Solution-chemistry control of Mg$^{2+}$-calcite interaction mechanisms: Implication for biomineralization

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ABSTRACT

We investigated the effect of Mg$^{2+}$ 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$^{2+}$ quantity in the hillock structure and the Mg$^{2+}$-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., $\sim$0.45), Mg$^{2+}$ 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-drop” followed by the development of linear ruptures along [108] and [44T] 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$^{2+}$ on calcite growth, which mainly resulted from the interplay among three major factors: (1) the size-mismatch between Mg$^{2+}$ and Ca$^{2+}$ 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$^{2+}$ incorporation patterns in the hillock structure; and (3) the step advancing rate (i.e., the calcite growth kinetics) that affects both Mg$^{2+}$ incorporation and the accommodation of Mg$^{2+}$-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$^{2+}$ in CaCO$_3$ mineralization, and thus, have important implication for a range of processes that involve the growth of Mg-Ca-CO$_3$ systems, such as biomineralization, carbon capture and storage, and scale controls in industrial settings.

Keywords: Mg-Ca-CO$_3$, biomineralization, lattice strain and stress

INTRODUCTION

Mineralization of calcium carbonate (CaCO$_3$), a ubiquitous process in natural and anthropogenic settings, can be affected by various trace elements and xeno compounds including metal cations, anions, organic polymers, and biomolecules (Reddy and Nancollas 1976; Mucci and Morse 1983; Reeder 1996; Hemming et al. 1998; Parsiegla and Katz 1999; Astilleros et al. 2000; Davis et al. 2000; Freund et al. 2001; Wasylenki et al. 2011; Montes-Hernandez et al. 2011; Xu et al. 2013; Long et al. 2014). Chief among the modifiers in sedimentary environments and calcifying organisms are magnesium cations (Mg$^{2+}$), which were demonstrated to impact the morphology, composition, and crystal structure of the formed CaCO$_3$ phases. The current scientific interests in the Mg-Ca-CO$_3$ system mainly stemmed from the close tie of Mg$^{2+}$ and CaCO$_3$ in nature, manifested by the prevalence of Mg-bearing carbonates (i.e., magnesian calcite and dolomite) in geological records, but also have extended far beyond the traditional sedimentology and mineralogy, well into the biomineralization, paleoclimatology, and material science as well as industrial practices.

It has been well recognized that the presence of Mg$^{2+}$ alters the growth morphology of CaCO$_3$ (i.e., calcite). The best-known correlation between solution Mg$^{2+}$ content and calcite growth morphology was reported in early 1970s, when Folk (1974) observed that with increasing Mg/Ca ratios in the growth medium, the resultant calcite crystals were elongated parallel to the c-axis. Various models were subsequently proposed to explain this elongation phenomenon (including Folk 1974; Lahann 1978; Given and Wilkinson 1985), and significant attention was directed to the potential selective effect of Mg$^{2+}$ on different crystal faces of calcite. The validity of these models remained controversial however, until direct field and experimental evidence became available in late 1980s. One important piece of such evidence was the (intra)sectoral zoning of trace elements (including Mg, Sr, Mn, and etc.) in calcite crystals, identified by Reeder et al. using a range of analytical tools (Reeder and Grams 1987;