

## Amino acid and chitin controlled Ca-Mg carbonate precipitation

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Calcium carbonate minerals, such as calcite and aragonite, are the most common mineral components in biominerals across geologic time. Ca-Mg carbonates, such as proto-dolomite and dolomite, are known to be more resistant to physical weathering, and are potentially more impervious to dissolution in an increasingly acidifying ocean compared to pure calcium carbonates. These Ca-Mg carbonates also have a greater potential for carbon sequestration due to the availability of both Ca and Mg cations to bond with carbonate groups. However, the high kinetic energy barrier for the dehydration of the  $\text{Mg}^{2+}$ -water complex restricts Mg incorporation in carbonates at Earth surface conditions, making Mg-bearing carbonates relatively rare biominerals. In this study, we show that chitins and amino acids that are acidic and hydrophilic can catalyze mineral surface  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  dehydration to allow for Ca-Mg carbonate precipitation via *in vitro* experiments, which may explain the mechanism for templating of Ca-Mg carbonate minerals in biomineralization systems. Our results also show that solid surfaces with adsorbed organic substrates contribute to specific crystal morphologies in experimental biomineral analogs, some of which resemble natural high magnesium calcite (HMC)/proto-dolomite crystals on leaf-cutter ant exoskeletons. This fundamental research on how Mg-rich carbonate crystals grow in the presence of organic substrates, and how these substrates impact their morphology and crystal chemistry not only has direct implications for the fields of low temperature geochemistry, carbonate biomineralogy, and climate proxies, but it also has applications in biomimetic crystal growth and carbon sequestration engineering.