

Solution-chemistry control of Mg²⁺-calcite interaction mechanisms: Implication for biomineralization

JIE XU^{1,*}, JIANHUA WANG², MINA HONG³, AND H. HENRY TENG^{3,*}

¹Geosciences Department, Virginia Tech, Blacksburg, Virginia 24060, U.S.A.

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

³Chemistry Department, George Washington University, Washington, D.C. 20052, U.S.A.

ABSTRACT

We investigated the effect of Mg²⁺ on calcite hillock growth over a broad range of solution conditions in terms of supersaturation (Ω_{calcite}) and Mg/Ca ratios using atomic force microscopy and secondary ion mass spectrometry. We found that both the incorporation pattern/incorporated Mg²⁺ quantity in the hillock structure and the Mg²⁺-induced morphological change of the hillock surface showed strong dependence of the growth conditions. Specifically, when Mg/Ca was high (i.e., >5) and Ω_{calcite} was low (i.e., ~0.45), Mg²⁺ 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 Ω_{calcite} were in intermediate ranges (i.e., Mg/Ca < 5, and 0.45 < Ω_{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 Ω_{calcite} were high (i.e., Mg/Ca > 5, and Ω_{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 Mg²⁺ on calcite growth, which mainly resulted from the interplay among three major factors: (1) the size-mismatch between Mg²⁺ and Ca²⁺ 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 Mg²⁺ incorporation patterns in the hillock structure; and (3) the step advancing rate (i.e., the calcite growth kinetics) that affects both Mg²⁺ incorporation and the accommodation of Mg²⁺-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 Mg²⁺ in CaCO₃ mineralization, and thus, have important implication for a range of processes that involve the growth of Mg-Ca-CO₃ systems, such as biomineralization, carbon capture and storage, and scale controls in industrial settings.

Keywords: Mg-Ca-CO₃, biomineralization, lattice strain and stress