Carbonate ion concentration as a master variable in the formation of geological and biological $CaCO_3$

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An understanding of chemical and physical controls on $CaCO_3$ formation has continued to challenge our community for more than a century. During the 1970's, magnesium ion became widely recognized for its polymorph-directing influence on the formation of calcite versus aragonite. Evidence from field observations enlarged the conversation to also consider the carbonate ion as a variable in polymorph selection. McCauley and Roy (1974) and Fernández-Diaz et al. (1996) noted high carbonate levels favored aragonite, but a widely-accepted model was not adopted.

With the realization that carbonate mineralization via metastable intermediates is widespread in natural systems, a new generation of studies is underway to decipher the physical basis for $CaCO_3$ crystallization. This effort is supported by advances in quantitative synthesis, structural analysis methods as well as theoretical capabilities.

To quantify the control of solution composition on the transformation of amorphous $CaCO_3$ (ACC) into crystalline polymorphs, Blue et al. (2017, *GCA*) developed a mixed flow reactor to synthesize ACC under controlled conditions of pH, Mg/Ca, and total carbonate concentration. ACC was transformed in the output suspension while characterizing the evolving solutions/solids. The findings provide a quantitative framework that predicts the initial crystalline polymorph from the ratios of Mg/Ca and CO_3/Ca.

New structural evidence that reiterates the importance of carbonate ion is emerging in our in-situ study using high energy x-rays and PDF analysis (Mergelsberg et al., in prep). The findings suggest carbonate ion concentration may be a master variable in directing incipient structure during the amorphous stage— long before crystallization to final products. The findings again show the urgency to revisit traditional models of carbonate formation and long-held dogmas regarding the environmental conditions that led to extensive carbonate deposits in the geological record.