



Coupled dissolution-precipitation as a mechanism for amorphous-to-crystalline calcium carbonate phase transition

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Growing evidence shows that several calcium carbonate biominerals form via an amorphous precursor phase. Such a biomineralization strategy could also be applicable for the biomimetic synthesis of novel functional materials. A crucial step in this process is the transformation of amorphous calcium carbonate (ACC) into calcite. However, controversy exists as to what is the actual mechanism of this transformation: Is it a solid-solid (solid state) or a dissolution/precipitation mechanism? Determining the transition mechanism is critical for example in interpreting the formation of oriented crystalline structures in biominerals (e.g., echinoderm spicules). We studied calcium carbonate precipitation and phase transitions according to the overall reaction $\text{Ca(OH)}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$. Mineral phase transformations during this reaction were studied using transmission electron microscopy (TEM). Our TEM analysis showed that two different types of ACC are sequentially formed during this reaction. Type I ACC shows no well-defined short-range order, while Type II ACC shows a short-range order corresponding to calcite. Following e-beam irradiation, Type I ACC particles transform into randomly oriented CaO nanocrystals, while irradiation of Type II ACC leads to the formation of pseudomorphs made up of perfectly oriented aggregates of calcite nanocrystals. Moreover, calcite crystals formed in solution or in air (85 % relative humidity) after Type II ACC are also pseudomorphs made up of porous aggregates of preferentially oriented calcite nanocrystals. Our results give experimental evidence showing that the ACC to calcite transformation under relevant biomineralization conditions (low T and P), also applicable in the biomimetic synthesis of calcite, is a pseudomorphic dissolution-precipitation process. This mechanism involves the tightly interface-coupled dissolution of the precursor amorphous phase (with the crystalline phase protostructure) and concomitant deposition of the crystalline product (calcite) on the remaining (not fully dissolved) precursor phase via epitaxial crystallization. The solubility and molar volume differences between parent and product phase explain the generation of porosity, which enables the progress of the reaction leading to a calcite pseudomorph.