Modelling spiral growth at dislocations and determination of critical step lengths from pyramid geometries on calcite \{10\overline{1}4\} surfaces

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Abstract

To visualise the morphologic changes of a growing spiral pyramid, a mathematical model was developed and implemented in an algorithm that can loop through the sequential time-frames in a growth sequence. The algorithm simulates growth of spiral pyramids with geometries reflecting variation in the step velocity ratio and critical lengths of inequivalent steps. We have developed a new mathematical model that implements a set of equations describing the relationship between time-dependent change of step length and orientation around dislocation sources. These step length relationships can be used for extracting the critical step lengths that restrict step growth at dislocations. This allows determination of the critical thermodynamic parameters from post-growth AFM images that do not rely on real-time AFM fluid-flow experiments.

The model was tested on experimental results obtained from calcite \{10\overline{1}4\} surfaces. A shift in pyramid apex geometry resulting from velocity anisotropy for the obtuse and acute steps was observed for pyramids grown from solutions of variable Ca\(^{2+}\) to CO\(_3^{2-}\) activity ratio. Relative step velocity and pyramid apex angle were correlated with activity ratio. AFM images of rhombic spiral pyramids on calcite surfaces were used for measuring the length of sequential steps for the four step orientations. Step length plots show the same trend in the experimental data as was predicted by the theoretical model. Critical step lengths were determined using linear regression analysis of the experimental results. The step edge energy was calculated to be 3.6 \(\cdot\) 10\(^{-14}\) J nm\(^{-1}\) for obtuse step edges and 1.3 \(\cdot\) 10\(^{-15}\) J nm\(^{-1}\) for acute edges. These values are consistent with previous experimental and computational studies.

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1. INTRODUCTION

Spiral growth at dislocations was described in the classical BCF model, named after the authors, Burton, Cabrera and Frank, as a dominant mechanism for crystal growth (Burton et al., 1951; Frank, 1952). This model described the growth of spirals protruding from dislocations using the physico-chemical parameters of a vapour phase equilibrium system and was developed from Kossel crystal theory, which implements a simple cubic lattice with only one type of ion in the unit cell (Kossel, 1927). Since then, research has focused on understanding the atomic-scale processes responsible for crystal growth (e.g., Cabrera and Vermilyea, 1958; Nielsen, 1984) and extensive efforts have been made to interpret the role of the thermodynamic driving force on these processes (e.g., Lasaga and Kirkpatrick, 1981; Chernov, 1993; Voronkov and Rashkovich, 1994; Sangwal, 1998). For non-Kossel crystals, which includes most naturally occurring compounds that contain more than one type of ion in the unit cell, there is a kinetic dependence of growth both on the ion activity ratio and the degree of supersaturation (e.g., Paquette and Reeder, 1995; Alimi and Gadri, 2004; Kucher et al., 2006; Nehrke et al., 2007).

Zhang and Nancollas (1998) presented a theoretical model based on experimental observations of NaCl crystals that described the kinetics of step growth processes as a...
function of the ion activity ratio and the ion activity product, i.e., the degree of supersaturation. For calcite, given that the Ca\(^{2+}\) to CO\(_3^{2-}\) ratio of natural waters largely exceeds unity (Zuddas and Mucci, 1994; Cai et al., 2000; Zeebe and Westbrook, 2003), the ion activity ratio is an important variable for evaluating calcite growth processes. Paquette and Reeder (1995) recognised the influence of the ion activity ratio on crystal morphology grown from solutions supersaturated with excess Ca\(^{2+}\). Recently, Nehlke et al. (2007) and Tai et al. (2006) also reported a significant kinetic dependence on ion activity ratio from bulk growth experiments. Thus, the kinetic control by differences in stoichiometry of the growth solution should be considered in models describing crystal growth.

Although a crystal surface may appear flat on a macroscopic scale, natural surfaces are rarely perfect or flat at the atomic scale. They have defects such as vacancies, substituted ions and localities where the atomic structure is disrupted. The driving force for ion incorporation is often higher at defect sites than in the surrounding atomic structure because of less satisfied bonds and local disorder. This higher energy favours growth (Lasaga and Kirkpatrick, 1981; Putnis, 1992). Dislocations are an important type of linear defect (Fig. 1). They can be edge or screw dislocations, depending on the orientation of the Burgers vector relative to the dislocation line. Such dislocations play an important role in crystal growth, thereby producing pyramids consisting of overlapping steps in a continuous spiral.

It is known that steps containing kinks with high formation energy have a relatively low kink density, producing straight step edges (e.g., Chernov et al., 2007). Spirals with well-defined, straight step edges are perfect for experimental investigations of changes in pyramid geometries. Hence, calcite was an obvious choice for comparing experimentally produced spirals with theoretical growth models. Furthermore, calcite is an interesting mineral because it precipitates biogenically and inorganically and is the main component of about 10% of all sedimentary rocks on the Earth’s surface.

The perfect cleavage face, \{10\(\overline{1}4\}\}, gives calcite its typical rhombohedral form (Fig. 2). These planes have the largest interplanar spacing, i.e., 3.036 Å, thus the weakest interplane attractive forces, resulting in low surface energy and perfect cleavage. The intersection of \(\{10\overline{1}4\}\) faces produces angles of 102\(^\circ\) and 78\(^\circ\) within cleavage planes, so steps tip away from or towards the underlying terrace producing obtuse and acute angles at terrace edges (Fig. 2c). The \(\{10\overline{1}4\}\) faces have high stability and low growth rate (de Leeuw and Parker, 1997). In a pure system, where no impurities interact with the surface, calcite ought to grow with rhombohedral morphology confined by \(\{10\overline{1}4\}\) faces. Experimental evidence shows that the growth mechanism depends on the degree of supersaturation. At intermediate degrees of supersaturation, dislocation-assisted growth dominates, producing spiral pyramids (Gratz et al., 1993; Teng et al., 1999). Better understanding of growth on rhombohedral surfaces is necessary for more effective interpretation of growth phenomena for calcite in natural systems. The aim of this study was: (i) to develop a new model for determining the critical step lengths associated with growth at dislocation sites and (ii) to test the model against experimental AFM data from rhombic spirals grown on calcite.

2. METHODS AND PROCEDURES

Freshly cleaved Iceland spar (Chihuahua, Mexico) single crystals, typically 5 × 5 × 3 mm, were prepared (Stipp and Hochella, 1991) in air and immersed in solutions with a saturation index, SI = log(Ω) = 0.6, where Ω represents the degree of supersaturation defined as the ion activity product in solution, in ratio to the equilibrium ion activity. pH was adjusted to 8.5 ± 0.1 by titration with KOH. The Ca\(^{2+}\) to CO\(_3^{2-}\) activity ratio, \(\xi\), was varied from 0.1 to 100 by adding analytical grade CaCl\(_2\)-2H\(_2\)O and KHCO\(_3\), to solutions where the ionic strength was maintained at 0.1 M using KCl. All experiments were performed at about 25 °C. A constant flow rate through the experimental mixing cell, containing the calcite crystal, was maintained by peristaltic pumping at 1.2 ml/min. Solutions of Ca\(^{2+}\) and CO\(_3^{2-}\) were injected from separate reservoirs into the cell by in-line mixing to prevent homogeneous precipitation before injection. All solution compositions were calculated using PhreeqC with fixed pH, SI and ionic strength. Alkalinity and carbonate concentration were verified on separate aliquots immediately after preparation by titration and total Ca concentration was determined by atomic absorption spectroscopy.

All Atomic Force Microscopy (AFM) images of Iceland Spar crystals were acquired ex-situ with a Digital Instruments Multimode IV on areas ranging from 2 to 10 μm in width, using standard Si\(_3\)N\(_4\) tips at scan rates of about 2–4 Hz. Images were corrected for distortion by defining linear drift vectors between successive up- and down-scan images, thereby producing corrected AFM images by means of affine transformations, with the matrix-based computing program, MATLAB (Mathworks, 2007). A detailed description of the correction procedure will be published separately. The AFM images were used to determine the geometric relationships for spiral pyramids grown from supersaturated solutions with variable Ca\(^{2+}\) to CO\(_3^{2-}\)
activity ratio on calcite \{10\overline{1}4\} surfaces. MATLAB was also used to develop an algorithm for the theoretical model and to simulate growth at dislocation sites.

3. RESULTS AND DISCUSSION

3.1. Growth of a spiral pyramid

A mathematical model describing the geometric constraints of growing spiral pyramids was used to interpret the morphology observed from experiments. The model was embedded in a MATLAB algorithm that could loop through sequential time-frames of a spiral originating from a single dislocation, thus producing an output-image of the growth process. The algorithm accounts for variation in inequivalent step velocities, as well as differences in critical length for the acute and obtuse steps arising from a single dislocation outcrop. Studying the geometry of a growth pyramid can provide estimates of the critical step lengths that restrict growth at dislocations. The critical length, \( l_c \), is defined in Fig. 3. Growth of a step in the direction normal to its edge is blocked if the step is shorter than its critical length (Frank, 1952; Chernov, 2001; De Yoreo and Vekilov, 2003).

For simplicity, step velocities are considered constant when \( L_i > l_{ci} \), thereby ignoring step-length limited growth near the dislocation source when \( L_i \) is close to \( l_{ci} \) (e.g., Burton et al., 1951). This simplification is consistent with experimental observations of a rapid increase in step velocity when the critical step length has been exceeded, as documented for calcite (Teng et al., 1998), barium sulphate (Higgins et al., 2000), lysozyme (Rashkovich et al., 2001) and potassium hydrogen phthalate (Rashkovich et al., 2003). After exceeding their critical length, steps reach their maximum growth velocity almost immediately. In general, this indicates that length-dependent step velocity can be assumed to be insignificant for crystal surfaces containing steps with low kink densities (Chernov et al., 2007). Hence, once this critical length is exceeded, the step advances with constant velocity, \( v_i \), so the velocity perpendicular to any step edge emerging from the dislocation outcrop can be expressed as:

\[
v = \begin{cases} v_i, & L_i \geq l_{ci} \\ 0, & L_i < l_{ci} \end{cases}
\]

where \( L_i \) represents the length of the respective step with orientation, \( i \); \( l_{ci} \), the critical step length; and \( v_i \), the step velocity.
velocity. Eq. (1) accounts for the velocities of the four step orientations, which we refer to as the two obtuse steps, O₁ and O₂, and the two acute steps, A₁ and A₂. (Fig. 4) The O₁ step is equivalent to the O₂ step and the A₁ step is equivalent to the A₂ step.

The spiral rotation period, \( \tau \), i.e., the time it takes the spiral to make one turn around the dislocation source, depends on the critical step lengths of the specific steps in addition to acute and obtuse step velocities:

\[
\tau \equiv t_{\text{lcot}(1)} + t_{\text{lcot}(2)} + t_{\text{lcat}(1)} + t_{\text{lcat}(2)} = (l_{\text{co}} + l_{\text{ca}}) \cos \alpha \left( \frac{1}{v_o} + \frac{1}{v_a} \right),
\]

where \( \alpha \) is the angle between the step normal of the next step and the direction of the critical step. For the \{10/14\} face of calcite, this angle is 12°, the difference between 90° and the rhombohedral angles, 102° and 78°. \( v_o \) and \( v_a \) represent the velocity of the obtuse and acute steps; \( l_{\text{co}} \) and \( l_{\text{ca}} \), the critical step lengths; and \( t_{\text{lcot}(1)}, t_{\text{lcot}(2)}, t_{\text{lcat}(1)} \) and \( t_{\text{lcat}(2)} \), the time it takes the step to exceed the critical step length for the obtuse (O₁ or O₂) and acute (A₁ or A₂) steps:

\[
\begin{align*}
  t_{\text{lcot}(1)} &= \cos \alpha \cdot \frac{l_{\text{cot}(1)}}{v_o}, \\
  t_{\text{lcot}(2)} &= \cos \alpha \cdot \frac{l_{\text{cot}(2)}}{v_a}, \\
  t_{\text{lcat}(1)} &= \cos \alpha \cdot \frac{l_{\text{cat}(1)}}{v_o}, \\
  t_{\text{lcat}(2)} &= \cos \alpha \cdot \frac{l_{\text{cat}(2)}}{v_a}.
\end{align*}
\]

For an isotropic square spiral, \( \alpha = 0° \), \( l_{\text{co}} = l_{\text{ca}} \) and \( v_o = v_a \), so \( \tau \) in Eq. (2) reduces to:

\[
\tau = 4 \cdot t_{unct} = \frac{4l_{\text{c}}}{v_a}.
\]

More detail on the theoretical background of spiral pyramid growth, based on both computational and experimental results can be found in Burton et al. (1951), Vekilov et al., (1992), De Yoreo et al. (1997), Lasaga and Lütte (2003) and Thomas et al. (2004).

From geometric considerations, the relationship between the apex angle, \( \theta \), and step velocity ratio can be expressed as:

\[
\log \left( \frac{v_o}{v_a} \right) = \log(\cos(0.5 \cdot \theta - 39°)) - \log(\sin(0.5 \cdot \theta - 27°)).
\]

This equation is similar to the relationship published by Teng et al. (1999). The apex angle is only dependent on the ratio of obtuse and acute step velocities, \( v_o/v_a = (T_o/T_a) \), where \( T \) denotes the terrace width between successive steps), and consequently reflects relative differences in growth velocity for the acute and obtuse steps. For the simulation presented in Fig. 4, the acute and obtuse step velocities are equivalent, i.e., \( v_o/v_a = 1 \). This results in \( \theta = 180° \).

Fig. 5 presents simulations illustrating the influence of inequivalent step velocities on pyramid geometry.

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**Fig. 4.** Example simulation illustrating time sequences in dislocation-assisted growth of spiral steps. The screw dislocation with a unit Burgers vector is rotating clockwise with the lower side on the right of the dislocation edge and the upper side on the left. The dislocation source is marked by a dot in the centre of the spiral. In this example, the critical step lengths were equivalent for all steps and the velocity ratio, \( v_o/v_a = 1 \). The stippled grey line pointing north from the dislocation represents the dislocation edge and the solid grey lines between spiral step edges represent sequential time steps in the growth sequence. A zoom out of the resulting spiral pyramid after several turns around the dislocation is illustrated to the right. The rhombic angular relationship between steps in this example represents those of a spiral on the \{10/14\} surface of calcite.
Fig. 4 shows a modelled time series of a growing rhombic spiral at a screw dislocation. Steps grow by an upward clockwise rotation. The two obtuse step edges face east and south and the two acute edges face west and north. Growth of the first monomolecular layer occurs on the right side of the dislocation edge. The first time frame, \( t_1 \), corresponds to the time when \( L_{O2} > l_{co(2)} \), so growth normal to the \( O_2 \) step edge (east) has proceeded. The obtuse \( O_1 \) step has not yet exceeded its critical length, i.e., \( L_{O1} < l_{co(1)} \), so growth is blocked normal to this step (south), i.e., \( v_o = 0 \) in the direction of \( O_1 \). At \( t_2 \), \( L_{O1} > l_{co(1)} \), so the \( O_1 \) step expands south at velocity, \( v_o \). The new critical step length becomes \( l_{cat(1)} \) and growth continues north, east and south, but not west. At \( t_3 \), the \( A_1 \) step exceeds its critical length, i.e., \( L_{A1} > l_{cat(1)} \). Now growth proceeds normal to all of the initial step edges, i.e., north, east, south and west. The next \( A_2 \) step reaches its critical length, \( l_{cat(2)} \), and the spiral has made one full turn around the dislocation source. At \( t_4 \), \( l_{cat(2)} \) is exceeded, so the second \( A_2 \) step grows north at a velocity \( v_o \). Once \( l_{co(2)} \) is exceeded again, growth normal to the second \( O_2 \) step (east) proceeds and the monomolecular layer stretches over the dislocation edge (\( t_5 \)). Looping through this growth sequence produces a clockwise rotating rhombic spiral.

### 3.1.1. Time-dependent step lengths of spirals

Growth of the polygonal spiral can be described in terms of the rate of change of step lengths around the dislocation source as the spiral grows. The length of a step edge at a given time in a growth sequence is related to the critical step length and to the velocity by which the step expands out from the source. Thus, the relative length of steps around the dislocation gives information about step growth. The initial growth events illustrated in Fig. 4 can be resolved by evaluating the relative time-dependent length change of the four spiral step orientations. At early times, the change in length of short steps close to the dislocation source is affected by the initial step growth events. For example, the time-dependent length change of the \( O_2 \) step, \( L_{O2}(t) \), can be resolved as: for a clockwise rotating spiral, when \( L_{O2} < l_{co(2)} \), growth perpendicular to the \( O_2 \) step is blocked, so its change in length is only defined by the velocity, \( v_o \), of the \( A_2 \) step (Eq. (6a)). Once \( l_{co(2)} \) has been exceeded, but not \( l_{co(1)} \), then \( O_2 \) progresses east (\( t_1 \) in Fig. 4). Now, the increase in length of the \( O_2 \) step, \( L_{O2}(t) \), is defined by the step velocity, \( v_o \), of the \( A_2 \) step, the critical length \( l_{co(2)} \) and the velocity, \( v_o \), of the \( O_2 \) step (Eq. (6b)). Once the critical length \( l_{co(1)} \) is reached, the southern expansion of the \( O_2 \) step edge is no longer blocked (\( t_2 \) and later in Fig. 4) and \( L_{O2}(t) \) is defined by both the velocity in the direction of the \( A_2 \) and \( O_1 \) steps, \( v_a \) and \( v_o \), and the obtuse critical step lengths, \( l_{cat(2)} \) and \( l_{co(1)} \) (Eq. (6c)):

\[
\begin{align*}
L_{O2}(t) &= \frac{v_o}{\cos \alpha} \cdot t, \\
&\text{for } t < t_{co}:
\end{align*}
\]

\[
\begin{align*}
L_{O2}(t) &= \frac{v_o}{\cos \alpha} \cdot t - \frac{\tan \alpha}{C_1} \cdot v_o \cdot (t - t_{co}), \\
&\text{for } t_{co} < t < 2 \cdot t_{co}:
\end{align*}
\]

\[
\begin{align*}
L_{O2}(t) &= \frac{v_o}{\cos \alpha} \cdot t - \sin \alpha \cdot l_{co} + \frac{v_o}{\cos \alpha} \cdot (t - 2 \cdot t_{co}).
&\text{for } t \geq 2 \cdot t_{co}:
\end{align*}
\]

Similar relationships can be written for the time-dependent change in length, \( L_{A2}(t) \), for the other steps. Solution of the set of series equations in the algorithm produces the resulting spiral at a specific time, \( t \), as shown in Fig. 4. A series of \( O_2 \) step lengths, \( L_{O2} \), after \( l_{co(1)} \) is exceeded are numbered from \( n_1 \) to \( n_m \). The initial \( O_2 \) step with number \( n_{(m-6)} \) is furthest down the pyramid slope. This increase in the length of sequential steps down the pyramid slope is equivalent to the time-dependent length change of a single step, because this step expands out to replace the lateral position of the former step at a distance defined by the terrace width, \( T \). So, \( L_{O2}(t) \) in Eq. (6c) can be replaced by \( L_{O2}(n) \).

Combining the step-length functions provides estimates for the critical step lengths, given that the step velocity ratio (Eq. (5)) can be determined. For example, the \( O_2 \) step length, \( L_{O2} \), can be described in terms of the length of the subsequent (shorter) step, \( L_{A1} \), in the direction of spiral rotation, i.e., clockwise in the present example. When the extension of steps \( O_2 \) and \( O_1 \) is no longer restricted by

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Fig. 5. Simulations illustrating the influence of step velocity anisotropy on the apex angle and thus the geometry of growth pyramids.
growth of new steps near the dislocation source, i.e., $t \geq (t_{ca} + 2t_{ac})$ (Fig. 3 and later in Fig. 4), the following relationship applies:

$$L_{O2}(t) = L_{O1}(t) + \left( \left( \frac{v_o}{v_a} \right)^{-1} \sin \alpha \right) \cdot (l_{co} + l_{ca}),$$

$$t \geq (t_{ca} + 2t_{ac}).$$

(7)

This time-dependent linear relationship describes a line with a slope of 1. The sum of obtuse and acute critical step lengths, $l_{ca} + l_{ac}$, at a given $v_o/v_a$ ratio can be determined from the intercept.

Fig. 6 illustrates the correlation of $L_{O2}(t)$ with $L_{O1}(t)$ at a given $v_o/v_a$ ratio. It shows how the length of the two obtuse step edges increases as the spiral grows and the step edges extend. There are four growth zones. Close to the dislocation, step expansion is affected by initial step formation events (zone I to III). The first zone, I, shows the relationship between the lengths of the $O_2$ and $O_1$ steps, $L_{O2}$ and $L_{O1}$, when $t < t_{O2}$, i.e., before $l_{O2}$ has been reached. The $O_1$ step does not extend yet. The second growth zone, II, shows the relationship for $l_{O2} \leq t < (t_{O2} + t_{O1})$, i.e., $l_{O2}$ is now exceeded ($t_1$ in Fig. 4). In the third zone, III, the critical step length of the $O_1$ step, $l_{O1}$, has been exceeded so the $O_2$ step extends in both ends. The western extension of the $O_1$ step is still suppressed, so $L_{O2}$ increases faster than $L_{O1}$ ($t_3$ in Fig. 4). In the fourth zone, IV, all initial growth events restricting obtuse step growth have been exceeded. $O_2$ and $O_1$ extend at the same pace ($t_5$ in Fig. 4), so the slope is now 1. This constant linear relationship between $L_{O2}$ and $L_{O1}$ in zone IV is fixed by Eq. (7). It represents the time-dependent step lengths for obtuse steps when $t \geq (t_{ca} + 2t_{ac})$. Further growth away from the dislocation source produces obtuse step lengths that plot within this zone. Therefore, plotting step lengths that are not restricted by the initial step formation processes at the source results in a linear regression corresponding to Eq. (7).

Similar step length relationships for each of the other steps in zone IV can be defined as:

$$L_{O1}(t) = L_{A1}(t) + (1 + 2 \sin \alpha) \cdot l_{ca} + l_{ac},$$

$$t \geq \tau,$$

(8)

$$L_{A1}(t) = L_{A2}(t) + \left( \frac{v_o}{v_a} - \sin \alpha \right) \cdot (l_{ca} + l_{ac}) - l_{ca} \left( \frac{v_o}{v_a} \right)^{-1},$$

$$t \geq (\tau + t_{ca}),$$

(9)

$$L_{A2}(t) = L_{O2}(t) + (1 + 2 \sin \alpha) \cdot l_{ca} + l_{ac},$$

$$t \geq (\tau + t_{ca} + t_{ac}).$$

(10)

Eqs. (8) and (10) show that the relationship between the lengths of two inequivalent steps, i.e., obtuse versus acute or vice versa, is independent of the velocity ratio, $v_o/v_a$, whereas the relationship between two equivalent steps, i.e., two acute or two obtuse, depends on $v_o/v_a$ (cf. Eqs. (7) and (9)). These trends are reflected in simulated step length plots presented as Fig. 7. Given that length measurement of sequential steps down the slope of a post-growth pyramid (Fig. 4) is equivalent to measuring the change in length of a single step as a function of time, $L(t)$ in equations 7 through 10 can be replaced by $L(n)$. Therefore, real-time AFM experiments are not necessary. One needs only a single, post-growth AFM image where a number of steps are present.

3.2. Experimental observations on calcite spirals

The straight-edge, rhombic pyramids that can be grown on calcite in a few hours make this mineral ideal for evaluating the theoretical model. Previous experiments showed that varying the Ca$^{2+}$ to CO$_3^{2-}$ activity ratio in supersaturated solutions dramatically changes the relative velocities of obtuse and acute step edges (Paquette and Reeder, 1995). High Ca$^{2+}$ to CO$_3^{2-}$ ratio shifts the pyramid apex toward acute–acute corners, correlating with higher obtuse step velocity relative to acute; low ratios shift the pyramid apex toward obtuse–obtuse corners, correlating with relatively higher acute step velocity. Fig. 8 shows representative AFM-images of spiral pyramids grown from solutions with $\xi = [10.0; 1.0; 0.1]$. The relationship between the activity ratio of Ca$^{2+}$ and CO$_3^{2-}$ in the growth solution and step velocity ratio, $v_o/v_a$, is evident by comparing pyramid morphology from experiments (Fig. 8) with the simulation re-
The experimental data demonstrated a clear relationship between \( v_o/v_a \) and \( n_{Ca/C0} \):

\[
\log\left(\frac{v_o}{v_a}\right) = \frac{0.381}{C1} \log(n) - 0.034, \quad \Omega = 10^{0.6}.
\]  

(11)

Previous observations also showed that there is a different dependence of step advance velocity on the degree of supersaturation for obtuse and acute step edges. The velocity of obtuse steps increases faster as a function of supersaturation than acute steps (Teng et al., 1999). This means that the velocity ratio also increases as a function of the degree of supersaturation, so equation 11 is only valid when \( \Omega = 10^{0.6} \). To derive a relationship that accounts for both activity ratio and degree of supersaturation will require further experiments.

3.2.1. Experimental step length plots

Drift-corrected AFM-images were used to measure lengths on sequential steps down the slope of spirals using the approach illustrated in Fig. 4. The pyramids were produced from solutions with ion activity ratios ranging from 0.1 to 100 and the data are plotted as a function of the neighbouring steps in Fig. 9. Lines representing step length correlations in zone IV data were found by linear regression of step lengths longer than 500 nm. Growth after extraction of the crystal from the growth solution, before solution removal with a jet of N\(_2\), would be constrained within this range by the relatively slow growth of calcite \{10\(1/2\)/C22\} faces. Also, restricting the step-length analysis to include steps longer than 500 nm excludes steps that are restricted by the growth processes near the dislocation source. As expected from Eqs. (7)–(10), the slope for each set of experimental data is approximately 1, which reflects that step length increases at a constant velocity after step expansion is no longer controlled by the initial growth events near the dislocation source.

From Eqs. (8) and (10), plots of step length for inequivalent edges, such as comparing \( O_1 \) and \( A_1 \) or \( O_2 \) and \( A_2 \), are expected to be independent of velocity ratio (Fig. 7) and we...
know from Eq. (11) that \( \frac{v_0}{v_a} \) depends on \( n \). This independence of \( n \) for inequivalent steps is reflected in the plots of experimental data, Fig. 9a and b. Slope for the data regression is near 1 and the \( y \)-intercept is positive, consistent with the model predictions. Fig. 9c and d, which compare equivalent step lengths, show the expected dependence of the velocity ratio from Eqs. (7) and (9). The model (Eq. (9)) predicts the largest effect of an increasing velocity ratio when comparing the relative length of acute edges, \( L_{A1} \) vs. \( L_{A2} \) (Fig. 7d). This trend is clear in the experimental data (Fig. 9d). The \( y \)-intercept increases with \( n \), corresponding to an increase in \( \frac{v_0}{v_a} \). According to Eq. (7), \( y \)-intercepts in a plot of \( L_{O2} \) vs. \( L_{O1} \) decrease slightly with increasing \( \frac{v_0}{v_a} \) (Fig. 7c). This corresponds to an increase in \( \xi \) for the experimental data. This trend is difficult to resolve from the experimental data (Fig. 9c), because the decrease in intercepts becomes smaller with increasing velocity ratio. Step length plots for equivalent steps, such as \( L_{O2} \) vs. \( L_{O1} \) and \( L_{A1} \) vs. \( L_{A2} \), derived from Eqs. (7) and (9), can provide an estimate of the sum of critical step lengths, i.e., \( l_{co} + l_{ca} \), and therefore an average value of \( l_c \). However, the implementation of \( \frac{v_0}{v_a} \) as a variable in these equations makes a large data set necessary for precise estimation.

On the other hand, step length plots for two inequivalent steps, such as \( L_{O2} \) vs. \( L_{A1} \) and \( L_{O1} \), derived from Eqs. (8) and (10), are independent of the step velocity ratio. Linear regression of the data gathered from step growth, independent of initial growth effects, provide an estimate of the absolute values of \( l_{co} \) and \( l_{ca} \), according to Eqs. (8) and (10). The linear regressions for the two plots (Fig. 9a and b) provide two equations with two unknowns. Their solution for data from the calcite spirals grown with a saturation index of 0.6, gives a critical length for \( l_{co} \) of 26 nm and \( l_{ca} \) of 9 nm. These values can be used to calculate the step edge energies from:

\[
l_{ai} = \frac{2bc\beta_i}{\Delta\mu},
\]
where $b$ represents the inter-atomic distance along the step (6.4 Å for calcite); $c$, the distance between atomic rows perpendicular to the step edge (3.2 Å for calcite); and $\beta_i$, the step edge energy of the $i$th step orientation. For obtuse steps, the step energy was $3.6 \pm 0.6 \text{ (2sd)} \cdot 10^{-19} \text{ J m}^{-1}$ and for acute steps, $1.3 \pm 3.9 \text{ (2sd)} \cdot 10^{-19} \text{ J m}^{-1}$. These values are consistent with previous results from real-time AFM growth experiments and computer simulations (Paloczi et al., 1998; Teng et al., 1998; Kristensen et al., 2004). However, a larger data set would provide a better fit and an estimate with smaller uncertainty.

For calcite, the rhombohedral symmetry causes the slip plane running along the dislocation to make either an obtuse or an acute angle with the underlying terrace. For this reason, different orientations of the dislocation relative to the rhombohedral structure produce slip planes with different structure, thereby changing the energy environment. Depending on solution composition, such energy differences could lead to changes in critical length, resulting in faster growth for one sign of the dislocation vector. However, given that obtuse and acute step energies are very similar, this would probably not have a dramatic influence on dislocation-assisted growth. The C glide of the rhombohedral structure results in an equal probability of obtuse and acute slip planes and, therefore, most likely a random rotation direction of the spirals. In this study, spirals with both rotation directions were observed at about equal probability, but the statistical sampling was small. Eqs. (7)–(10) applies equally for counter-clockwise rotating spirals; the $L_i$ variables simply switch place.

Previous experimental determinations of critical step lengths have typically used the ability of real-time AFM to acquire images during fluid-flow. From this approach, the critical lengths can be determined by the time when growth normal to the corresponding steps is no longer blocked and the critical length is directly measured from the AFM-image (Paloczi et al., 1998; Teng et al., 1998; Rashkovich et al., 2006). However, accurate length determination from real-time AFM images is hindered by artefacts. Image distortion, mainly resulting from hysteretic behaviour of the piezoelectric scanner and tip asymmetries introduce uncertainty (Henriksen and Stipp, 2002). Also, very high scan rate and high resolution images are necessary for precise determinations. Most important, determinations from real-time AFM requires the use of fluid-flow over the sample while acquiring the images, so growth may be affected by the scanning tip. The approach described here does not require real-time AFM imaging. It uses only the geometric restrictions of any polygonal spiral pyramid to predict growth at a dislocation site and neglects the immature steps near the apex, at the dislocation source. Therefore, post-growth AFM images can be used for measuring on a number of sequential steps in the same image to decrease uncertainty.

### 4. CONCLUSIONS

The polygonal spiral geometry was valuable in the development of a new method for determining the critical step lengths restricting growth at a dislocation site. The general method relies on the step-length relationships between spiral steps and can be applied to all spiral systems in which the step velocity can be assumed to be independent of its length, as is true for most minerals with relatively low solubility. The method was tested on and found to predict experimental observations from rhombic spiral growth on calcite surfaces and critical step lengths for obtuse and acute step orientations were extracted. These thermodynamic critical parameters were used for calculating a step edge energy of $3.6 \pm 0.6 \cdot 10^{-19} \text{ J m}^{-1}$ for obtuse steps and $1.3 \pm 3.9 \cdot 10^{-19} \text{ J m}^{-1}$ for acute steps. These estimates correspond well with literature values determined from other approaches. Implementation of the mathematical model in an algorithm produces spirals predicting the influence of a variable ion activity ratio on spiral geometry.

The spiral model and corresponding experimental results presented here represent a step forward in comprehensive understanding of processes responsible for growth of natural crystals. Methods for determining critical step parameters tell us something about the thermodynamics of a given chemical system. The influence of solution composition in pure systems on the morphology and growth rate of calcite is far from fully understood. Better understanding of calcite behaviour in systems, where Ca$^{2+}$ and CO$_3^{2-}$ activities are inequivalent and where the presence of impurities can significantly modify the kinetics of growth or dissolution, will improve our predictions of growth modification processes in natural systems. Implementing the ion activity ratio in growth models will facilitate a better understanding of the inhibiting effects of growth modifiers present in natural systems.

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