

# Induced Growth of Calcium Carbonate Using an Atomic Force Microscope

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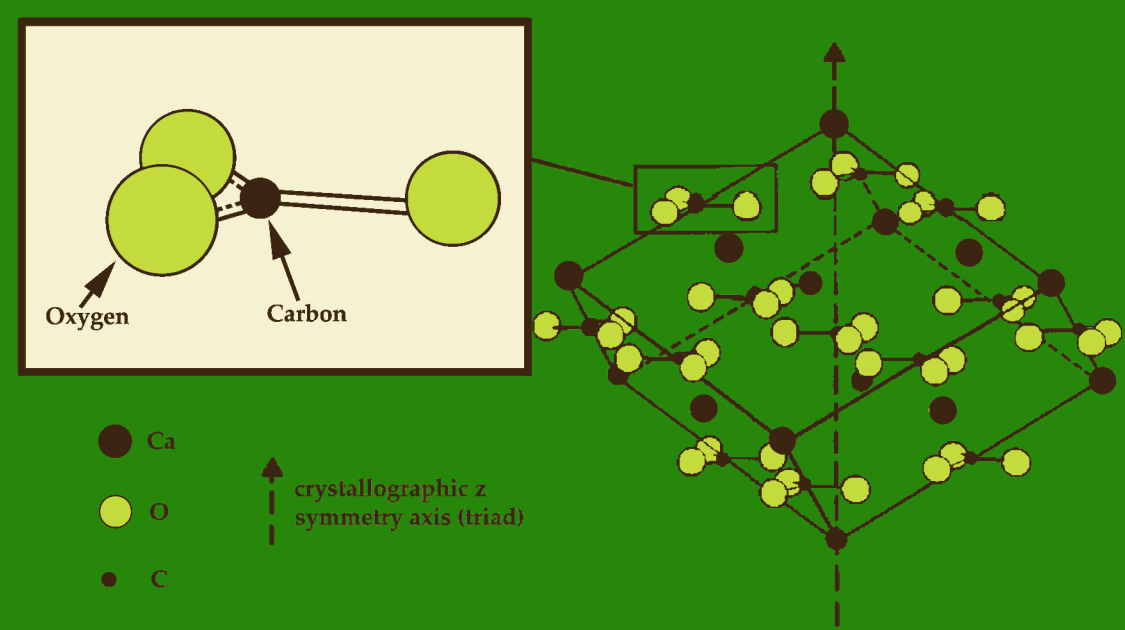
## Introduction

Bond breaking at surfaces due to stimuli such as exposure of materials to radiation, mechanical stress, or chemical agents are well established. We examine the consequences of combining localized mechanical stress on the surface of calcium carbonate, in the form of an AFM tip, and exposure to aqueous solutions. We show for the first time that we can induce highly localized crystal growth on the [10 $\bar{1}$ 4] surface of CaCO $_3$  through combined exposure to supersaturated solutions and mechanical stress applied by an AFM tip. The experiment simulates many features of mineral deposition within mammalian joints. Better understanding of the process of calcification can lead to improved biological implants and alleviation of pathologies such as arthritis and tendonitis. Experimental evidence is presented which supports a mechanism of tip-enhanced transport of ions to nucleation sites.

## Calcium Carbonate (Calcite)

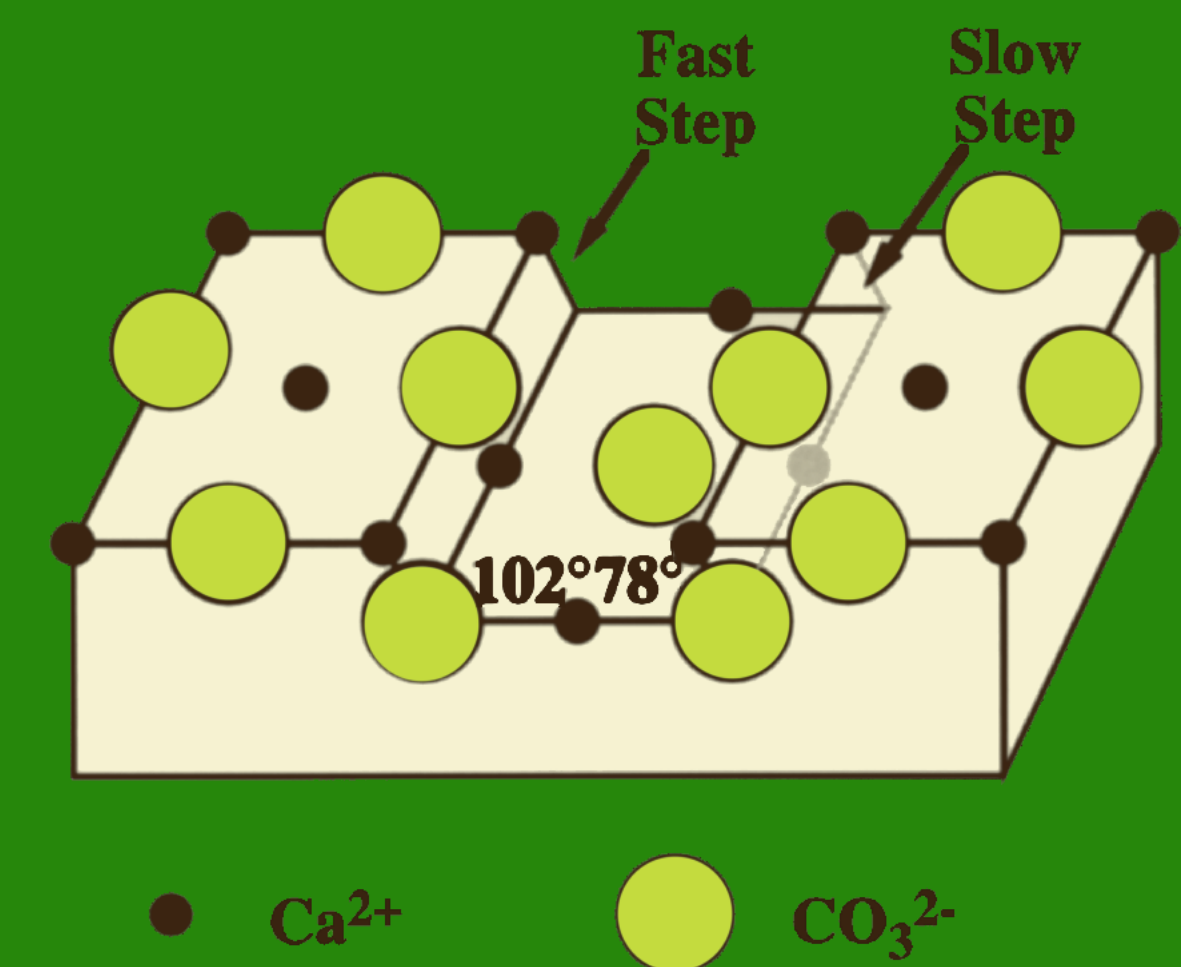
- Calcium carbonate minerals are abundant in nature.
- Calcium carbonate in aqueous solutions is involved with mineral formation and the exchange of carbon dioxide between the atmosphere, lithosphere and the ocean.
- Calcite is an important biomineral involved in bone and shell development.

### Calcite Structure



## Etch Pit Dissolution

In undersaturated aqueous solutions rhombohedral etch pits are formed with two pairs of distinct crystallographic identical steps. The fast step allows for easier material deposition than the slow step due to its more open orientation.

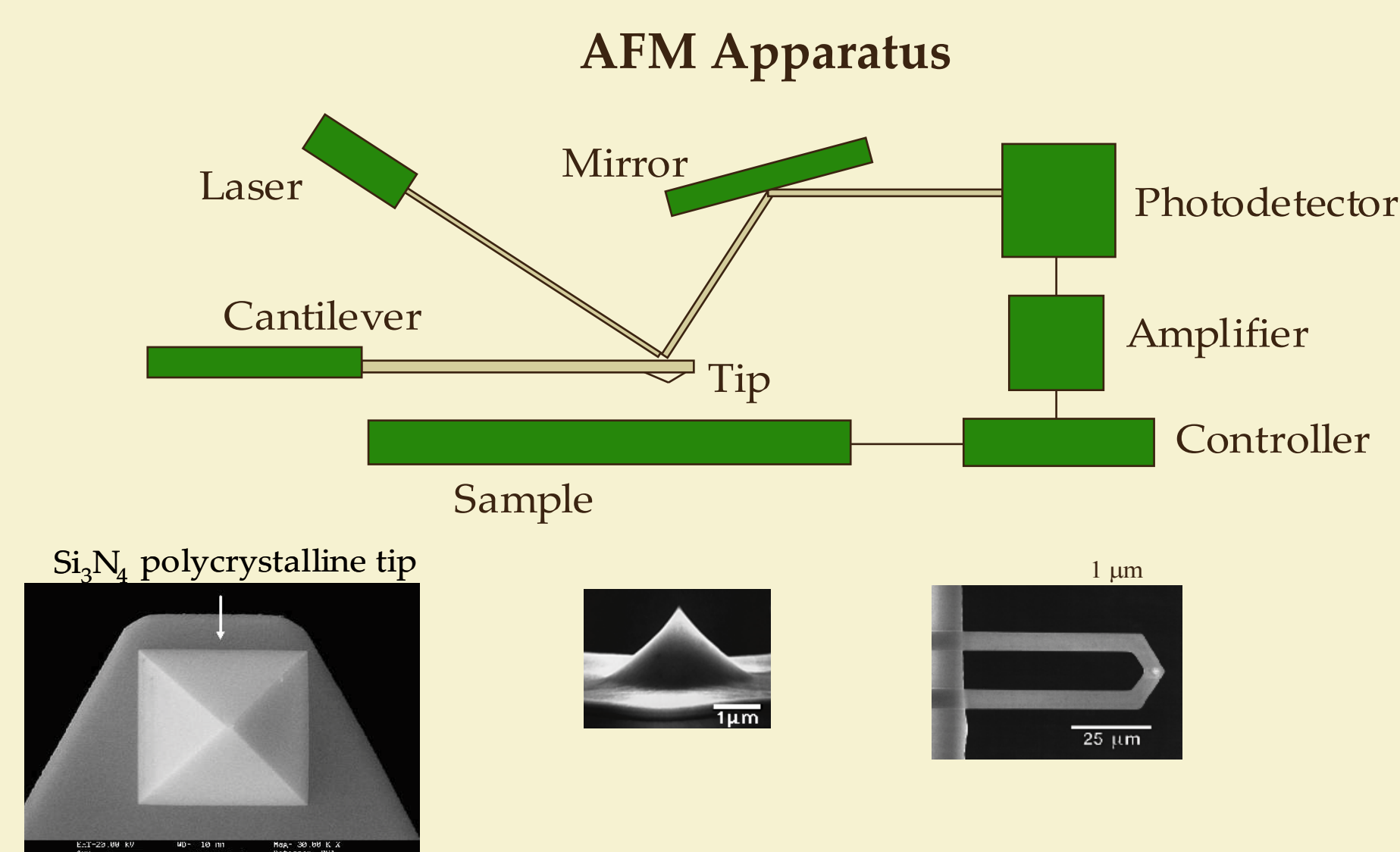


The fast steps are denoted as [441] $^+$  and [481] $^-$

The slow steps are denoted as [441] $^-$  and [481] $^+$

## AFM Setup

The AFM provides a topological map of an atomic surface by rubbing the tip over the surface. Freshly cleaved calcite was placed under the tip and scanned at low normal forces ( $F < 50$ nN) in various calcium carbonate solutions.



## Experimental

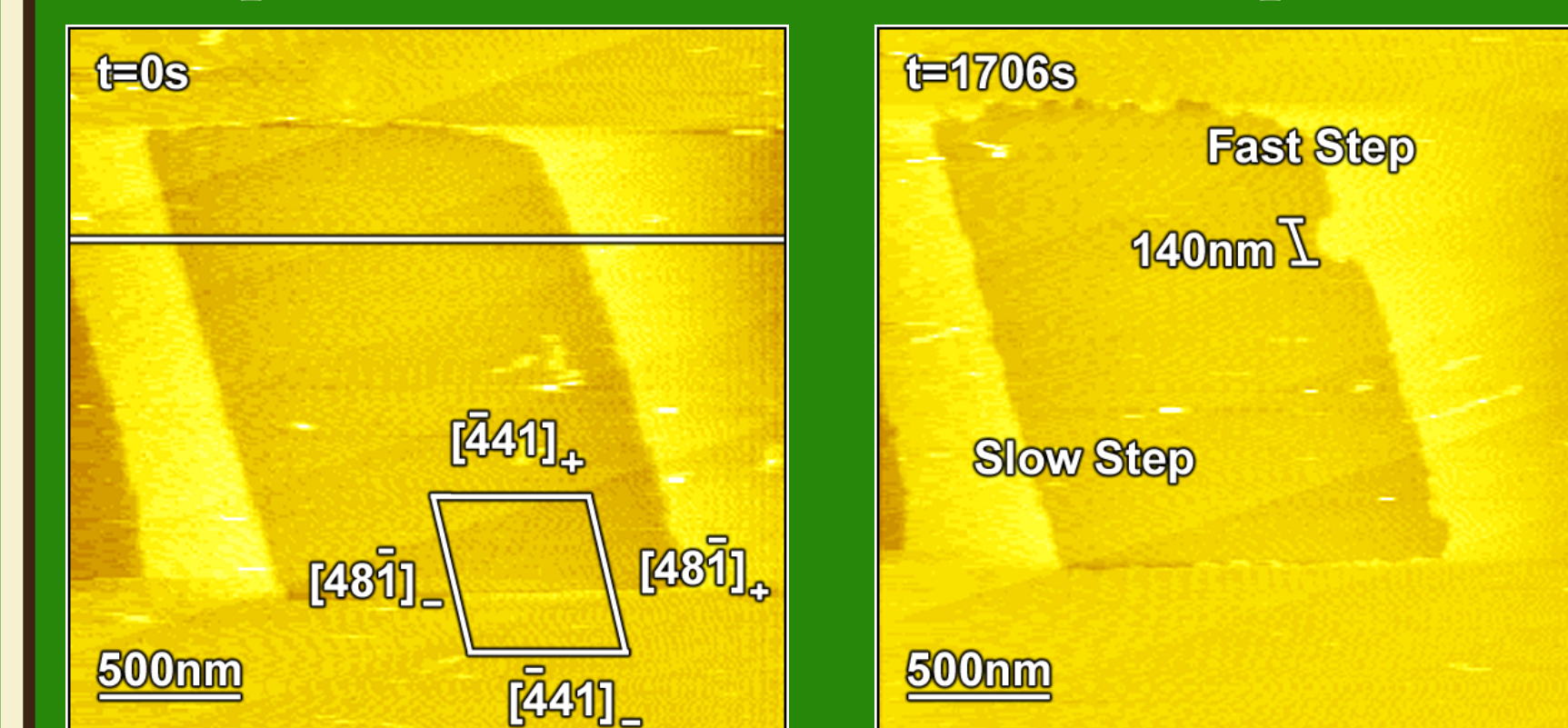
Optical-quality geological calcite was cleaved into fragments. In situ atomic force microscope (AFM) imaging was performed in contact mode using a Molecular Imaging PicoScan AFM. Nanoprobe AFM tips made of Si $_3$ N $_4$  were utilized. Experiments were done in calcium carbonate solutions of various supersaturations. All solutions had a fixed pH of 8.0-8.5. The supersaturation,  $\sigma$ , was calculated by:

$$\sigma = \ln \left( \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{sp}} \right)$$

where  $a$  is the activity of the ionic species and  $K_{sp} = 10^{-8.54}$  is the equilibrium solubility of calcite at zero ionic strength.

## Results and Discussion

### Localized Scanning on Steps of an Etch Pit Shows Growth is Induced by the Tip of the Atomic Force Microscope



Induced, localized growth of approximately 140 nm width produced after six continuous scans with the slow scan axis disabled. The figure on the left indicates the position of the line scans by the white line. The normal force of the

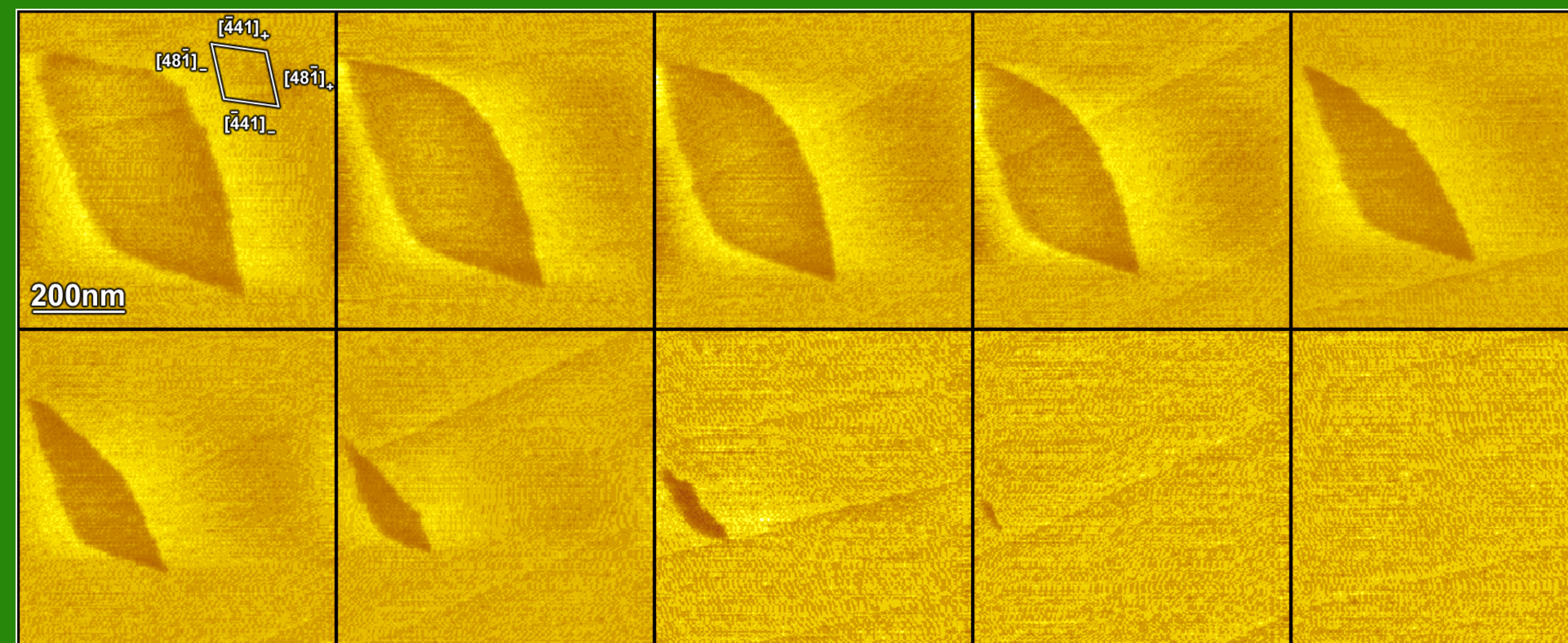
scan is 7.2 nN and the tip speed is 7  $\mu$ m/s in a solution concentration of  $\sigma = 1.3$ . Growth appears to be normal to the fast step as shown in figure on the left

### Localized Induced Growth on Pit Edges

- The white line on the image to the left indicates the position where the AFM tip was drawn back and forth along surface.
- Treatment was symmetric, but material was mainly deposited on the fast step.
- This is consistent with the relative ease of deposition along fast steps in general.
- Similar results were found for scanning on monolayer atomic steps with unknown crystal orientation.

### Induced Growth from an AFM tip Fills in an Etch Pit

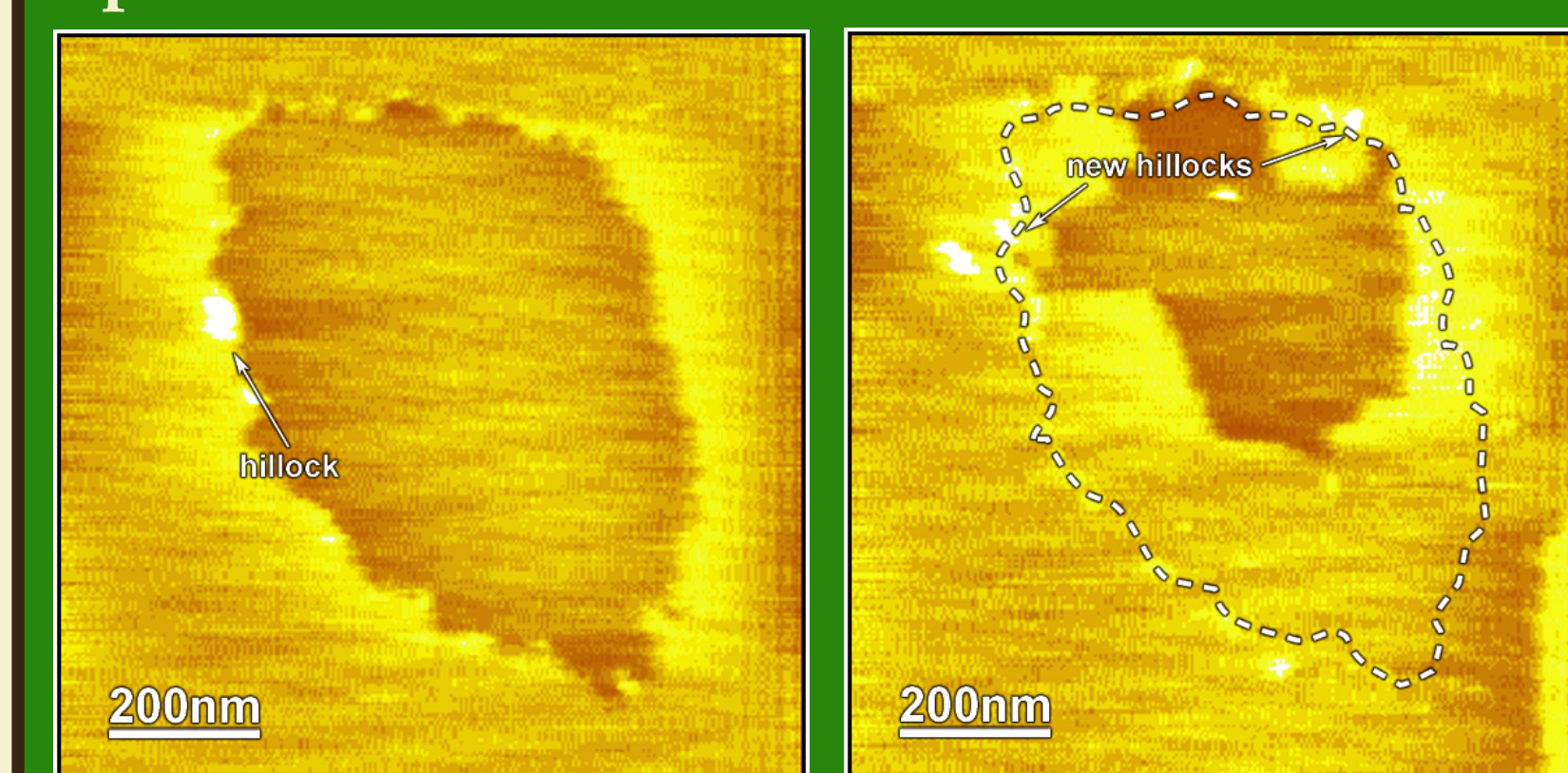
Ten selected images of a consecutive sequence of AFM images of a pit that is one atomic layer deep. All images were scanned in a solution of  $\sigma = 3.9$ . 12 scans (1068 s) were necessary to completely fill in the pit. Normal scanning force for all images is 11 nN and the scan rate is 2.9  $\mu$ m/s. Crystal orientation is shown on the right.



### Spontaneous Growth

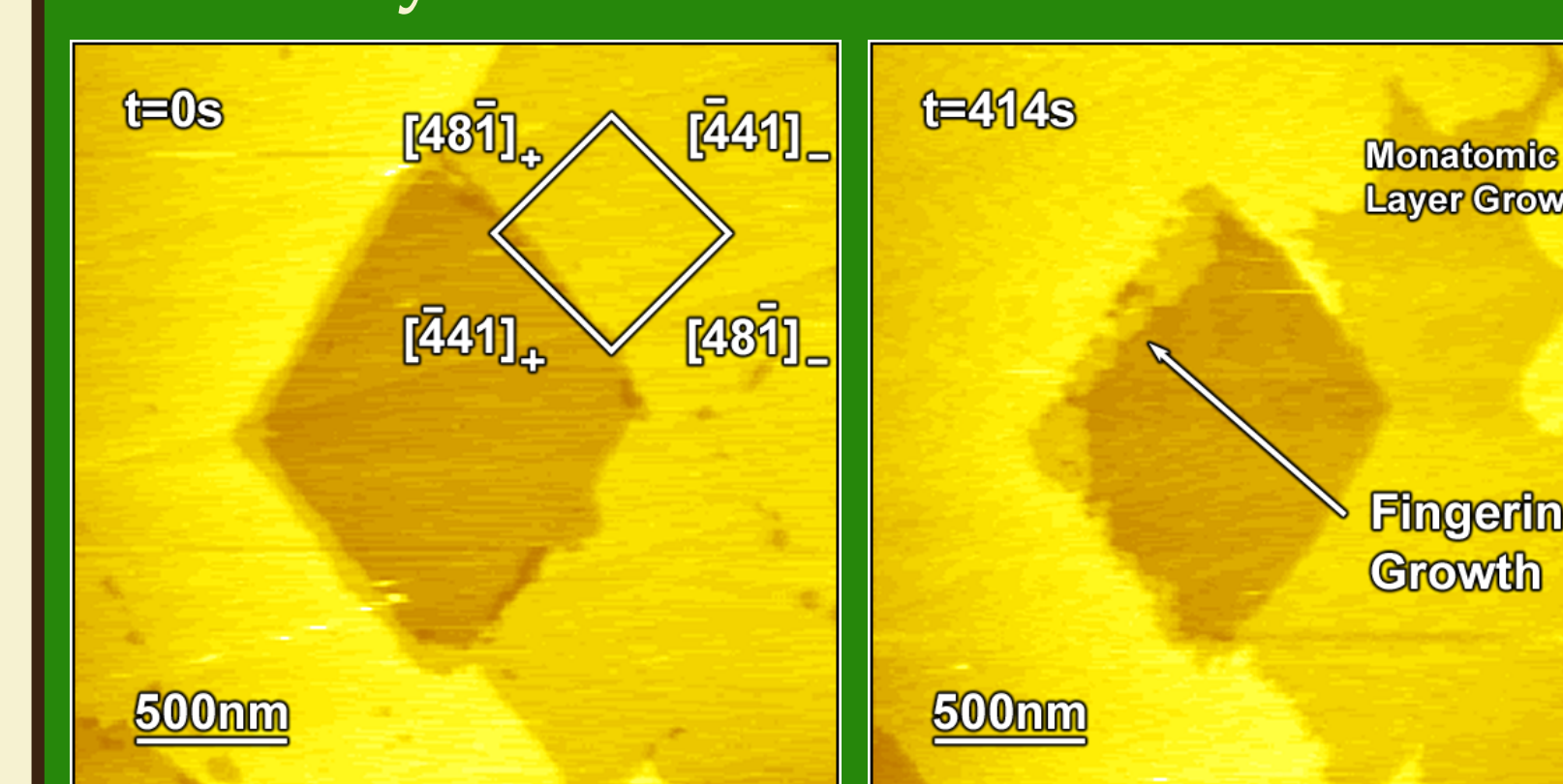
- In highly concentrated solution spontaneous growth occurs.
- Hillock formation suggests defects on the surface.
- Nucleation on the surface is not observed when growth is tip induced.

### Nucleation Around Pits on the Surface of Spontaneous Growth



When placed in very supersaturated solution, spontaneous growth occurs and new hillocks form around the boundaries of the old pit. This suggests that rapid growth causes defects which are not observed when the growth is induced. These images were taken at a  $\sigma = 6.9$ .

### Induced Growth Demonstrates "Fingering Instability"



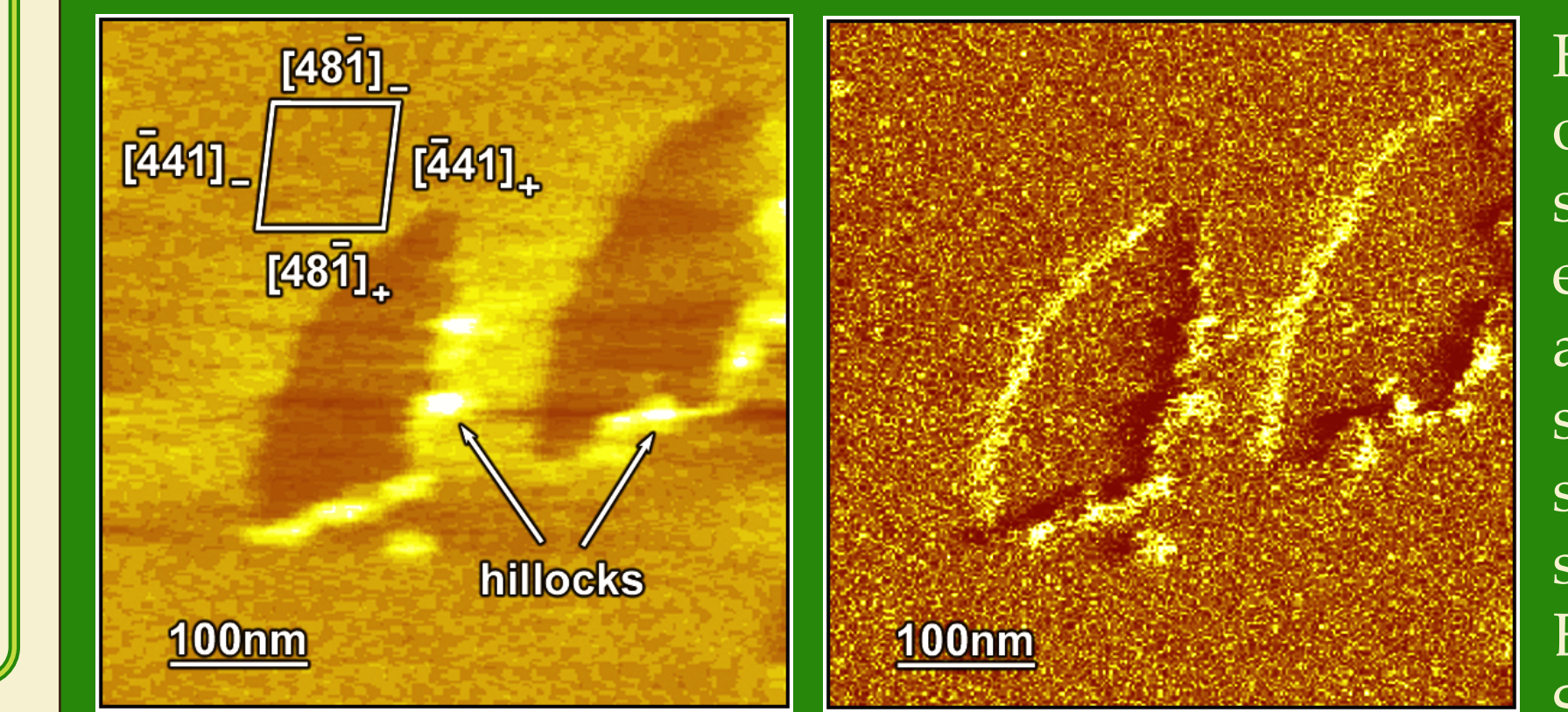
Fingered growth (as indicated by the white arrow) appears to be growing normal to the edge of the fast steps in the etch pit. The images were obtained at a normal force of 17 nN and a scan speed of 2.2  $\mu$ m/s. The scan on the left was taken in a solution concentration of  $\sigma = 0.7$  and the image on the right was placed in a more saturated solution of  $\sigma = 1.42$ , the new growth is shown by the arrow.

### Stability of Induced Growth

- Despite the apparent instability of the induced growth, a completely filled in pit does not demonstrate any topological defects in the surface.

Hillock Nucleation occurs less frequently on induced growth regions than on areas that spontaneously grew.

## Mechanism of Tip Induced Growth

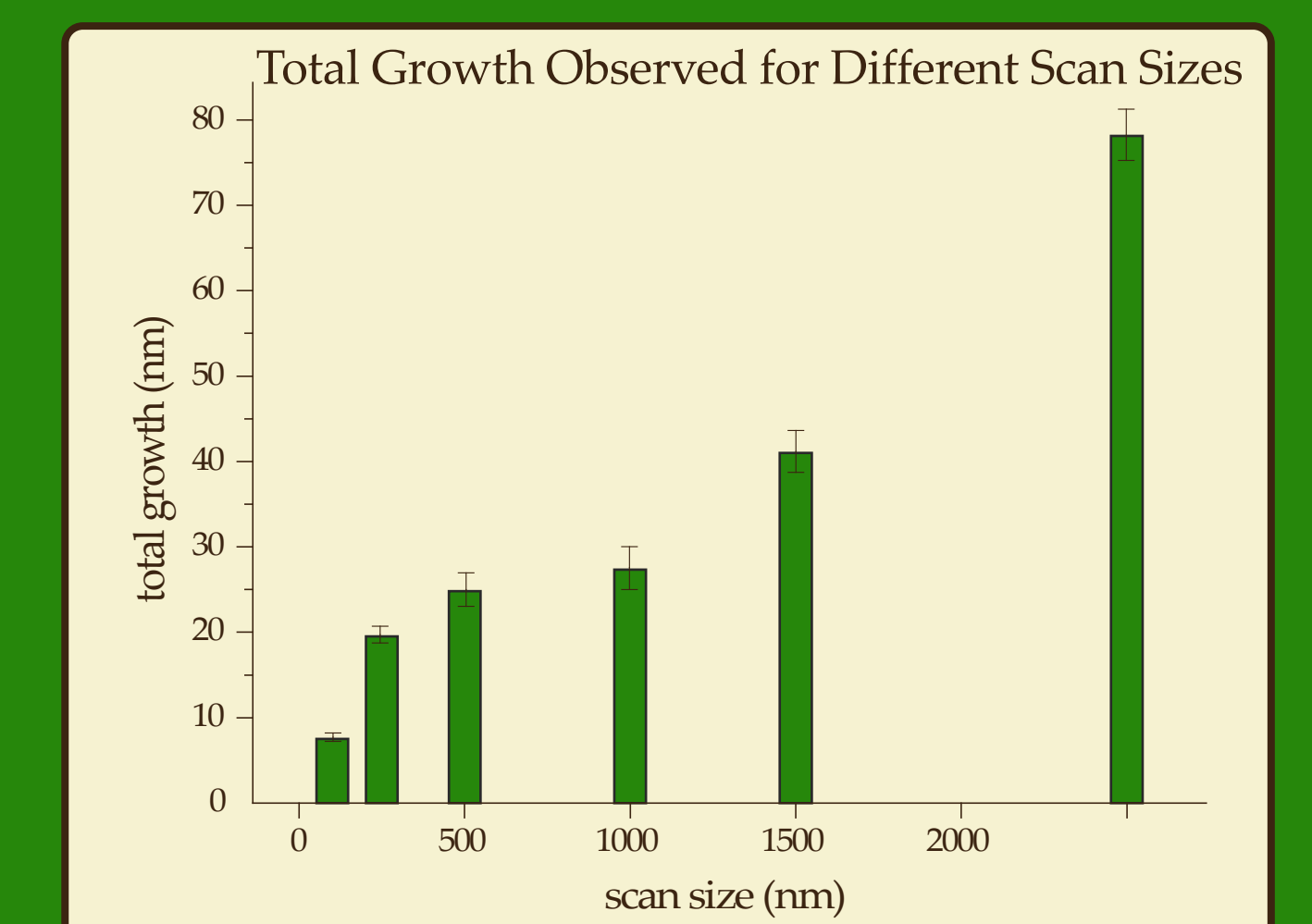


Hillocks form on the fast steps on the edge of pits and step in saturated solution suggesting an Ehrlich-Schwoebel

barrier that prevents material diffusing along a terrace from crossing a step down into a pit. These images were taken at a normal force of 16 nN, a scan rate of 6.2  $\mu$ m/s and a solution concentration of  $\sigma =$

The Barrier does not prevent deposition along the step since spontaneous growth can still be produced. The scanning induced growth rate does not depend on the location of scanning (more scanned area at top versus more scanned area at the bottom) so it shows that both the upper and lower terraces are good sources of adsorbed ions. In calcite, the diffusion of ions along both terraces is hindered, and both terraces maintain high density of adsorbed material for sweeping in order to contribute equally to growth

However, as shown below, the amount of total growth induced by the tip is related to the size of the scan, suggesting that the tip acts as a broom. Therefore, if number of ions the tip has access to increases, the growth observed increases.



## Conclusion

- Continuous, low force scanning induces deposition along calcium carbonate step edges.
- Growth rates depend strongly on step orientation and solution supersaturation.
- Scanning-induced deposition significantly increases the deposition rates in etch pits under supersaturated conditions.
- The tip is utilized as a tool to move sorbed ions over step edges and along terraces.
- The tip sweep ions over an Ehrlich-Schwoebel barrier and the tip acts as a broom causing more ions to adhere to the step edge.
- The location of the tip relative to the step edge does not effect growth rates of the induced growth in a consistent manner.
- Spontaneous growth exhibits defects that induced growth does not. Nucleation is inhibited by the tip, and topological defects are not observed with induced growth.

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