 \times 10^{-2}$ cm. Little influence of the DBL occurs when $\varepsilon < 2 \times 10^{-4}$ cm.

All the rate curves in Figs. 12 and 13 to a reasonable extent of accuracy ($\pm 25\%$) can be approximated by a linear relation.

$$R = \alpha \cdot ([Ca^{2+}]_{eq} - [Ca^{2+}])$$

(9)

where $\alpha$ is a rate constant in cm s$^{-1}$ and $[Ca^{2+}]_{eq}$ is the Ca equilibrium concentration. It should be noted that close to equilibrium for both dissolution and precipitation, inhibition mechanisms due to impurities in the limestone are operative (Busenberg and Plummer, 1986; Dreybrodt, 1988; Svensson and Dreybrodt, 1992; Dreybrodt et al., 1996a,b). Therefore, Eqn. 9 is valid only for concentrations $c/c_{eq} \leq 0.9$ for dissolution and $c/c_{eq} \geq 1.2$ for precipitation, respectively.

Furthermore, due to $CO_2$ conversion in the bulk controlled regime, the thickness $\delta$ of the turbulent bulk can also exert significant influence onto the rates. This is illustrated in Fig. 13, where both dissolution (a) and precipitation rates are shown for various values of $\delta$ depicted on the curves. For dissolution the rates are sensitive to values of $\delta$ below 1 cm. There is little change for higher values. In contrast the precipitation rates show a different behaviour. Here the limiting value of $\delta$, above which the rates stay unchanged with increasing $\delta$, is higher by a factor of 10 ($\delta = 10$ cm). To summarize such data, Table 2 lists the values of $\alpha$ and $[Ca^{2+}]_{eq}$ (cf. Eqn. 9) for dissolution rates with various $P_{CO_2}$, temperatures, $c$, and $\delta$. Table 3 gives corresponding data for precipitation. These in view of our experimental results can serve as a help to estimate rates in natural systems to an accuracy of about $\pm 25\%$. It should be noted here that the values in Table 3 are only valid for Ca concentrations $[Ca^{2+}] \approx 5 \times 10^{-3}$ mole/L. For higher concentrations the real rates are underestimated.

6. CONCLUSION

We have measured by use of the rotating disk technique dissolution rates of calcite in the system $H_2O - CO_2 - CaCO_3$ as they occur in natural waters of low $P_{CO_2}$, but also for high $P_{CO_2} > 10^{-2}$ atm up to 1 atm, which are not likely to occur in nature. The aim of these experiments was to reveal the role of the laminar diffusion boundary layer which separates the surface of the dissolving mineral from the well-mixed bulk of the solution. Our results give clear evidence that the diffusion boundary layer across which mass transport must be effected by molecular diffusion can reduce the rates significantly. Furthermore, the slow reaction $H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^-$ plays a significant role, which so far has not been sufficiently regarded in most studies dealing with dissolution or precipitation of calcite. We have found two regions where this reaction plays a dominant role. For

![Fig. 13. Theoretical dissolution rates (a) and precipitation rates (b) for various values $\delta$ of the turbulent core (cf. Fig. 6). The values of $\delta$ are related to the numbers on the curve by the corresponding insets. $\varepsilon = 5 \times 10^{-3}$ cm.](image)
rates on calcite measured by Herman (1982) compared well with the actual data. This is in agreement with the observation that the dissolution rates do not depend on the lithology of the limestone sample. Consequently we have measured rates with otherwise unchanged conditions for marble, for two limestone samples of Devonian origin from Guilin, and a single crystal of calcite. Within the limits of error all samples exhibited identical rates. Similar results were also obtained by Buhmann and Dreybrodt (1985a) who showed that during dissolution from thin stagnant films with thickness below 0.1 cm the dissolution rates are controlled by CO2 conversion and mass transport. Consequently different minerals (marble, limestone, and a calcite single crystal) exhibited identical behaviour.

Often the rate equation of PWP is applied to explain field observations by employing the activities of the corresponding species measured in the bulk water. Thus one neglects the presence of the diffusion boundary layer and considerable overestimations of the rates are the consequence (Liu et al., 1995). A nice example of the influence of the hydrodynamic conditions on dissolution rates in phreatic limestone caves has been given by Lauritzen (1986). He has shown that the dissolution rates in a cave consisting of a single phreatic conduit increased with increasing flow of water. At high yields of 10 m3 s−1 the rates were higher by about 1 order of magnitude, compared to those at yields of about 1 m3 s−1.

It is, of course, not easy to give values for ε in rivers or caves. Some estimations can be made by measuring dissolution rates on gypsum samples, which have suitable shapes to fit into the geometry of the limestone surface (Opdyke et al., 1987; Dreybrodt et al., 1992). Even if this is not possible, the values of the kinetic constants can be used to give some crude estimation of the rates, which are based on a sound understanding of calcite dissolution and precipitation in such complex systems.

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Table 3. Numerical values of α = α (T, Pco2, ε, δ), cf. Eqn 9, for calcite precipitation in the open system.

<table>
<thead>
<tr>
<th>ε (cm)</th>
<th>Pco2 = 3 × 10⁻⁴ atm</th>
<th>Pco2 = 1 × 10⁻¹ atm</th>
<th>Pco2 = 5 × 10⁻¹ atm</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>δ (cm) 5°C 10°C 20°C</td>
<td>δ (cm) 5°C 10°C 20°C</td>
<td>δ (cm) 5°C 10°C 20°C</td>
</tr>
<tr>
<td>0.001</td>
<td>0.1 3.75 5.59 11.39</td>
<td>0.1 4.44 5.74 11.1</td>
<td>0.1 3.44 4.72 7.94</td>
</tr>
<tr>
<td>0.005</td>
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<td>1.94 2.92 5.98</td>
<td>1.35 1.96 3.44</td>
</tr>
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<td>0.01</td>
<td>1.58 2.48 5.54</td>
<td>1.45 2.19 4.52</td>
<td>1.08 1.55 2.77</td>
</tr>
<tr>
<td>0.02</td>
<td>1.30 2.05 4.54</td>
<td>1.18 1.75 3.59</td>
<td>0.96 1.39 2.52</td>
</tr>
<tr>
<td>0.001</td>
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<td>9.32 13.23 23.33</td>
<td>4.93 6.78 9.93</td>
</tr>
<tr>
<td>0.005</td>
<td>5.19 8.24 18.21</td>
<td>5.53 5.01 10.00</td>
<td>1.48 2.10 3.62</td>
</tr>
<tr>
<td>0.01</td>
<td>3.48 5.48 12.45</td>
<td>2.01 3.04 6.15</td>
<td>1.09 1.56 2.77</td>
</tr>
<tr>
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<td>2.25 3.57 7.91</td>
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<tr>
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<td>3.86 5.78 11.25</td>
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<tr>
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<td>2.15 3.78 6.52</td>
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<tr>
<td>0.02</td>
<td>2.85 4.47 9.35</td>
<td>1.36 2.06 4.10</td>
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</tr>
<tr>
<td>0.001</td>
<td>100 31.67 40.15 56.80</td>
<td>100 14.36 19.47 30.30</td>
<td>100 4.94 7.08 9.98</td>
</tr>
<tr>
<td>0.005</td>
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<td>3.93 5.80 11.38</td>
<td>1.48 2.14 3.62</td>
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<td>5.46 8.64 17.38</td>
<td>2.16 3.30 6.56</td>
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<tr>
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<td>2.95 4.62 9.85</td>
<td>1.37 2.06 4.11</td>
<td>0.96 1.39 2.53</td>
</tr>
</tbody>
</table>

| [Ca²⁺] | 10⁻³ mmol/cm² | 6.75 6.30 5.60 | 10.10 9.30 8.30 | 17.10 16.20 14.30 |

Pco2 < 10⁻² atm and thicknesses of the boundary layer below 10⁻³ cm the carbonate ions released from the solid react to HCO₃⁻ consuming the protons delivered by hydration of CO₂. In this bulk controlled regime the influence of CO2 conversion becomes evident by the dependence of the rates on the thickness of the bulk layer.

For large Pco2 > 0.01 atm and thickness of the DBL above 10⁻³ cm, CO₂ conversion takes place in a small region adjacent to the calcite surface and almost all carbonate ions released from the solid react to HCO₃⁻ in this narrow region. The protons needed for this reaction are delivered by CO₂ molecules, diffusing from the bulk and reacting to H⁺ + HCO₃⁻ close to the solid surface. This mechanism is only relevant in the case of low control rates are weakly dependent on the thickness of the turbulent zone, since CO2 conversion in the DBL is rate limiting. This is corroborated by the enhancement of dissolution rates upon addition of carbonic anhydrase.

This has some important consequences. Many dissolution experiments using the rotating disk technique have employed a partial pressure Pco2 = 1 atm and thicknesses of the DBL between 10⁻³ up 1 × 10⁻⁸ cm (Herman, 1982; Herman and White, 1985). In these cases rates are determined entirely by CO2 conversion, and no valid conclusion can be drawn on the dissolution mechanisms at the surface of the mineral. This is in agreement with the observation that the dissolution rates on calcite measured by Herman (1982) compared well with the predictions of our model (Dreybrodt and Buhmann, 1991). If CO2 conversion controls the rates then one would expect no influence of the lithology of the limestone sample to the rates. Consequently we have measured rates with otherwise unchanged conditions for marble, for two limestone samples of Devonian origin from Guilin, and a single crystal of calcite. Within the limits of error all samples exhibited identical rates. Similar results were also obtained by Buhmann and Dreybrodt (1985a) who showed that during dissolution from thin stagnant films with thickness below 0.1 cm the dissolution rates are controlled by CO2 conversion and mass transport. Consequently different minerals (marble, limestone, and a calcite single crystal) exhibited identical behaviour.

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