



Chemical and physical controls on the transformation of amorphous calcium carbonate into crystalline CaCO₃ polymorphs

C.R. Blue^{a,1}, A. Giuffrè^{a,2}, S. Mergelsberg^a, N. Han^a, J.J. De Yoreo^{b,c}, P.M. Dove^{a,*}

^a Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA

^b Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352, USA

^c Department of Materials Science and Engineering, U. Washington, Seattle, WA 98195, USA

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Abstract

Calcite and other crystalline polymorphs of CaCO₃ can form by pathways involving amorphous calcium carbonate (ACC). Apparent inconsistencies in the literature indicate the relationships between ACC composition, local conditions, and the subsequent crystalline polymorphs are not yet established. This experimental study quantifies the control of solution composition on the transformation of ACC into crystalline polymorphs in the presence of magnesium. Using a mixed flow reactor to control solution chemistry, ACC was synthesized with variable Mg contents by tuning input pH, Mg/Ca, and total carbonate concentration. ACC products were allowed to transform within the output suspension under stirred or quiescent conditions while characterizing the evolving solutions and solids. As the ACC transforms into a crystalline phase, the solutions record a polymorph-specific evolution of pH and Mg/Ca.

The data provide a quantitative framework for predicting the initial polymorph that forms from ACC based upon the solution $a\text{Mg}^{2+}/a\text{Ca}^{2+}$ and $a\text{CO}_3^{2-}/a\text{Ca}^{2+}$ and stirring versus quiescent conditions. This model reconciles discrepancies among previous studies that report on the nature of the polymorphs produced from ACC and supports the previous claim that monohydrocalcite may be an important, but overlooked, transient phase on the way to forming some aragonite and calcite deposits. By this construct, organic additives and extreme pH are not required to tune the composition and nature of the polymorph that forms.

Our measurements show that the Mg content of ACC is recorded in the resulting calcite with a $\approx 1:1$ dependence. By correlating composition of these calcite products with the $\text{Mg}_{\text{tot}}/\text{Ca}_{\text{tot}}$ of the initial solutions, we find a $\approx 3:1$ dependence that is approximately linear and general to whether calcite is formed via an ACC pathway or by the classical step-propagation process. Comparisons to calcite grown in synthetic seawater show a $\approx 1:1$ dependence. The relationships suggest that the local $\text{Mg}^{2+}/\text{Ca}^{2+}$ at the time of precipitation determines the calcite composition, independent of whether growth occurs via an amorphous intermediate or classical pathway for a range of supersaturations and pH conditions.

The findings reiterate the need to revisit the traditional picture of chemical and physical controls on CaCO₃ polymorph selection. Mineralization by pathways involving ACC can lead to the formation of crystalline phases whose polymorphs and compositions are out of equilibrium with local growth media. As such, classical thermodynamic equilibria may not provide a reliable predictor of observed compositions.

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* Corresponding author.

E-mail address: dove@vt.edu (P.M. Dove).

¹ Current address: eScience Labs, Sheridan, CO 80110, USA.

² Current address: Department of Physics and Chemistry, University of Wisconsin, Madison, WI 53706, USA.

1. INTRODUCTION

Amorphous calcium carbonate (ACC) and other metastable CaCO_3 phases are increasingly recognized as prevalent during calcification. Insights from these studies are motivating an extensive effort to revisit long-standing assumptions regarding CaCO_3 mineralization and the factors that allow nonclassical, multistep pathways to mineralization (De Yoreo et al., 2015). Of particular interest are the relationships between chemical composition of the local environment and the crystalline polymorphs that form. For example, the formation of calcified skeletons can involve the accumulation of ACC within the organic matrix followed by its transformation to anhydrous crystalline polymorphs (calcite, aragonite, and vaterite) or the hydrated polymorph, monohydrocalcite. Examples include sea urchin spicules (Beniash et al., 1997; Politi et al., 2008), sponge spicules (Aizenberg et al., 1996), mollusk shells (Weiss et al., 2002; Nudelman et al., 2007), pillbug cuticles (Tao et al., 2009) and crayfish gastroliths (Akiva-Tal et al., 2011).

ACC has received relatively little attention in the context of carbonate mineral formation in geological environments. Field observations, however, suggest ACC may precipitate when conditions promote high local supersaturations for short periods of time. For example, some marine porewaters undergo pulses of increased alkalinity levels—due to either intrinsic (e.g., photosynthesis, respiration) or extrinsic (e.g., degassing, alkaline water input) factors (Dupraz et al., 2009)—on short time scales to produce ACC. More extreme environments such as saline lakes, sabkhas, and closed basin lakes can also achieve sufficiently high alkalinities to form ACC (Ingerson, 1962; Ross, 1991; Señorale-Pose et al., 2008; Sánchez-Román et al., 2011; Katz and Nishri, 2013). ACC has also been identified in microbial mats (Dupraz et al., 2009) and hot spring deposits (Jones and Peng, 2012). The resulting crystalline polymorphs exhibit diverse morphologies, and a complex spread of elemental and isotopic signatures that are extensively documented (Thompson and Ferris, 1990; Solotchina et al., 2009; Katz and Nishri, 2013; Nielsen and DePaolo, 2013). Indeed, mineralization by ACC and other nonclassical pathways may be the missing link to interpreting unusual carbonate compositions and textures that are found in modern and ancient carbonates but not predicted by traditional crystal growth models (Wang et al., 2012; Han et al., 2013; De Yoreo et al., 2015).

Given the importance of Mg as an indicator of paleoenvironmental conditions raises the question of whether the mineralization process, in itself, influences calcite composition. The many investigations that use Mg content of calcite to infer conditions of formation (e.g. Nürnberg et al., 1996; Rosenthal et al., 1997; Lea et al., 1999; Russell et al., 2004) implicitly assume that (1) growth occurs by the classical step-growth process of ion-by-ion attachment or (2) composition is independent of growth process, including mineralization by an amorphous pathway.

Recent studies of the crystalline transformation of ACC provide important insights, but a quantitative picture of chemical controls on the polymorphs that form and their compositions are not yet established. For example, Table 1 shows that ACC can transform to different crystalline poly-

morphs, often as mixtures, and with highly variable Mg content. Discrepancies between the results of these studies are due, in part, to the experimental methods, which could not control the evolution of the solution chemistry during ACC precipitation. The most common experimental approach uses variations on the batch-reactor method. This method involves stirring the solutions during the transformation (Rodríguez-Blanco et al., 2012; Nishiyama et al., 2013) or allowing the transformation to proceed without stirring (Loste et al., 2003; Han et al., 2013). Most experiments mixed solutions of CaCl_2 with NaHCO_3 or began at higher pH values using Na_2CO_3 (Radha et al., 2012). Other methods achieved rapid (and unknown) supersaturations by sublimating a nearby $(\text{NH}_4)_2\text{CO}_3$ salt into CaCl_2 solutions (Raz et al., 2000; Wang et al., 2012).

Although the observations reported in Table 1 are variable, they suggest the interplay of chemical and physical factors determine the initial polymorph that forms during mineralization via an amorphous pathway. To test this idea, we designed a series of experiments to quantify the control of local chemical composition on polymorphs and compositions (calcite) that transform from ACC. The first part of the study used the mixed-flow reactor (MFR) method to synthesize a suite of ACC materials under controlled chemical conditions (Blue et al., 2013; Blue and Dove, 2015). By this approach, the Mg content of ACC is regulated by tuning initial solution Mg/Ca, total inorganic carbon concentration, and pH. In the second part of the study, the characterized ACC was allowed to transform into crystalline products under physically mixed (stirred) or quiescent (unstirred) conditions.

The findings identify chemical and physical conditions that reproducibly direct the ACC to transform into specific CaCO_3 polymorphs and reiterate the importance of monohydrocalcite as another potentially important metastable end-product phase (Rodríguez-Blanco et al., 2014). This framework also shows the conditions that regulate the Mg content of calcite from low to very high Mg values and do not require extreme solution pH or the presence/addition of organic molecules. The resulting construct provides a chemical and physical basis for better understanding CaCO_3 polymorph selection, and calcite composition, while also reconciling apparent discrepancies in the literature.

2. METHODOLOGY

2.1. ACC synthesis

ACC was synthesized at 25 °C (± 1 °C) using a mixed flow reactor (MFR) method adapted from Blue et al. (2013) (Fig. 1). Advantages of the MFR over previous synthesis methods include: (1) synthesis at constant, quantified supersaturation under controlled chemical conditions, (2) continuous formation of the amorphous phase at steady-state conditions, and (3) production of large amounts of ACC with reproducible compositions for characterization by complementary methods.

The experimental design used a syringe pump to input two 100 mL solutions that contained variable concentrations of the salts (1) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and

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