

## **Morphological consequences of differential Mg<sup>2+</sup> incorporation at structurally distinct steps on calcite**

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### **ABSTRACT**

Magnesium is considered the principal modifier of calcite morphology in many natural environments. However, the physical mechanism by which magnesium alters the external form of calcite has remained controversial due to a lack of direct experimental insight. Here we use in situ AFM observations of step dynamics and growth-hillock morphology to resolve the role of Mg<sup>2+</sup> in governing calcite surface morphologies. We show that Mg<sup>2+</sup> directly modifies the surface morphology of calcite as a consequence of differential interaction with four crystallographically controlled step directions. Step-specific interactions are especially evident at low Mg/Ca ratios in solution, where steps with acute step-edge geometries ([441]<sub>-</sub> and [48 $\bar{1}$ ]<sub>-</sub>) are observed to be rough while obtuse steps ( $\bar{[441]}$ <sub>+</sub> and [48 $\bar{1}$ ]<sub>+</sub>) remain smooth. Higher Mg/Ca solution ratios cause the edges of both step-types to become rough and the growth spiral to approach an elliptical form. During this process, new [42 $\bar{1}$ ] step directions are generated by decreased growth velocities at the intersection of the  $\pm$  directions. As these steps flow along the [010] vector, they accumulate and result in the formation of pseudofacets with an orientation that approximates a (010) face. We propose that this phenomenon is the result of strain at the intersection of nonequivalent step-types, resulting in differential Mg<sup>2+</sup> incorporation across the boundary between those steps. This hypothesis is supported by estimates of the incorporated strain as well as observations of growth-hillock recovery from impurity poisoning that indicate the presence of “remembered” strain at the boundary of the nonequivalent step-types. The results of this study offer a plausible molecular-scale explanation for elongate calcite crystals that are commonly observed in sedimentary environments. This novel explanation for habit modification of calcite by impurities arises from step-specific impurity interactions rather than the face-specific interactions commonly assumed in previous models (Folk 1974; Lahann 1978).