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Establishing the Physical Basis for Calcification by Amorphous Pathways

Christina R. Blue

Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
In
Geosciences

Patricia M. Dove, chair
J. Donald Rimstidt
Michael F. Hochella, Jr.
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ESTABLISHING THE PHYSICAL BASIS FOR CALCIFICATION BY AMORPHOUS PATHWAYS

Christina R. Blue

ABSTRACT

The scientific community is undergoing a paradigm shift with the realization that the formation of carbonate minerals with diverse compositions and textures can be understood within the framework of multiple pathways to mineralization. A variety of common minerals can form via an amorphous pathway, where molecules or clusters aggregate to form a metastable amorphous phase that later transforms to one or more crystalline polymorphs. Amorphous calcium carbonate (ACC) is now recognized in a wide variety of natural environments. Recent studies indicate the chemical signatures and properties of the carbonate polymorphs that transform from an ACC pathway may obey a different set of dependencies than those established for the "classical" step-growth process. The Mg content of ACC and calcite is of particular interest as a minor element that is frequently found in ACC and the final crystalline products of calcified skeletons or sediments at significant concentrations. Previous studies of ACC have provided important insights into ACC properties, but a quantitative understanding of the controls on ACC composition and the effect of mineralization pathway on Mg signatures in calcite has not been established.

This study utilized a new mixed-flow reactor (MFR) procedure to synthesize ACC from well-characterized solutions that maintain a constant supersaturation. The experimental design controlled the input solution Mg/Ca ratio, total carbonate concentration, and pH to produce ACC with systematic chemical compositions. Results show that ACC composition is regulated by the interplay of three factors at steady state conditions: 1) Mg/Ca ratio, 2) total carbonate concentration, and 3) solution pH. Findings from transformation experiments show a systematic and predictable chemical framework for understanding polymorph selection during ACC transformation. Furthermore, results suggest a chemical basis for a broad range of Mg contents in calcite, including high Mg calcite. We find that the final calcite produced from ACC is similar to the composition of the initial ACC phase, suggesting that calcite composition reflects local conditions of formation, regardless of the pathway to mineralization. The findings from this study provide a chemical road map to future studies on ACC composition, ACC transformation, polymorph selection, and impurities in calcite.