

## Transformation of synthetic amorphous calcium carbonate: *In situ* X-ray total scattering study

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Despite much interest in the industrial, environmental, and biological applications of amorphous calcium carbonate (ACC), few studies have been able to examine the amorphous to crystalline transformation *in situ*. We used synchrotron X-ray total scattering and pair distribution function analysis to characterize the *in situ* transformation of ACC, examining samples prepared by different synthesis methods and at different hydration states. ACC samples were allowed to react in capillaries at ambient P and T with deionized water or a calcite-equilibrated solution. Reaction progress could be followed using multiple regressions of *in situ*  $I(Q)$  data, with calcite, vaterite, and fresh ACC end-members.

The different ACC samples exhibited a range of results in terms of both transformation rate and pathway. Transformation kinetics varied according to ACC synthesis method, and in turn transformation pathway was affected strongly by kinetics. Experiments with slower transformation kinetics showed ACC transforming directly to calcite, while experiments with the fastest transformation rates yielded a mixture of calcite and vaterite. In experiments where transformation produced a mixture of phases, the initial crystallization of vaterite and calcite was simultaneous. Transformation of ACC directly to calcite and the simultaneous formation of vaterite and calcite both indicate that vaterite is not an essential precursor phase in the formation of calcite. However, *ex situ* analysis of capillaries long after *in situ* analysis did show a secondary transformation from vaterite to calcite, with slower reaction kinetics than either of the initial crystallization reactions from the amorphous phase.

Reactions involving calcite-equilibrated solution and partially dehydrated ACC both correlated with an overall decrease in the transformation kinetics. We attribute these effects to a decreased departure from equilibrium and the distinct structural roles of the various hydrous components of the partially dehydrated ACC. The *in situ* structural analyses used in this study shed light on the possible controls manipulated by organisms to direct transformation *in vivo* with potential applications for biomimetic synthesis.