Biologically Inspired Controls over Assembly of Crystalline Nanostructures

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ABSTRACT

In an effort to understand the physical principles governing the controls on the growth of nanocrystals exerted by living organisms during tissue mineralization, we have performed *in situ* AFM studies of crystal growth from solution on a number of systems in which inorganic and organic modifiers have been added to alter morphology and kinetics. The results reveal a variety of mechanisms by which modifier-surface interactions affect growth to generate new facets or pseudo-facets, but suggest that, in general, controls over morphology and kinetics are maintained by step-specific interactions on pre-exisitng crystal faces.

Keywords: biomineralization, crystallization, atomic force microscopy, crystal growth modulation

1 INTRODUCTION

By utilizing small molecules and proteins to modulate crystal nucleation and growth, living organisms produce single nanocrystals and nanocrystal composites that provide materials solutions to their functional requirements.[1,2] In doing so, they exhibit control over the location, phase, and crystallographic orientation of the nuclei, as well as the morphology, growth rate, and size of the growing crystals. The resulting structures typically exhibit facets or pseudofacets not expressed in crystals grown from pure solutions. The mechanism by which these modulators affect growth have generally been explored either through bulk crystallization experiments[1,2], or with molecular models focused on the interactions between the impurities and atomic planes on the newly expressed faces.[3] These studies have generally attributed the expression of new faces to the stabilizing effect of the growth modulators on the new faces. However, few studies have either tried to quantify the changes in growth dynamics at the molecular scale or looked at interactions between impurities and atomic steps, particularly on the crystal faces expressed in the absence of the impurities, despite their obvious importance in determining many aspects of growth dynamics and morphology. Here we report the results from *in situ* AFM investigations of growth modification in a number of crystal-impurity systems, which allow us to quantify the effect of growth additives on step morphology and kinetics. The results argue for the importance of modifier interactions specific to atomic steps on existing crystal faces in determining the overall evolution of crystal morphology. The systems we have examined include carbonates[4,5,6], phosphates[7], oxalates[8], and pthalates[9] grown in the presence of inorganic ions[5,7], amino acids[4,6], small organic moloecules[8,9], and proteins[8]. Using examples from a number of these systems, here we show how the growth kinetics and resulting crystal habit are defined by modifications to existing atomic steps and that these modifications vary dramatically depending on the step direction, even on a single crystal face.

2 EXPERIMENTAL

The systems investigated were: calcium carbonate (calcite) plus Mg^{2+}, glycine, aspartic acid, glutamic acid, and serine; potassium dyhydrogen phosphate (KDP) plus Fe^{3+} and Al^{3+}; calcium oxalate monohydrate (COM) plus citrate and uropontin; and potassium acid pthalate (KAP) plus euriglaucine. Growth solutions were prepared by dissolving high purity starting materials in deionized water with a resistivity of $>18M\Omega$. The impurity contents of the starting materials were determined from inductively coupled mass spectrometry. Metal impurities levels were $<$ 1ppm.

The ionic strength, pH, supersaturation, and temperature were all controlled parameters. For example, the pH of the calcium carbonate solutions was adjusted by small additions of NaOH and the ionic strength was fixed by using NaCl as a background electrolyte. The supersaturation, σ, was calculated from:

$$\sigma \equiv \frac{\Delta\mu}{k_B T} = \ell n\left(\frac{a}{a_e}\right) \qquad (1)$$

where $\Delta\mu$ is the change in chemical potential per molecule upon crystallization, k_B is Boltzmann's constant, T is the absolute temperature, and a and a_e are the actual and equilibrium activites of solute respectively. (In the case of KDP and KAP, the actual and equilibrium concentrations in units of molarity, C and C_e were used in place of the activities.) For the carbonate and oxalate solutions, σ was varied by keeping all parameters constant except the solute concentration. For the phosphate and pthalate solutions, σ was controlled by varying the temperature.

In situ AFM experiments were performed using a Digital Nanoscope III force microscope in contact mode with standard SiN cantilevers having a nominal force constant of 0.1 Nm^{-1}. Seed crystals ranging in size from 0.02 to 100 cm^2 were mounted on glass cover-slips and

placed within a commercial AFM fluid cell. Growth solution was continuously flowed through the cell. The evolution of surface morphology, step shape, step speed, and growth source structure was recorded by collecting a continuous series of images during growth of the crystal. Flow rates were chosen to be sufficiently high to ensure that the step speed was independent of flow rate (i.e, growth rate was limited by surface kinetics) and ranged from 0.5 to 6 ml·min⁻¹ depending on the system.

The temperature of the fluid cell was controlled to within ±0.05°C using a Peltier heater/cooler and a commercial temperature controller. A coated type-T thermocouple was inserted through the tubing just inside the outlet port of the fluid cell in order to determine the exact temperature of the solution in the cell. Details of the experimental method can be found in previous publications [4,5,6,7,10].

3 RESULTS AND DISCUSSION

Fig. 1 a and 1b shows the effect of citrate on the growth of the COM {-101} face. In both examples, the effect of the additive on step morphology is dramatically different for different step directions. The <-10-1> step train (moving to the left) loses its stability (Fig. 1b) and exhibits a step speed reduction that is more than an order of magnitude greater than that exhibited by the <120> steps (moving to the right). Both step directions exhibit the characteristic step-edge morphology caused by impurity pinning. Most importantly, the resulting growth hillock shape closely resembles that of the macroscopic crystal (Fig. 1b inset). In contrast, citrate has no effect on any of the step directions expressed on the {010} (side) faces of the crystal (not shown here). Hence, the change in crystal morphology, particularly the appearance of the new, rounded pseudo-facets appears to be controlled by the interaction between the citrate molecule and the steps on the existing {-101} face. Furthermore, the strength of the interaction is highly step-specific.

Fig. 1 c-e shows the effect of the L- and D- forms of aspartic acid on the growth of the calcite {104} face. Three important effects are observed. First, the chirality of the amino acid impacts the morphological modifucation of the steps with the resulting hillock shape exhibiting an asymmetry across the calcite glide plane that reflects the chirality of the individual amimo acid enantiomer. Second, the upper steps (referred to as obtuse in the calcite literature) show little or no modification. Third, the steps do not show the dramatic effect of step pinning by impurities as seen with citrate on COM or Fe^{3+} and Al^{3+} on KDP (not shown here). Once again, as the insets to Fig. 1d and 1e show, the overall modification to the crystal morphology, including the appearance of rounded pseudo-facets along the sides of the crystal, closely resembles that exhibited by the elementary steps on the existing {104} faces, and the interaction of the growth modifier with the crystal surface is highly step specific.
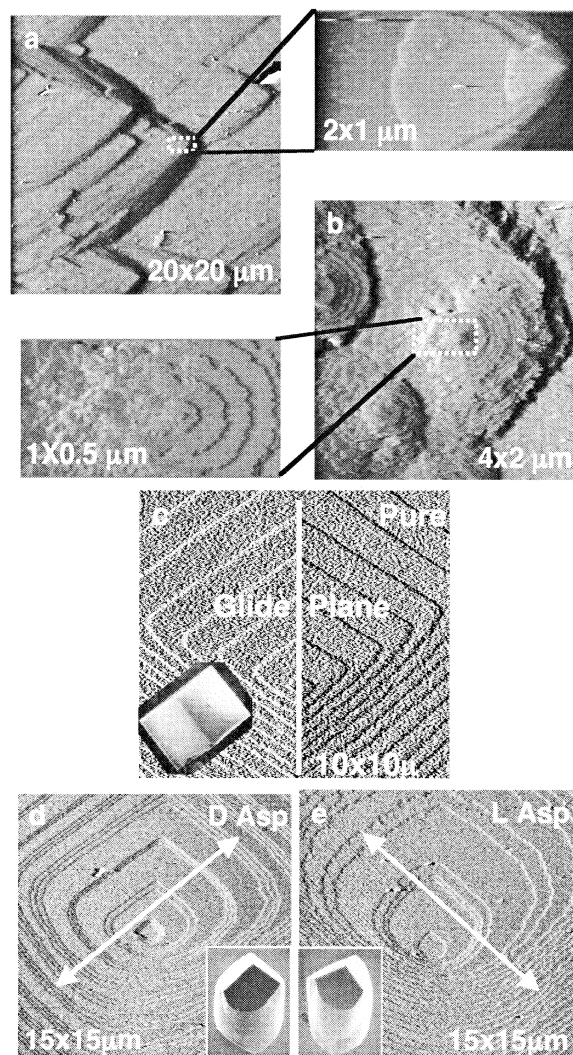

Fig. 1: (a-b) Hillock and step morphology of calcium oxalate monohydrate during growth in (a) pure and (b) citrate-bearing solutions. Effect on step morphology and kinetics is dramatically different for the two step types. (c-e) Step morphology and crystal habit of calcite grown in (c) pure, (d) D-aspartic acid-bearing and (e) L-aspartic acid-bearing solutions. Addition of the chiral amino acids breaks the glide plane symmetry. Insets show SEM images of macroscopic crystals

Similar step-specific interactions as well as relationships between altered crystal morphologies and modifications to the elementary step structures are seen in the calcite-$^{Mg2+6}$ and KAP-euorglaucine[9] systems. In the case of the latter, although the modifier is only incorporated into one step type, apparently it has little impact on the lattice and leads to little or no change in step shape. Correspondingly, the resulting crystals show no change in morphology.

4 CONCLUSIONS

Analyses of other growth characteristics in these systems, such as the dependence of step speed and critical size on supersaturation show that numerous and fundamentally differenty mechanisms are responsible for the observed modifications of growth morphology and dynamics including: 1) Step-blocking due to impurity pinning, 2) Changes in equilibrium activity, a_e, and strain-induced step retardation due to impurity incorporation, 3) Alterations of the orientational dependence of step-edge energy, and 4) Blocking of kink-sites. However, in all cases, the basis for growth modification is a modulator-crystal interaction that is dominated by step-specific binding at the step edges on existing crystal faces. Thus the appearance of <u>new</u> facets or pseudo facets does not appear to be the result of thermodynamic stabilization of the new facets, but rather a direct manifestation of kinetic limitations to step motion imposed on the steps of the <u>pre-exisiting</u> facets.

5 ACKNOWLEDGMENTS

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