

## **Solution-chemistry control of Mg<sup>2+</sup>-calcite interaction mechanisms: Implication for biomineralization**

**JIE XU<sup>1,\*</sup>, JIANHUA WANG<sup>2</sup>, MINA HONG<sup>3</sup>, AND H. HENRY TENG<sup>3,\*</sup>**

<sup>1</sup>Geosciences Department, Virginia Tech, Blacksburg, Virginia 24060, U.S.A.

<sup>2</sup>Department of Terrestrial Magnetism, Carnegie Institutions of Washington, Washington, D.C. 20015, U.S.A.

<sup>3</sup>Chemistry Department, George Washington University, Washington, D.C. 20052, U.S.A.

### **ABSTRACT**

We investigated the effect of Mg<sup>2+</sup> on calcite hillock growth over a broad range of solution conditions in terms of supersaturation ( $\Omega_{\text{calcite}}$ ) and Mg/Ca ratios using atomic force microscopy and secondary ion mass spectrometry. We found that both the incorporation pattern/incorporated Mg<sup>2+</sup> quantity in the hillock structure and the Mg<sup>2+</sup>-induced morphological change of the hillock surface showed strong dependence of the growth conditions. Specifically, when Mg/Ca was high (i.e., >5) and  $\Omega_{\text{calcite}}$  was low (i.e., ~0.45), Mg<sup>2+</sup> was predominantly incorporated into the negative sectors of the hillock structure, resulting in gradual loss of step structure and morphological amorphism on these vicinal surfaces. When Mg/Ca and  $\Omega_{\text{calcite}}$  were in intermediate ranges (i.e., Mg/Ca < 5, and 0.45 <  $\Omega_{\text{calcite}}$  < 1), the originally straight edges of the hillock steps exhibited curvatures of varying degrees and formed “tear-drop” morphologies. It is noted that such “tear-drop” morphology was stable within the duration of the experiments and did not evolve into other surface patterns. By contrast, when both Mg/Ca and  $\Omega_{\text{calcite}}$  were high (i.e., Mg/Ca > 5, and  $\Omega_{\text{calcite}}$  > 1.1), the growing hillocks experienced two phases of morphological changes, initiated with the formation of “tear-drops” followed by the development of linear ruptures along  $[\bar{4}81]$  and  $[44\bar{1}]$  directions. And the occurrence of these ruptures segmented the hillock surface effectively into multiple isolated plateaus. Significantly, we revealed the underlying mechanisms for these condition-specific effects of Mg<sup>2+</sup> on calcite growth, which mainly resulted from the interplay among three major factors: (1) the size-mismatch between Mg<sup>2+</sup> and Ca<sup>2+</sup> that causes structural strains in magnesian calcite and leads to morphological amorphism in high-Mg carbonate; (2) the asymmetry of the calcite crystal structure that sets a physical limitation for Mg<sup>2+</sup> incorporation patterns in the hillock structure; and (3) the step advancing rate (i.e., the calcite growth kinetics) that affects both Mg<sup>2+</sup> incorporation and the accommodation of Mg<sup>2+</sup>-induced structural strains in the hillock structure. Detailed discussions were given for each growth scenario. The results of our study provide a theoretical base to decipher the roles of Mg<sup>2+</sup> in CaCO<sub>3</sub> mineralization, and thus, have important implication for a range of processes that involve the growth of Mg-Ca-CO<sub>3</sub> systems, such as biomineralization, carbon capture and storage, and scale controls in industrial settings.

**Keywords:** Mg-Ca-CO<sub>3</sub>, biomineralization, lattice strain and stress