

Formation of amorphous calcium carbonate and its crystalline transformation

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The formation of biominerals from an amorphous precursor phase is a common phenomenon in biomineralization. Organisms from various phyla use this strategy to form different crystalline materials, including the transformation of a disordered ferrihydrite phase into magnetite, amorphous calcium phosphate into hydroxyapatite, and amorphous calcium carbonate (ACC) into the crystalline CaCO₃ mineral (e.g., calcite, aragonite, vaterite or monohydrocalcite). The increasing evidence shows that such transformation process widely follows non-classical nucleation and growth pathways, where amorphous precursor phase can play a crucial role. Among the more than 70 biogenic minerals known so far, calcium carbonate most widely occurs. Despite recent extensive research, the crystallization of biogenic CaCO₃ from amorphous precursor is not fully understood. Herein, a series of ACCs with different contents of Mg²⁺ were first biomimetically synthesized in the presence of polyaspartic acid (PASP), and then their phase transformation processes were investigated under different medium conditions. Our results show that the ACC with lower Mg²⁺ content can transform into magnesium calcite and aragonite, whereas the ACC with higher Mg²⁺ content can exclusively form monohydrocalcite. Furthermore, a series of Ca L-edge NEXAFS analyses revealed that the ACCs with different contents of Mg²⁺ and PASP possess distinct short-range structure, and it can be attributed to the combined effect of PASP and Mg²⁺. These short-range structures must somehow be preserved during the crystallization, though the crystallization follows a dissolution/precipitation process, and it may provide a blueprint for the ultimate transformation product of the ACC.

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