Evolution of Calcite Growth Morphology in the Presence of Magnesium: Implications for the Dolomite Problem

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Abstract

The effect of magnesium on calcite growth morphology was known to occur as step rounding in some cases and surface segmentation in others. What remain unknown are the conditions for and the relations between the different effects, suggesting a lack of comprehensive understanding in the fundamental cause. Here we investigated the evolution of spiral hillock morphology on calcite cleavage surfaces in solutions with increasing Ca to Mg ratios and supersaturation levels using *in situ* atomic force microscopy. We isolated the effects of Mg and saturation by conducting experiments under conditions of constant pH, ionic strength, and $\text{Ca}^{2+}/\text{CO}_3^{2-}$. Our results revealed three types of morphological variations, ranging from step rounding in one direction (type I), to all directions (type II), and finally to a mosaic-like surface segmentation associated with monolayer buckling and step bunching (type III). These results suggest that the effect of magnesium on calcite growth depends upon multiple parameters including the concentration of Mg in solution, the step speed, as well as the extensiveness of Mg for Ca substitution in calcite lattice. We propose that the morphological variation may be understood by a model that takes into consideration of (1) the lifespan and flux size of Mg ions at kinks in comparison to step kinetics, and (2) the diffusion and alignment of point defects created by the substitution of Mg for Ca in the crystal lattice. Stress calculations show that the maximum amount of Mg which calcite lattice can sustain before plastic deformation is ~40%, suggesting that lattice stress due to the mismatch between MgCO_3 and CaCO_3 is likely the ultimate cause for the difficulty of ambient condition dolomite crystallization.

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1. INTRODUCTION

The incorporation of magnesium ions into calcium carbonate minerals is a critical subject to understanding the ‘dolomite problem’, biomineralization processes, and, more recently, the *foraminiferal Mg/Ca*-paleothermometry (e.g. [Lippmann, F. 1973; Berner, R. A. 1975; Bischoff, W. D., Bishop, F. C. et al. 1983; Mucci, A. and Morse, J. W. 1983; Lear, C. H., Rosenthal, Y. et al. 2002; Barker, S., Greaves, M. et al. 2003; Gayathri, S., Lakshminarayanan, R. et al. 2007; Evans, D. W., Muller-Loennies, S. et al. 2012; Xu, J., Yan, C. et al. 2013]). In a broad sense, the presence of Mg in the lattice of CaCO_3 phases renders three types of effects on the mineralization of calcium carbonate. Firstly, many studies indicated that Mg reduces the thermodynamic stability of calcite [Busenberg, E. and Plummer, L. N. 1989; Konigsberger, E. and Gamsjager, H. 1992; Davis, K. J., Dove, P. M. et al. 2000; Davis, K. J., Dove, P. M. et al. 2004; Kulik, D. A. 2006]. This decrease is believed to be caused by the introduction of disorder [Berner, R. A. 1975; Mucci, A. and Morse, J. W. 1983] and lattice strain [Glodsmith, J.R. and Graf, D. L. 1958; Goldsmith, J. R., Graf, D. L. et al. 1961; Althoff, P. L. 1977; Bischoff, W. D., Bishop, F. C. et al. 1983; Paquette, J. and Reeder, R. J. 1990] in the calcite structure due to the size difference between Ca^{2+} ($r = 1.14 \text{ \AA}$) and Mg^{2+} ($r = 0.86 \text{ \AA}$) [Shannon, R. D. 1976]. Measurements of calcite step propagation rates in the presence of Mg demonstrated that the incorporation of Mg as an impurity increases the local solubility at kinks [Davis, K. J., Dove, P. M. et al. 2004; Wasylenki, L. E., Dove, P. M. et al. 2005; Stephenson, A. E., DeYoreo, J. J. et al. 2008], in support of the thermodynamic consideration. Secondly, a plethora of experimental work documented the significant retardation of Mg ions on the growth kinetics of CaCO_3 [Davis, K. J., Dove, P. M. et al. 2000; Davis, K. J., Dove, P. M.

et al. 2004; Wasylenki, L. E., Dove, P. M. et al. 2005; Stephenson, A. E., DeYoreo, J. J. et al. 2008; Astilleros, J. M., Fernandez-Diaz, L. et al. 2010]. Compared to Ca^{2+} , Mg^{2+} is 24.56% smaller, leading to a 1.76 times higher charge density and, in turn, a considerably stronger hydration. The presence of such a strong water shell is suggested to increase the kinetic barrier for calcite nucleation and growth when magnesium is adsorbed onto mineral surfaces [Lippmann, F. 1973; Loste, E., Wilson, R. M. et al. 2003; De Yoreo, J. J., Zepeda-Ruiz, L. A. et al. 2009]. A step pinning model in which the binding of Mg^{2+} ions to calcite surface edges prevents the attachment of Ca^{2+} at kink sites [De Yoreo, J. J. and Vekilov, P. G. 2003; Arvidson, R. S., Collier, M. et al. 2006; Xu, M. and Higgins, S. R. 2011] provides a very reasonable explanation for such a kinetic effect.

The third widely reported magnesium effect is the modification of calcite growth morphology. Earlier observations focused primarily on the more rounded rhombohedral appearance of calcite crystals grown in the presence of Mg [Davis, K. J., Dove, P. M. et al. 2000; Davis, K. J., Dove, P. M. et al. 2004; Stephenson, A. E., DeYoreo, J. J. et al. 2008; Zhang, F. F., Yan, C. et al. 2013]. Given and Wilkinson [1985] hypothesized that that morphological change results chiefly from the supply rate of carbonate ions instead of Mg effect. However, later studies using differential interference contrast (DIC) imaging technique [Northrup, P. A. and Reeder, R. J. 1994; Tang, Y. Z., Elzinga, E. J. et al. 2007] revealed an uneven distribution of Mg on calcite growth surfaces with higher concentrations confined to the $\langle \bar{4}41 \rangle$ vicinal faces. This observation led the authors to suggest that, based upon the size and geometric differences in kink sites at steps of different orientations on calcite surfaces, the smaller Mg^{2+} prefers to enter the smaller and more closed acute steps [Paquette, J. and Reeder, R. J. 1990; Reeder, R. J. 1996]. This

hypothesis was later supported by *in situ* atomic force microscopy (AFM) data [Davis, K. J., Dove, P. M. et al. 2000; Davis, K. J., Dove, P. M. et al. 2004; Wasylenki, L. E., Dove, P. M. et al. 2005; Stephenson, A. E., DeYoreo, J. J. et al. 2008; Astilleros, J. M., Fernandez-Diaz, L. et al. 2010; Sethmann, I., Wang, J. W. et al. 2010; King, H. E., Satoh, H. et al. 2013] which showed that Mg incorporation at calcite growth steps is indeed crystallographic direction specific. It was further suggested that the preferential incorporation of Mg in acute steps hinders the growth kinetic and weakens the surface energetic control on step orientations, and ultimately leads to the rounding of growth steps [Falini, G., Gazzano, M. et al. 1994; Zhang, Y. P. and Dawe, R. A. 2000; Meldrum, F. C. and Hyde, S. T. 2001; Davis, K. J., Dove, P. M. et al. 2004]. A careful examination of the literature data, however, reveals a less discussed observation that shows that the directional development of step rounding appears to be dependent on solution supersaturation (with respect to calcite): whereas significant rounding occurs in the acute side at low supersaturation conditions, step deformation develops in both $\langle \bar{4}41 \rangle_+$ and $\langle \bar{4}41 \rangle_-$ when supersaturations rise to result in growth hillocks elongated along the c-glide [Davis, K. J., Dove, P. M. et al. 2000; Davis, K. J., Dove, P. M. et al. 2004; Wasylenki, L. E., Dove, P. M. et al. 2005; Stephenson, A. E., DeYoreo, J. J. et al. 2008].

Step rounding was the prevalent morphological change known for the Mg effect until recently, when a different growth feature – surface segmentation – was reported [Astilleros, J. M., Fernandez-Diaz, L. et al. 2010; Sethmann, I., Wang, J. W. et al. 2010; King, H. E., Satoh, H. et al. 2013]. This type of morphology is characterized by the development of a mosaic-like feature where individual tiles take on a rhombic appearance following the original cleavage directions of calcite. The interpretation to this

morphological development invoked lattice strain derived from the mismatch between MgCO_3 and CaCO_3 structures [Astilleros, J. M., Fernandez-Diaz, L. et al. 2010; Sethmann, I., Wang, J. W. et al. 2010; Pimentel, C., Pina, C. M. et al. 2013]. For example, [Sethmann, I., Wang, J. W. et al. 2010] combined AFM observations with molecular dynamic simulations and suggested that strain energy may be released by the formation of disordered linear zones cutting through monolayers on calcite growing surfaces to cause a surface bulge. [Pimentel, C., Pina, C. M. et al. 2013] suggested the generation of screw dislocations at the initial buildup of lattice strain as evidenced by growth spirals on individual tiles, and ultimately the formation of "sub-nano step" along the original step direction when crystal fails to sustain the internal stress.

Suffice it to say that these findings depict a complex morphological effect of Mg on calcite growth and suggest that a clear understanding of the conditions under which specific morphology manifests and of how the different morphologies are related is still missing. In the present work we attempt to address these issues by conducting calcite growth experiments under conditions of varying supersaturation and Mg to Ca ratio in the solutions while maintaining pH, ionic strength, and $a_{\text{Ca}^{2+}}/a_{\text{CO}_3^{2-}}$ constant. We postulate that the Mg effect depends not only on the level of Mg content in the solution but upon the step kinetics as well. In addition, we suspect that regional lattice strain buildup due to local accumulation of point defects formed by Mg substitution for Ca causes plastic deformation that ultimately leads to the inhibition of calcite growth.

2. EXPERIMENTAL DETAILS

Growth solutions were made by dissolving reagent grade NaHCO_3 , CaCl_2 , NaCl and MgCl_2 (Sigma Aldrich) into deionized water (resistivity 18.2 m Ω). Solution pH (8.0), ionic strength IS (0.1) and $a_{\text{Ca}^{2+}}/a_{\text{CO}_3^{2-}}$ (1.0) were fixed while the supersaturations of calcite and dolomite as well as $a_{\text{Mg}^{2+}}/a_{\text{Ca}^{2+}}$ ($R_{\text{Mg}/\text{Ca}}$) vary. Solution speciation calculations were performed by PHREEQC [Parkhurst, D. L. and Appelo, C. A. J. 1999] with the Davies equation [Davies, C. W. 1962] applied for activity correction. Supersaturation indexes for both calcite and dolomite are defined as follows:

$$\gamma_{\text{cal}} = \log \frac{a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}}{K_{\text{sp}}(\text{calcite})} \quad (1) \text{ and}$$

$$\gamma_{\text{dol}} = \log \frac{a_{\text{Ca}^{2+}} a_{\text{Mg}^{2+}} a_{\text{CO}_3^{2-}}^2}{K_{\text{sp}}(\text{dolomite})} \quad (2)$$

where a_i is the activity of species i and K_{sp} is the solubility product (calcite $10^{-8.48}$ and dolomite $10^{-16.70}$ at 25 °C). Freshly cleaved calcite chips of optical-quality Iceland spar (Ward's Scientific, Chihuahua, Mexico) were used for *in situ* AFM fluid cell experiments where γ_{cal} varied from 0.5 to 1.2, γ_{dol} from 1.83 to 3.22, and $R_{\text{Mg}/\text{Ca}}$ from 1 to 7 (Fig. 1). AFM Images of calcite growing surfaces were collected by a Nanoscope IIIc Scanning Probe Microscope (Digital Instruments, contact mode) while experimental solutions were continuously introduced in the cell by a syringe pump at a flow rate of 40 mL/h. Step growth rates were measured in both obtuse and acute directions, respectively if possible, on consecutive (alternating upward and downward scan directions) images from the changes in the angles bisecting two adjacent steps [De Yoreo, J. J., Land, T. A. et al. 1997].

3. RESULTS

Consistent with previous reports [Davis, K. J., Dove, P. M. et al. 2004; Wasylenki, L. E., Dove, P. M. et al. 2005; Zhang, F. F., Yan, C. et al. 2013], the presence of Mg^{2+} ions in growth solutions significantly retarded calcite monolayers propagation. For example, at $\gamma_{cal} = 0.5$, the introduction of 1.2 mM Mg solution induced an 85% decrease in calcite step speed within 20 seconds. In contrast to the sharply visible hindrance to step kinetics, changes in the morphology of the inherent rhombohedral growth hillocks appeared to be transitory and complex. Broadly speaking, three types of modified morphologies, depending upon the solution chemistry, manifested during our experiments. The first type (Fig. 2a) is characterized by step alteration confined chiefly to the acute side. Compared to the intact (or weakly affected) obtuse steps, changes in the acute orientation are featured by varied degrees of loss of step directions (i.e. rounding) and structures (i.e. uniform step spacing and homogenization of steps and terraces). Type I morphology develops primarily at low γ_{cal} or low $R_{Mg/Ca}$ conditions.

A tear-drop morphology (type II, Fig. 2b), where both the obtuse and the acute sides become roughened and rounded, emerges in association with a modest increase in $R_{Mg/Ca}$ and γ_{cal} . In the cases where rounding is severe, the surface feature appears to completely lose the inherent rhombohedral frame as no clearly defined crystallographic directions are identifiable on the growth hillocks. Instead, the spirals become elongated parallel to the c-glide and evolve into a pseudo-oval shape with wider step spacing in the $\langle \bar{4}41 \rangle_+$ directions, the only remaining feature of the original spirals.

A third type of morphology (Fig. 2c) featuring surface segmentation develops from type II and becomes dominated by continuous elevation of γ_{cal} and $R_{Mg/Ca}$; however, the minimal levels of $R_{Mg/Ca}$ and γ_{cal} required for the transition seem to be

inversely related to one another. The fragmented surfaces are characterized by ridges with several tens of nanometers in height, constituting the boundaries of the ‘mosaic-like’ surface segments. Instead of rounding, these edges run along the original cleavage directions of $\langle 48\bar{1} \rangle$ and $\langle \bar{4}41 \rangle$ with occasional occurrences of the $\langle 42\bar{1} \rangle$. The initial transition from type II to type III morphology appears to start at the acute sides instigated by a sudden rupturing of curved steps snapping into straight segments or when in-plan bulging develops across multiple terraces (Fig. 2d). Furthermore, despite no detectable movement in the ridges, monolayer nucleation and growth continue within each segment but stop at the boundaries (i.e. ridges) as if the steps hit a wall. A summary view of growth morphologies at each experimental solution chemistry conditions is given in Fig. 1.

4. DISCUSSION

Results from our experiments clearly show that the morphological effect of Mg on calcite growth is more complex than previously reported. More importantly, the results suggest that there is no single factor that dominates in controlling the morphology change; instead, multiple parameters, including $a_{Mg^{2+}}/a_{Ca^{2+}}$ and supersaturations, are collectively in play. Here we attempt to combine the various controls to offer a more comprehensive view for the role of Mg in calcite growth.

1. Type I and II morphology

Assuming the observed morphological variations result from the Mg effect, the development of type I morphology indicates selective adsorption/incorporation of Mg at the acute steps. Given the preference of Mg for the geometrically more closed and

smaller sites at the $\langle\bar{4}41\rangle$ steps [Paquette, J. and Reeder, R. J. 1995], the observed selectivity does not come as a surprise. In fact, the persistent development of Type I morphology in solutions with elevated $R_{Mg/Ca}$ (up to 7) at low $\gamma_{cal} = 0.5$ or at high calcite supersaturation ($\gamma_{cal} = 1.2$) but low $R_{Mg/Ca} = 0.5$ appears to indicate that the differences in kink sites in different crystallographic directions are the chief governing forces that direct the Mg effect regardless of step kinetics and the relative abundance of Mg in growth media.

The development of type II at conditions of higher γ_{cal} and $R_{Mg/Ca}$, however, calls into question this explanation. Type II morphology is characterized by Mg affecting both the acute and obtuse steps, and can be regarded simply as a strengthened Mg effect leading to the loss of directional preference for Mg adsorption/incorporation. If kink size and geometry are the sole controlling factors, increased surface coverage of Mg (i.e. higher $R_{Mg/Ca}$ in solutions) and growth rates (i.e. higher γ_{cal}) should not alter the shape of obtuse steps. Experimental observations, on the contrary, showed the development of type II morphology when both γ_{cal} and $R_{Mg/Ca}$ go beyond 0.5. For example, transformation of type I to type II was observed when the calcite supersaturation was increased from 0.5 to 0.7 at $a_{Mg^{2+}}/a_{Ca^{2+}} = 5$, or the Mg to Ca ratio went up from 3 to 5 at $\gamma_{cal} = 0.7$ (Fig. 1), revealing the roles of both surface coverage and step kinetics in the morphological variation. The multifaceted effects cannot be fully accounted for by the conventional impurity theories. For example, in the equilibrium adsorption model [Botsaris, G.D., Mason, E. A. et al. 1967], it is assumed that the surface coverage of impurity particles depends fully upon the step propagation rate. At low supersaturation conditions when step growth is slow and new layers cannot rapidly sweep through the

growth surfaces, impurity adsorption reaches maximal (i.e. equilibrium) value and, consequently, exerts the strongest effect. On the other hand, when the surface is quickly overlain by newly grown layers at high supersaturations, the impurity cannot adsorb effectively and the effect therefore should be weakened. Following this model, one should expect to see the strongest Mg effect at low supersaturation conditions, contradicting the experimental observations.

We propose that the Mg effect may be understood by considering the lifespan and flux size of Mg at kinks in comparison to step kinetics. Following the classical approach to step kinetics [Chernov, A. A. 1961], one can assume that the Mg attachment rate ϖ at a step is a function that combines ion attachment frequency f_a , the average lifetime τ of Mg ions at kinks, and the size of Mg flux J near growth sites. The magnitude of J (defined as $-D_{Mg}\nabla_{Mg}$ by Fick's Law where D is the diffusion coefficient and ∇ the concentration gradient) in the present study is directly proportional to the absolute population of Mg particles in the solution, but is also a function of γ_{cal} because it is constrained by the magnitude of $R_{Mg/Ca}$. Since calcium concentration in our experimental solutions (where $a_{Ca^{2+}}/a_{CO_3^{2-}}$ was made to be unity) can be represented by $(10^{\gamma_{cal}}K_{sp})^{1/2}$, one can show that the size of J for Mg is a function of $D_{Mg}R_{Mg/Ca}(10^{\gamma_{cal}}K_{sp})^{1/2}$. Collectively, we have the relation

$$\varpi = \phi[f_a\tau D_{Mg}R_{Mg/Ca}(10^{\gamma_{cal}}K_{sp})^{1/2}] \quad (3)$$

to predict the rate for Mg attachment at steps.

On the other hand, the classical crystal growth theory [Burton, W. K., Cabrera, N. et al. 1951; Chernov, A. A. 1961] predicts that the growth rate of monomolecular steps is positively correlated to supersaturation in the form of $v_s = \phi(a - a_e)$ where $(a - a_e)$ is

the deviation of the solute activity a from its equilibrium value a_e [Chernov, A. A. 1961]. In our experimental system a and a_e are equivalent to $(10^{\gamma_{cal}} K_{sp})^{1/2}$ and $(K_{sp})^{1/2}$, respectively. Inserting the two expressions into the classic step kinetic equation, one shows that step velocity in the present study may be estimated by

$$v_s = \phi[(K_{sp})^{1/2}(10^{1/2\gamma_{cal}} - 1)] \quad (4)$$

in the absence of the impurity effect.

In isotropic crystal systems where steps are identical in all directions, the effect of Mg on step morphology can be examined by simply comparing the relative size of ϖ and v_s : if $\varpi/v_s > 1$, significant Mg adsorption/incorporation develops leading to step rounding; when $\varpi/v_s < 1$, Mg adsorption/incorporation is trivial, and steps are not subject to the strong impurity effect and will maintain straight morphology. In an anisotropic system such as calcite, additional consideration on τ (the average lifespan of Mg at kinks) and the surface coverage of Mg at individual steps (A_i where i is the direction with a longer τ) is needed to understand the direction preference of Mg adsorption or incorporation. As long as $A_i < 100\%$, Mg will be preferentially incorporated into steps in direction i , otherwise the direction preference will diminish due to the saturation of Mg ions at the preferred steps.

In our experiments, the attachment frequency f_a and the Mg flux J should, to a first order approximation, not differ significantly in different orientations because these two parameters are chiefly dependent on temperature and solution concentration, respectively. Such reasoning leaves the lifetime τ of Mg^{2+} at kinks to be the primary responsible factor for the step preference. Given the closer matching between Mg and the acute sites detailed by Paquette and Reeder [Reeder, R. J. and Paquette, J. 1989; Paquette, J. and

Reeder, R. J. 1990], it is reasonable to assume $\tau_- > \tau_+$ for calcite. As such, at conditions of low step velocity (e.g. low γ_{cal}) where $\varpi/v_s > 1$, step rounding in the acute directions should occur; any increase in $R_{Mg/Ca}$ will further augment the magnitude of ϖ (Eq. 3), leading to an even stronger preferential adsorption/incorporation of Mg at the acute steps. This explains the experimental observations made in the range of $R_{Mg/Ca}$ rising from 0.5 to 7 at $\gamma_{cal} = 0.5$ (Fig. 1). On the other hand, when J is kept low and $\Lambda_i < 100\%$, increasing supersaturation does not change the conditions of $\varpi/v_s > 1$ because ϖ scales with $10^{1/2\gamma_{cal}}$ whereas v_s scales with $(10^{1/2\gamma_{cal}} - 1)$ (Eqs. 3 and 4), indicating a continuous occurrence of preferential Mg adsorption/incorporation at the acute steps and consistent with the observations made at conditions of $0.5 < \gamma < 1.2$ when $R_{Mg/Ca}$ was kept constant at = 0.5.

Now consider the cases where both the solution supersaturation and the cation ratio vary. Whereas increasing γ_{cal} leads to a faster increase in ϖ than in v_s (Eqs. 3 and 4) and hence a stronger incorporation of Mg in all growth fronts, higher $R_{Mg/Ca}$ intensifies Mg surface coverage and ultimately triggers the saturation of Mg at the acute steps, i.e. $\Lambda_{acute} \approx 100\%$. The development of this condition now forces Mg to adsorb at the less favored sites (in our case the obtuse steps). This explains the development of type II morphology in solutions of higher γ_{cal} and $R_{Mg/Ca}$. Still, due to the inequality of $\tau_- > \tau_+$, the incorporation of Mg remains more substantial in the acute orientations, as indicated by the more severe step rounding shown in experimental observations (Fig. 1b).

2. Type III morphology

2.1 plastic deformation and maximal Mg substitution

Consistent with an earlier report [Sethmann, I., Wang, J. W. et al. 2010], our data also indicated the existence of a minimal level of γ_{cal} and $R_{Mg/Ca}$ for the development of surface segmentation. The minimal supersaturation and cation ratio revealed by our experiments were $\gamma_{cal} \approx 0.7$, or $\Omega_{calcite} \approx 5$ (Ω is defined as $10^{\gamma_{cal}}$) and $R_{Mg/Ca} \approx 1$, lower than that of $\Omega_{cal} \approx 33$ and $R_{Mg/Ca} \approx 2$ suggested by the data from [Sethmann, I., Wang, J. W. et al. 2010]. This difference could be due to the solution chemistry effects reported previously by [Hong, M. and Teng, H. H. 2014] given that our solutions had fixed pH (8.0), ionic strength (0.1) and $R_{Mg/Ca}$ (1.0) while the *Sethmann's* study had varied values in these parameters. Because of the mutual dependence between the minimal $R_{Mg/Ca}$ and γ_{cal} required for type III morphology development (Fig. 3), the supersaturation of dolomite γ_{dol} (Eq. 2) becomes a more intuitive and composite indicator to signal the morphology change even though dolomite is not formed in the experiments. For instance, at the opposite ends of our experimental conditions, $\gamma_{cal} = 0.5$ and $R_{Mg/Ca} = 7$, and $\gamma_{cal} = 1.2$ and $R_{Mg/Ca} = 0.5$, only type I morphology was observed because these conditions were associated with lower γ_{cal} (1.98 and 2.22, respectively). On the other hand, a modest condition of $\gamma_{cal} = 0.9$ and $R_{Mg/Ca} = 3$ brought about the full development of type III morphology when γ_{dol} reached 2.41. A value of $\gamma_{dol} \approx 2.39$ appears to be a reasonably accurate demarcation for the onset of type III morphology.

The existence of such a minimum suggests that the development of segmented surfaces with mosaic-like morphology probably results from the lattice stress buildup in calcite due to Mg for Ca substitution surpassing a certain threshold value. In agreement with *Sethmann et al.*'s observation, *in situ* AFM images from our experiments showed the

occurrence of monolayers buckling to form intra-layer ridges along calcite cleavage directions (Fig. 2d). Moreover, our data also revealed an abrupt aggregation of steps in association with the rupture of curvature (Fig. 2d) at the onset of type III morphology. Whereas molecular dynamics modeling in *Sethmann et al.*'s study suggests a correlation between lattice relaxation and surface bulging, suffice to say that lattice deformation in the form of either layer buckling or step aggregation/curvature breakup results in the release of stress.

The Mg^{2+} ion ($0.86\text{\AA}$) is about 30% smaller than Ca^{2+} ($1.14\text{\AA}$) in ionic radius [Shannon, R. D. 1976]. As a consequence, the d_{104} value in the Mg-substituted calcite decreases constantly with increase $\text{MgCO}_3\%$ [Zhang, F. F., Xu, H. F. et al., 2010]. Due to the size difference, a spherical local compressive stress field will be generated within monomolecular layers upon Mg^{2+} substitution of Ca^{2+} in calcite lattice. It is reasonable to assume that the stress can build up initially but will be released through plastic strain (i.e. permanent deformation) once the stress surpasses the elastic limit of calcite with increasing Mg presence. The minimal concentration of Mg in the lattice required for plastic strain to occur may be determined theoretically by comparing the elastic limit and the bulk modulus of calcite. *Ab initio* calculation of Mg-substituted calcite [Elstnerova, P., Friak, M. et al. 2010] gives a volume change of $18.36\text{\AA}^3$ for the replacement of a Ca by a Mg in a calcite unit cell with dimensions of $383.56\text{\AA}^3$. Assuming a spherical volume with an initial radius of R , the Mg-substitution reduces the cell radius to be $0.984R$. It then follows that the strain energy U generated due to the volume decrease is the summation of work done by the compressive force over the entire spherical surface of the stress field associated with the decrease of the unit cell from R to $0.984R$:

$$U = \int_0^{4\pi R^2} \sigma ds \int_R^{0.984R} dr = -0.064\pi\sigma R^3 \quad (5)$$

where σ is the stress. On the other hand, [Elstnerova, P., Friak, M. et al. 2010] also indicated a calcite formation energy change of 0.05 eV/atom resultant from the Mg for Ca substitution, allowing one to obtain from (Eq. 5) a value of 1.37 GPa for σ , which further leads to the determination of the ratio of stress to relative volume change upon the substitution of a Ca by a Mg, i.e. $\sigma/(\frac{\Delta V}{V}) = 28.62 \text{ GPa}$. Using either the experimental [Pavese, A., Catti, M. et al. 1996] or theoretical [Elstnerova, P., Friak, M. et al. 2010] value of 70.13 and 70.3, respectively, for the bulk modulus of calcite, one finds that the minimal number of substitution of Mg for Ca in a calcite unit cell (6 formula units) before plastic deformation is around 2.4, or ~40%.

2.2 Mechanistic consideration

In the presence of impurities or doping agents, mismatches can occur at the growth front of individual epi-layers subject to two lattice periodicities, that of the existing monolayer and that of the substrate. These mismatches may be accommodated by misfit strain (MS) or misfit dislocations (MD) with the latter often entering at some critical threshold strain levels [Matthews J. W. and Blakeslee, A. E. 1974; van der Merwe, J. H., 1991; Vdovin, V. I., 1999]. In the present study, misfits develop both horizontally (within a growing layer between the existing CaCO_3 and the newly grown $(\text{Ca,Mg})\text{CO}_3$ domains), and vertically between the calcite substrate and the overlaying Mg-containing calcium carbonate. When Mg content is low, as in the case of type I and II morphology, the growth morphology is modified by the gradual buildup of MS as indicated by the progressively loss of step directions. With increasing Mg incorporation, MD breaks in leading to the appearance of type III morphology.

A critical issue for the development of type III morphology is the restoration of the original cleavage directions on the growing surfaces at the onset of MDs. A point defect is created in the lattice when a Ca is replaced by a Mg. If these defects immediately produce MDs at steps (i.e. edge dislocation), a surface pattern (MD networks) in the epitaxial hetero-layer will evolve into a mosaic structure (i.e. type III morphology), similar to that reported on the $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ system where SiGe was grown epitaxially on Si [Vdovin, V. I., 1999]. In our study, however, the defects initially only produced MS that transformed the straight steps in calcite to curved ones in the resultant magnesian calcite, and MDs did not come into play until a later stage when Mg content was high. A reasonable mechanism to explain the timing of MD occurrence may be defect diffusion. It is well known that point defects are mobile and move stochastically in lattices following Fick's diffusion law (e.g. [Antoniadis, D. A. and Moskowitz, I. 1982; Gremaud, G., Ho, L. P. et al. 1983; Hwang, I. S., Theiss, S. K. et al. 1994; Libal, A., Reichhardt, C. et al. 2007]). More importantly, it was documented that point defects tend to exhibit surprising memory effects and diffuse along certain easy directions [Pertsinidis, A. and Ling, X. S. 2001]. It is conceivable, from an energetics point of view, that the Mg sites, that is, the point defects in our case, will ultimately align themselves along the most stable directions (i.e. calcite $[\bar{4}41]$) to release the accumulated misfit stress, leading to the nucleation of linear MDs. If and when this occurs, the local Mg concentration may reach the theoretical maximum of ~40%, and the individual spherical stress field associated with each point defect will coalesce to give rise to a cylindrical field along the low energy direction (Fig. 4). This is because, whereas the σ_{yy} component (i.e. parallel to the alignment) of individual stress fields around each Mg site will largely cancel out, the σ_{xx}

components overlap to produce a stronger compressive force perpendicular to the alignment directions and ultimately cause monolayer buckling. Furthermore, if the linear field is near steps, the σ_{zz} components may lead to attractive stress between layers to cause steps to bunch or aggregate [Schindler, A. C., Gyure, M. F. et al. 2003]. In both cases, the resultant ridges or macro-steps, now following the original calcite cleavage directions, should have a lower surface energy than the curved steps.

2.3 Implications for the dolomite problem

Complete inhibition of monolayer growth was never observed in the full range of our experimental conditions (γ_{cal} from 0.5 to 1.2; $R_{Mg/Ca}$ from 0.5 to 7) prior to the formation of surface ridges in type III morphology. Even within the ‘mosaic-like’ tiles on the segmented surfaces, curved steps of individual layers still advance at detectable speeds (Fig. 2c). Rather, it is the emergence of the surface ridges that finally stops the growth process as the advance of all individual steps comes to an end upon reaching the segmentation boundaries. We surmise that the magnesium concentration in these ridges probably has reached the maximal value (~40%) calculated from the stress-strain consideration. If this is the case, the observation may imply that the inhibition of Mg to calcite growth and the difficulty of dolomite formation at ambient conditions are ultimately attributed to the lattice stress buildup originated from the continuous substitution of Mg for Ca. That is, lattice distortion at ~40% Mg presence is so severe that further growth cannot proceed. The threshold value of ~40% Mg calculated in this study is in fact in good agreement with the HRTEM measurements in modern protodolomite (MgCO₃% ~ 40 to 44%) [Xu, H. F., 2010] and synthetic disordered dolomite (MgCO₃% ~ 45%) [Zhang, F. F., Xu, H. F. et al., 2010], and with the composition of the

(Ca,Mg)CO₃ phase synthesized in anhydrous conditions (amorphous precipitate when Mg > ~37%) [Xu, J., Yan, C. et al. 2013]. It is important to note that, whereas ~40% Mg is needed to induce the ridge structure formation to completely stop growth at monolayer level, less than 20% may be enough to render bulk growth unnoticeable given the widely reported observation that, in the absence of additives or biological activities, Mg content in ambient laboratory grown (Mg,Ca)CO₃ phases never exceeded 20% [Mucci, A. and Morse, J. W. 1983; Mucci, A. 1986; Sethmann, I., Wang, J. W. et al. 2010; Zhang, F. F., Yan, C. et al. 2013].

5. CONCLUSION

We investigated the evolution of growth morphology on the cleavage surfaces of calcite with changing Mg to Ca ratios and supersaturation in the solutions, and found three types of morphological variations. When either $R_{Mg/Ca}$ or γ_{cal} is low, step rounding in the acute side was observed; increased Mg concentration and supersaturation first engendered morphological changes in both the acute and the obtuse directions, followed by the development of monolayer buckling and step aggregation in the original cleavage direction to form surface segmentation, indicating Mg effects propagating from one dimension (individual crystallographic directions) to two dimensions (i.e. the entire growth surface). These observations suggest that the morphological evolution is controlled by a combined effect of solution Mg flux and step kinetics, and may result from the lattice stress buildup derived from cation substitution. We propose that, at low $R_{Mg/Ca}$ or γ_{cal} conditions, the Mg effect is governed by the relative rate of Mg attachment at kinks relative to step speed. Increasing Mg concentration and

supersaturation ultimately leads to a significant presence of point defects in association with the extensive substitution of Mg for Ca. We further propose that the diffusion and the resultant alignment of these defects are responsible for the release of lattice stress in the form of plastic deformation (monolayer buckling and step aggregation) observed in high $R_{Mg/Ca}$ and γ_{cal} solutions. Calculations indicate that the Mg content needed to generate lattice stress exceeding the elastic limit of calcite is around $\sim 40\%$, beyond which growth comes to a complete stoppage at the monolayer level. This result suggests that the excessive lattice stress due to the size difference in Mg for Ca may be the ultimately cause for Mg inhibiting calcite growth and for the lack of dolomite formation in ambient conditions.

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CAPTIONS

Fig 1. Summary of calcite surface morphologies in solutions of different compositions depicted by calcite supersaturation (x-axis) and Mg to Ca ratio (y-axis). Images on the left side of the zigzag line are types I and II morphologies whereas on the right side is type III. Literature data from Davis et al. (2004) and Sethamann et al. (2010) are also included for reference.

Fig 2. AFM images of calcite growth spirals at different levels of supersaturation and $a_{Mg^{2+}}/a_{Ca^{2+}}$. All images are oriented with the obtuse side on the top and acute side on the bottom as marked in (a). In type I morphology (a), only the acute steps on the growth spiral are affected and rounded in the presence of Mg while the obtuse ones remain straight and maintain their original crystallographic directions. In type II morphology (b), both obtuse and acute steps are rounded although the change in acute side appears to be more severe as the steps have completely lost their growth directions. Type III morphology (c) exhibits a segmented surface where individual sections are bordered by multi-layer thick ridges oriented in the original cleavage directions. No detectable movement is observed at these ridges, but monolayers with rounded edges continue to grow inside the individual segments. The transition from type II to type III morphology (d) is characterized by a snapping of curved steps into straight segments followed by step aggregation upstream (arrow 1), or a sudden buckling of terraces that cuts through multiple steps (arrow 2). Both the snapping and the buckling lead to the formation of ridges parallel to the original calcite $\langle \bar{4}41 \rangle$ directions.

Fig 3. Inverse relation between calcite supersaturation (x-axis) and solution Mg^{2+} concentration required for the development of type III morphology. Dash line indicates the minimum conditions separating type III morphology from type II.

Fig 4. Schematics showing the occurrence of point defects in calcite due to Mg (small green spheres) substitution of Ca (large red spheres) and resultant individual compressive stress field (a). Upon diffusion, these point defects may align themselves in a low energy direction (parallel to y-axis) and subsequently produce a cylindrical compressive stress field (b). The compressive stress (parallel to x-axis) can be released through layer buckling that forms a ridge parallel to the y-axis.

Fig. 1

Fig. 2

Fig. 3

Fig. 4