Calcite precipitation from aqueous solutions with different calcium and hydrogen carbonate concentrations
Kai Zeppenfeld

ABSTRACT

This paper describes the influence of different Ca\(^{2+}\) and HCO\(_3\) concentrations on the precipitation of calcite in aqueous solutions. Mixtures of CaCl\(_2\) and NaHCO\(_3\) solutions with different concentrations were stirred, covering a wide range of supersaturation and precipitation of calcite. The resulting reduction of the Ca\(^{2+}\) concentration was recorded as a function of time by measuring the electric conductivity and the pH value. The nucleation rate increased with increasing supersaturation and can be described with the classical theory of nucleation. For different solutions with similar values of supersaturation, the hydrogen carbonate/calcium ratio had no significant influence on the rate of nucleation. At a given calcium concentration the precipitation rate increased with increasing supersaturation. This effect was more pronounced at higher supersaturations. Measurements at similar values of supersaturation showed that the calcite precipitation rate increased with increasing hydrogen carbonate/calcium ratio. These results can be explained by applying a surface complexation model. The crystal surface concentrations of the two species >CaCO\(_3\) and >CO\(_3\) and the adsorption of CaCO\(_3\)\(^0\) ion pairs are responsible for catalysing calcite precipitation.

Key words | calcite precipitation, crystal growth, hydrogen carbonate/calcium ratio, nucleation, supersaturation, surface complexation

INTRODUCTION

The precipitation of calcite (CaCO\(_3\)) is of great importance in natural environments, regulating the carbon composition of rivers, lakes and oceans (Stumm & Morgan 1996). Moreover CaCO\(_3\) scaling is often a major problem in natural water supply of industrial plants and various chemical engineering processes. The precipitation and crystallization of calcite as an insulating layer causes a decrease in the flow rate in pipes and reduced heat transfer in heat exchangers (Drew Ameroid 1997). Several publications report on the crystallization of CaCO\(_3\) in aqueous solutions. Apart from the temperature (Kabasaci et al. 1996; Johannsen et al. 1997), the pH value (Brown et al. 1993; Gomez-Morales et al. 1996) and the number of inoculating seed crystals (Reddy & Gaillard 1981; Takasaki et al. 1994) the crystal growth rate is strongly dependent on supersaturation with respect to calcite. With increasing supersaturation S the growth rate r follows an expression of the form \(r \sim (S - 1)^x\). Therefore r corresponds to a linear (\(x = 1\)) (Reddy & Nancollas 1971; Meyer 1979; Gutjahr et al. 1996) or parabolic (\(x = 2\)) dependence (Kazmierczak et al. 1982; Nielsen & Toft 1984; Lioliou et al. 2007) on the degree of supersaturation.

In addition, the kinetics of calcite precipitation is widely explained by surface reaction-controlled mechanisms. The surface reaction-controlled mechanisms consist of adsorption, dehydration and surface diffusion of lattice ions, spiral growth at screw dislocations, or two-dimensional nucleation on the mineral surface. The precipitation of calcite can also be diffusion controlled, depending on the degree of supersaturation and hydrodynamic conditions at which
the precipitation is initiated (Shiraki & Brantley 1995; Zeppenfeld 2005).

Apart from supersaturation, the growth rate of calcite may also be affected by the aqueous composition through the carbonate anion to calcium cation concentration ratio of the solution (van der Weijden et al. 1997; Lin & Singer 2005). These studies demonstrated that for different solution compositions with the same degree of supersaturation, the calcite precipitation rate increased with increasing carbonate/calcium ratio. This finding contradicts the generally accepted assumption that the degree of supersaturation is the sole factor for controlling precipitation kinetics. The precipitation experiments were initiated by adding calcite seed crystals to the solutions in a constant pH range from 7.2 to 9.0. Furthermore it could be demonstrated (Nehrke et al. 2007) that under a high and fixed pH (10.2) and at a constant degree of supersaturation, the growth rate of a single crystal was highest when the concentration ratio CO$_3^{2-}$/Ca$^{2+}$ of the solution equaled one. The growth rate decreased proportionally with positive or negative deviation of the CO$_3^{2-}$/Ca$^{2+}$ ratio from one.

In the current study the precipitation rates of calcite were measured as a function of supersaturation at different concentrations of hydrogen carbonate and calcium ions in non-seeded and homogeneous solutions. The unexpected results may explain the deposition of calcite in natural water systems and in natural water supply under conditions where Ca$^{2+}$ and HCO$_3^-$ are present as major components.

**MATERIALS AND METHODS**

All experiments were carried out in a 500 cm$^3$ glass vessel thermostatized at a constant room temperature of 25 $\pm$ 0.5°C. NaHCO$_3$ and CaCl$_2$ solutions were prepared from corresponding reagent grade crystalline solids (Merck) using deionised water (0.06 $\mu$S cm$^{-1}$). The concentration of the CaCl$_2$ and NaHCO$_3$ solutions were 5.0 to 9.0 mmol l$^{-1}$ and 6.0 to 20.0 mmol l$^{-1}$, respectively. Equal volumes (200 ml) of the calcium chloride and hydrogen carbonate solutions were rapidly mixed by injecting them at the same time under stirring (600 rpm) using a magnetic stirrer to achieve a critical supersaturation with respect to CaCO$_3$. The magnetic stirrer has no noticeable influence on CaCO$_3$ precipitation, as substantially higher intensities of a magnetic field (> 0.2 tesla) are needed for a noticeable effect (Tai et al. 2008). All systems were operated open, which included the exchange of CO$_2$ with the atmosphere. The initial pH value of all mixed solutions ranged from 8.22 to 8.38, measured by a WTW 320 pH meter (Merck Labor und Chemie Vertrieb West GmbH, Bochum, Germany). The electric conductivity was measured using a WTW 318 instrument (Merck Labor und Chemie Vertrieb West GmbH, Bochum, Germany). The conductivities of all prepared solutions ranged from 875 to 1,810 $\mu$S cm$^{-1}$. Before each new experiment the glass vessel was washed with hydrochloric acid and dried thoroughly.

$\kappa_{25}$ alterations in the Ca$^{2+}$ concentration $\Delta$[Ca$^{2+}$] in the solution were followed according to Equation (1) based on electric conductivity measurements.

$$\Delta [\text{Ca}^{2+}] = (\kappa_{25}^0 - \kappa_{25}) / \Lambda_{\text{molar}}$$ (1)

$\kappa_{25}^0$ is the electric conductivity of the solutions immediately after mixing and $\Lambda_{\text{molar}}$ denotes the average molar equivalent conductivity. A value of 180 $\pm$ 3 S cm$^{-2}$ mol$^{-1}$ was calculated for Ca(HCO$_3$)$_2$ solutions in the described concentrations range (Landolt & Börnstein 1960; Zeppenfeld 2001). The low concentrations dependency of $\Lambda_{\text{molar}}$ (Onsager & Fuoss 1932), causing an error of $\pm$ 3 S cm$^{-2}$ mol$^{-1}$ was neglected. In addition, an additional low dependency on dissolved CO$_2$ (House 1981) and NaCl causing a maximal error of 2%, was also neglected.

The conditions of the supersaturated solutions were selected so that the formation of calcium carbonate was initiated after an induction time. The onset of precipitation was accompanied by a reduction in the Ca$^{2+}$ concentration, which was determined by measuring the electric conductivity $\kappa_{25}$ as a function of time. The crystalline precipitation products were dried at room temperature and examined by X-ray powder diffractometry. The precipitate consisted only of calcite; the aragonite and the vaterite modifications were not observed.

**RESULTS AND DISCUSSION**

**Kinetics of calcite precipitation**

The calcite precipitation described above is considered to result from the following reactions:
\[
\text{CaCO}_3(s) \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \quad K_{\text{so}} \quad (2)
\]
\[
\text{CaCO}_3(s) + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \quad K_{\text{so}} K_2^{-1} \quad (3)
\]
\[
\text{CaCO}_3(s) + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \quad K_{\text{so}} K_1 K_2^{-1} \quad (4)
\]

The supersaturation \( S \) with respect to calcite is defined as:
\[
S = \frac{a(\text{Ca}^{2+}) a(\text{CO}_3^{2-})}{K_{\text{so}}} = \frac{a(\text{Ca}^{2+}) a(\text{HCO}_3^-)}{a(\text{H}^+) K_{\text{so}} K_2^{-1}}
\]
\[
= \frac{a(\text{Ca}^{2+}) a^2(\text{HCO}_3^-)}{a(\text{H}_2\text{CO}_3) K_{\text{so}} K_1 K_2^{-1}}
\]

where \( K_{\text{so}} \) is the thermodynamic solubility product of calcite \((\text{p}K_{\text{so}} = 8.42 \text{ (Stumm \\ & Morgan 1996)})\), \( K_1 \) the first acidity constant of \( \text{H}_2\text{CO}_3 \) \((\text{p}K_1 = 6.35)\), \( K_2 \) the second acidity constant of \( \text{HCO}_3^- \) \((\text{p}K_2 = 10.30)\), \( a(\cdot) \) the activities of the ions in the solution at time \( t \), with the activity coefficients \( \gamma_z \) determined by the Davies Equation \((\text{Stumm \\ & Morgan 1996})\):
\[
-\log \gamma_z = 0.51 z^2 [f(0.5/(1 + f(0.5)) - 0.3]
\]

in which \( f \) is the ionic strength and \( z \) the charge of the corresponding ion.

The resulting \( \text{Ca}^{2+} \) and \( \text{HCO}_3^- \) concentrations of all mixed solutions and the values of the supersaturation \( S \) calculated for an average initial \( \text{pH} \) of 8.30 \((\text{Equation (5)})\) are summarized in Table 1. Five calcium concentrations between 2.5 and 4.5 mmol l\(^{-1}\) were combined with hydrogen carbonate concentrations between 3.0 and 10.0 mmol l\(^{-1}\). The supersaturation increased with increasing calcium and increasing hydrogen carbonate concentration, whereby similar values of \( S \) can result from quite different hydrogen carbonate/calcium concentration ratios.

Figure 1 shows the time-related alteration in the \( \text{Ca}^{2+} \) concentration for a solution with 4.0 mmol l\(^{-1}\) \( \text{Ca}^{2+} \) and 5.0 mmol l\(^{-1}\) \( \text{HCO}_3^- \) and a supersaturation of 27.9. The alteration of the \( \text{pH} \) value with time is also shown. Because a certain supersaturation was achieved, the first stable nuclei were formed. These were growing to a detectable size while the formation of new nuclei was going on \((\text{Söhnle \\ & Mullin 1988})\) and the \( \text{Ca}^{2+} \) concentration and the \( \text{pH} \) value were decreasing slowly, resulting in a slightly turbid solution. After the formation of a sufficient area of nuclei, the crystal growth was the dominant process \((\text{Mullin 2001})\) and mass precipitation of calcite started, followed by a rapid decrease in the \( \text{Ca}^{2+} \) concentration. A drop in the \( \text{pH} \) value indicated the beginning of precipitation according to Equations (3) and (4), whereby the dissolved \( \text{CO}_2 \) was stripped partially by stirring and therefore a final \( \text{pH} \) value of 7.43 was attained at 160 min. The supersaturation decreased according to Equation (5) and a final value of \( S = 1.5 \) could be calculated. Therefore the solution was still supersaturated and the dissolution reaction of \( \text{CaCO}_3 \) could be neglected. This was valid for all experimental runs.

The required time for the initiation of calcite mass precipitation, in particular the turning point in the \( \text{Ca}^{2+} \) concentration versus time function, which was determined by a geometric method, is referred to as the induction period, \( t_{\text{Ind}} \) \((60 \text{ min})\). Table 1 shows the induction period at various values of supersaturation \( S \) and the hydrogen carbonate/calcium ratio. With increasing supersaturation the induction period decreased because higher supersaturation promotes the formation of nuclei \((\text{Mullin 2001})\). At a similar degree of supersaturation e.g. \( S = 22 \) or \( S = 33 \) the hydrogen carbonate/calcium ratio had no significant influence on the nucleation, as the values of the induction period were comparable.

The precipitation of calcite (Figure 1) follows a rate expression of the form
\[
- \frac{d[\text{Ca}^{2+}]}{dt} = k([\text{Ca}^{2+}] - [\text{Ca}^{2+}]_0)^2
\]

where \( k \) \((\text{L}/\text{mmol} \cdot \text{min})\) is the rate constant of precipitation, \([\text{Ca}^{2+}]_0\) is the concentration of calcium ions before precipitation is started and \([\text{Ca}^{2+}]\) is the \( \text{Ca}^{2+} \) concentration measured at time \( t \).

Analysis of calcite crystal growth data is facilitated by the integrated form of Equation (7):
\[
\frac{1}{[\text{Ca}^{2+}]} - \frac{1}{[\text{Ca}^{2+}]_0} = kt
\]

The linear plot of \(1/[\text{Ca}^{2+}] - 1/[\text{Ca}^{2+}]_0\) versus time presented in Figure 1 confirms that Equation (8) is valid to interpret the experimental results. The rate constants
Table 1 | Calculated values of the rate constant $k$ and the induction period $t_{\text{Ind}}$ versus the different $\text{Ca}^{2+}$ and $\text{HCO}_3^-$ concentrations, the resulting supersaturations $S$ (pH = 8.30) and the hydrogen carbonate/calcium concentration ratio $[\text{HCO}_3^-]/[\text{Ca}^{2+}]$. The errors in the value of the figures in the right-hand column are shown in parentheses.

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<th>$[\text{HCO}_3^-]$ (mmol l$^{-1}$)</th>
<th>$[\text{HCO}_3^-]/[\text{Ca}^{2+}]$</th>
<th>$S$</th>
<th>$t_{\text{Ind}}$ (min)</th>
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$k$ calculated via Equation (8) as a function of supersaturation $S$ and different hydrogen carbonate/calcium ratios are listed in Table 1. With increasing supersaturation the rate constant increased, whereby at similar values of supersaturation e.g. $S = 22$ or $S = 33$ the rate constant increased with increasing hydrogen carbonate/calcium ratio.

Nucleation

The formation of nuclei is the first step to produce a crystalline product. Nucleation mechanisms are considered to be either homogeneous, where collisions on the
molecular scale lead to the generation of nuclei, or heterogeneous, where surfaces of foreign solids catalyse the generation of nuclei. The rate of nucleation, $J_s$, in particular the number of nuclei per unit time per unit volume can be expressed as follows (Mersmann et al. 2000; Mullin 2001):

$$J_s = \Omega \exp \left[ \frac{-16\pi V_m^2 \gamma^2 f(\theta)}{3(K_B T)^3 \ln 2S} \right]$$

(9)

where $V_m$ is the molar volume of calcite, $\gamma$ the interfacial tension or surface energy of the solid in contact with the solution, $K_B$ the Boltzmann constant, $T$ the temperature, $S$ the supersaturation and $\Omega$ the pre-exponential factor. For heterogeneous nucleation the surface energy is corrected by the factor $f(\theta)$ which is related to the hypothetical contact angle of a solute nucleus spreading on the surface of a foreign particle. The contact angle is a function of the affinity between a cluster of the condensed solute and the uppermost layer of molecules of foreign particles, e.g. dust particles. For $f(\theta) = 1$, the nucleation is homogeneous and for $f(\theta) < 1$, the nucleation is heterogeneous.

If nucleation is followed by diffusional growth, the rate of nucleation $J_s$ is inversely proportional to the induction period $t_{\text{Ind}}$ (Sönnel & Mullin 1988):

$$t_{\text{Ind}} = J_s^{-1}$$

(10)

Substituting Equation (10) into Equation (11) and rearranging results produces

$$\log t_{\text{Ind}} = B(\log S)^{-2} - \log \Omega$$

(11)

with

$$B = \frac{16\pi V_m^2 \gamma^2 f(\theta)}{3(K_B T)^3 \ln 210}$$

(12)

The plot of the dependence of the measured induction times (Table 1) as a function of supersaturation for the five different $\text{Ca}^{2+}$ concentrations of the solutions is shown in Figure 2. The experimental data demonstrate that the log $t_{\text{Ind}}$ versus $(\log S)^{-2}$ function is linear, whereby the dependence can be separated into two linear parts with different slopes. This observed dependence results from the fact that at low values of supersaturation ($S < 25$) the nucleation is predominantly heterogeneous ($f(\theta) < 1$), whereas at high values of supersaturation ($S > 25$) homogeneous nucleation prevails ($f(\theta) = 1$). The two linear parts, corresponding to the different nucleation mechanisms, are expected to have different slopes ($B_{\text{hom}} > B_{\text{het}}$) as can be determined from Equation (12) and as found experimentally (Figure 2). These results are in good agreement with earlier published investigations by Sönnel & Mullin (1978), who determined induction periods of $\text{CaCO}_3$ precipitation as a function of supersaturation.

Furthermore, it could be demonstrated that different $\text{Ca}^{2+}$ concentrations and the resulting hydrogen carbonate/calcium ratio have no significant effect on heterogeneous
or homogeneous nucleation, because the slopes of the linear parts ($B_{\text{hom}}$ and $B_{\text{het}}$) are similar (Figure 2). Thus the rate of nucleation or the induction period is only dependent on supersaturation, expressed by Equation (9).

Crystal growth

As soon as enough stable nuclei have formed they begin to grow into calcite crystals of visible size. There are two steps in mass deposition: first a transport process, whereby solute ionic species are transported from the bulk of the fluid phase to the surface of solids (nuclei and growing crystals). This is followed by an integration reaction with solute species arranging themselves into the crystal lattice (Mersmann et al. 2000; Mullin 2001). The transport process determines the number of contacts resulting in crystal growth. If the stirrer speed is sufficiently high, the crystal growth is primarily determined by the integration of the solute species into the crystal lattice. At slower stirrer speeds the rate controlling mechanism change continuously from surface reaction control to primarily transport control (Zeppenfeld 2005). Because of the constant kind of stirring (600 rpm in all experiments) and the resulting constant transport process, the change of the crystal growth rate is only controlled by processes on the crystal surface and increases with increasing supersaturation.

For small supersaturation ($S \leq 1$) the system may be contained near the thermodynamic equilibrium. Based on the minimum of free energy, the crystal surfaces are very smooth. If a single ion is added to this surface, it can form a bond with only its nearest neighbour, resulting in a very low binding energy, which is a major barrier for crystal growth. With increasing supersaturation the roughness of the crystal surfaces increases on the basis of a development of screw dislocations (Dove & Hochella 1993) and finally of two-dimensional and polynuclear growth (Shiraki & Brantley 1995). Any molecule incident on a rough crystal surface has a greater probability of ending up with a higher binding energy than a crystal with a smooth surface. The rough surfaces tend to maintain their roughness during growth and molecules attach themselves at sites, creating new corners which are preferred sites for subsequent additions (Nielsen 1984). With increasing degree of supersaturation the growth rate increases with different exponents, respectively. A parabolic dependence appears only at small supersaturation ($S \approx 1.5$). With increasing supersaturation ($S \geq 2.2$) the dependence becomes linear, whereby the crystal growth is strongly dependent on the roughness of the crystal surfaces (Mersmann et al. 2000; Teng et al. 2000).

Figure 2 shows the experimental rate constant $k$, or the precipitation rate as a function of supersaturation $S$ for the five different Ca$^{2+}$ concentrations of the solutions.

![Figure 2](image)

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Figure 2 shows the experimental rate constant $k$, or the precipitation rate as a function of supersaturation $S$ for the solutions with the five different Ca$^{2+}$ concentrations listed in Table 1. With increasing hydrogen carbonate concentration and thereby increasing supersaturation the rate constant increased linearly. Therefore, it can be concluded that the growth rate increases with increasing roughness

![Figure 2](image)
of the surfaces and the crystal growth is mostly determined by two-dimensional and polynuclear growth. This experimental correlation can be separated into two linear parts with different slopes. At low supersaturation (S < 25) the slopes are substantially smaller than at higher supersaturation (S > 25). This dependence results from the fact that at low supersaturation the nucleation mechanism is heterogeneous whereas at higher supersaturation homogeneous nucleation prevails. The homogeneous nucleation results in an increasing formation of nuclei (Equation (9)), whereby the enhanced solid surfaces of nuclei promote the two-dimensional and polynuclear crystal growth.

Figure 2 shows that the slopes for both separated linear parts of the function $k(S)$ decrease with increasing Ca$^{2+}$ concentration. The slope $m = \frac{dk}{dS_{\text{Ca}^{2+}}}$ characterizes how the rate constant increases, i.e. how much for a given Ca$^{2+}$ concentration the precipitation is accelerated with supersaturation increase, which (owing to the experimental set up) corresponds to an increasing hydrogen carbonate/calcium ratio. A plot of $m$, calculated by linear regression, at the five different Ca$^{2+}$ concentrations is shown in Figure 3. It is clear that with increasing Ca$^{2+}$ concentration $m$ decreases. This tendency is more pronounced at higher supersaturation (S > 25). Therefore the above described acceleration of precipitation decreases with increasing Ca$^{2+}$ concentration. This is in agreement with the fact that an increasing hydrogen carbonate/calcium ratio results in a higher precipitation rate at similar values of supersaturation (Table 1).

These results can be explained by using surface complexation reactions as outlined in the following paragraphs. Calculations of the calcite surface characteristics under experimental conditions was based on the surface complexation model originally proposed by van Cappellen et al. (1993) and later modified by Pokrovsky et al. (2000). The surface complexation reactions and their intrinsic stability constants $K_{\text{int}}^0$ are summarized in Table 2.

![Figure 3](https://iwaponline.com/aqua/article-pdf/59/8/482/401685/482.pdf)  
**Figure 3** Calculated slopes $m = \frac{dk}{dS_{\text{Ca}^{2+}}}$ for the five Ca$^{2+}$ concentrations of the solutions.

### Table 2

<table>
<thead>
<tr>
<th>Surface complexation reaction</th>
<th>$\log K_{\text{int}}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&gt; \text{CaOH} + \text{H}^+ = &gt; \text{CaOH}_2^+$</td>
<td>11.5</td>
</tr>
<tr>
<td>$&gt; \text{CaOH} = &gt; \text{CaO}^- + \text{H}^+$</td>
<td>-12.0</td>
</tr>
<tr>
<td>$&gt; \text{CaOH} + \text{CO}_3^{2-} + 2\text{H}^+ = &gt; \text{CaHCO}_3^2 + \text{H}_2\text{O}$</td>
<td>23.5</td>
</tr>
<tr>
<td>$&gt; \text{CaOH} + \text{CO}_3^{2-} + \text{H}^+ = &gt; \text{CaCO}_3^2 + \text{H}_2\text{O}$</td>
<td>17.1</td>
</tr>
<tr>
<td>$&gt; \text{CO}_3^2 = &gt; \text{CO}_3^- + \text{H}^+$</td>
<td>-5.1</td>
</tr>
<tr>
<td>$&gt; \text{CO}_3^- + \text{Ca}^{2+} = &gt; \text{CO}_3\text{Ca}^2 + \text{H}^+$</td>
<td>-1.7</td>
</tr>
</tbody>
</table>

In aqueous solutions water molecules are ordered near the calcite surface by forming OH-groups (Perry et al. 2007). The precipitation of calcite requires the adsorption of the mineral lattice ions Ca$^{2+}$ and CO$_3^{2-}$ on the surface, followed by dehydration of the formed surface complexes. The major surface species under the experimental conditions described above (pH = 8.30) are $> \text{CaCO}_3$ and $> \text{CO}_3^-$, which were measured by diffuse reflectance infrared spectroscopy (Pokrovsky et al. 2000). These results are consistent with the observation that in an aqueous medium the surface charge of calcite is negative (Thomson & Pownall 1989) and that variation in pH does not affect the surface potential significantly (Cicerone et al. 1992). Furthermore the surface concentration of $> \text{CaCO}_3$ and $> \text{CO}_3^-$ are positively correlated with observed calcite precipitation rates (Lin & Singer 2005). These results suggest that $> \text{CaCO}_3$ and $> \text{CO}_3^-$ are the dominant species responsible for calcite precipitation. van der Weijden et al. (1997) observed a higher growth rate of calcite with increasing HCO$_3$/CO$_3^{2-}$ ratio or decreasing pH, which was explained by a contribution of hydrogen carbonate to calcite crystal growth. This is in line with the fact that dehydration of the mineral surface and the formation of $> \text{CaCO}_3$ (Table 2) are important steps in calcite precipitation. Therefore it can be concluded that the concentrations of the $> \text{CaCO}_3$ and $> \text{CO}_3^-$ increased with increasing hydrogen carbonate/calcium ratio.

Both Ca$^{2+}$ (aq) ions and CaCO$_3^2$ (aq) ion pairs can adsorb to the $> \text{CaCO}_3$ and $> \text{CO}_3^-$ surface species, by the
following reactions:

\[ > \text{CaCO}_3^- + \text{Ca}^{2+}(\text{aq}) \rightarrow \text{CaCO}_3^- - \text{Ca}^{2+} \]  
(13)

\[ > \text{CaCO}_3^- + \text{CaCO}_3^0(\text{aq}) \rightarrow \text{CaCO}_3^0(\text{s})^+ > \text{CaCO}_3^- \]  
(14)

\[ > \text{CO}_3^- + \text{Ca}^{2+}(\text{aq}) \rightarrow > \text{CO}_3^- - \text{Ca}^{2+} \]  
(15)

\[ > \text{CO}_3^- + \text{CaCO}_3^0(\text{aq}) \rightarrow \text{CaCO}_3^0(\text{s})^+ > \text{CO}_3^- \]  
(16)

in which the CaCO_3^0(aq) is about 20 times more reactive than Ca^{2+}(aq) at the calcite–water interface (Nilsson & Sternbeck 1999). However, the dehydration of the dissolved ionic species is required to incorporate lattice ions into the calcite structure during the precipitation process. It can be suggested that the carbonate ion has a greater water exchange rate than the calcium ion and the dehydration of the cation is the rate-determining step in calcite precipitation (Nielsen 1984). The complexation of the cation with a carbonate ligand enhances the dehydration of the remaining water molecules coordinated with the cation (Magerum et al. 1978), and thus promotes the adsorption of CaCO_3^0(aq) ion pairs at the > CaCO_3^- and > CO_3^- surface sites.

In Equation (14), > CaCO_3^- on the reactant side is incorporated into the calcite lattice when CaCO_3^0(aq) is adsorbed and dehydrated. The adsorbed CaCO_3^0(aq) becomes a new > CaCO_3^- surface site. Moreover > CO_3^- on the reactant side is incorporated into the calcite lattice, where the remaining CO_3^- from CaCO_3^0(aq) becomes a new > CO_3^- surface site (Equation (16)). At these new surface sites further CaCO_3^0(aq) species are adsorbed. With an increasing hydrogen carbonate/calcium ratio the concentration of the adsorbed CaCO_3^0(aq) ion pairs increased resulting in a higher precipitation rate of calcite, as described above. The results are supported by the observation that both the heterogeneous and homogeneous nucleation are independent of the hydrogen carbonate/calcium ratio at similar values of supersaturation. Therefore it can be concluded that solid calcite particles with > CaCO_3^- and > CO_3^- surface species (e.g. enough stable nuclei or calcite seeds) must be present in the solution, because these calcite particles adsorbed the CaCO_3^0(aq) ion pairs.

The observation of Nehrke et al. (2007) that the growth was greatest when the ratio CO_3^-/Ca^{2+} in the solution was equal to unity, can be explained by the high and fixed pH value of 10.2. Under this condition the carbonate concentration was probably similar to the hydrogen carbonate concentration and therefore the surface complexation model cannot be applicable. Therefore the results may be explained with the kink growth rate theory for non-Kossel crystals, assuming that the frequency factors for attachment to kink sites are the same for the cation and anion.

CONCLUSIONS

Calcite precipitation experiments were carried out at different supersaturations and different hydrogen carbonate/calcium ratios in an open system, which included the exchange of CO_2 with the atmosphere. Both the heterogeneous and the homogeneous nucleation rate increased with increasing supersaturation. At similar values of supersaturation the hydrogen carbonate/calcium ratio has no significant influence on the nucleation rate. For given Ca^{2+} concentrations it was observed that the precipitation rate increased linearly with increasing supersaturation. This acceleration of the precipitation increased significantly after a certain saturation was exceeded, which suggests a two-dimensional and polynuclear growth mechanism. The accelerations decreased with increasing Ca^{2+} concentrations. This is in accordance with the observation that, in contrast to nucleation, the growth rate increased with increasing hydrogen carbonate/calcium ratio at similar values of supersaturation. The calcite surface complexation model was used to explain the experimental results. An increasing hydrogen carbonate/calcium ratio results in a higher quantity of the dominant > CaCO_3^- and > CO_3^- surface species, resulting in an enhanced growth rate. Furthermore, the dehydration of Ca^{2+} ions and thereby the formation of CaCO_3^0 ions, which are adsorbed at the negatively charged calcite surfaces, is promoted by a higher hydrogen carbonate/calcium ratio.

Thus the deposition rate of calcite in natural water systems increased with increasing hydrogen carbonate content and decreasing calcium content at constant supersaturation. Moreover the precipitation rate of CaCO_3 in natural water supply as in pipes and heat exchangers increased with increasing hydrogen carbonate/calcium.
ratio at similar values of supersaturation. Therefore the supersaturation is not the sole factor controlling calcite precipitation under conditions where Ca\(^{2+}\) and HCO\(_3^−\) are present as major components.

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