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

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Abstract. Calcite and other crystalline polymorphs of CaCO₃ can form by pathways involving amorphous calcium carbonate (ACC). Previous studies of ACC provide important insights, but 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 apparent 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 the 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 the 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 the local growth media. As such, classical thermodynamic equilibria may not provide a reliable predictor of observed compositions.

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 the 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 (Nudelman et al., 2007; Weiss et al., 2002), 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 that 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-Roman 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, 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 the 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 polymorphs, 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 (Rodriguez-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

Na₂CO₃ (Radha, et al., 2012). Other methods achieved rapid (and unknown) supersaturations by sublimating a nearby (NH₄)₂CO₃ salt into CaCl₂ solutions (Raz et al., 2000; Wang et al., 2012).

**** TABLE 1 ****

Although the observations reported in **Table 1** are variable, they suggest that 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 the 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 CaCO₃ polymorphs and reiterate the importance of monohydrocalcite as another potentially important metastable end-product phase (Rodriguez-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 CaCO₃ 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 ($\pm 1^\circ\text{C}$) using a mixed flow reactor (MFR) method adapted from Blue et al. (2013) (**Figure 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 2) NaHCO_3 . All experiments contained magnesium so that the resulting ACC would be stable for short periods prior to the transformation to crystalline products. Small amounts of NaOH were added to the NaHCO_3 solution to adjust the initial pH to the desired value. Although the study was not designed to study pH specifically, the experiments were designed to span a portion of pH space with initial pH values ranging from 9.22-10.10 and the steady state values of 8.2-9.5. Input solution compositions are summarized in **Appendix Table A1**. The experimental design also used a range of saturation states to produce the ACC by varying carbonate concentration and pH. Saturation states are reported with respect to pure calcite:

$$(1)$$

where Ω_{calcite} is the saturation state with respect to pure calcite, a_i is the activity of species i , and the solubility product of calcite is given by $K_{sp,\text{calcite}} = 10^{-8.48}$ at 25°C (Plummer and Busenberg, 1982). The experiments began with Ω_{calcite} in the range 27–82 such that all solutions precipitated ACC. Our ability to produce ACC at relatively low calcite supersaturation is consistent with previous studies (Hamm et al., 2014; Kellermeier et al., 2014) suggesting the published ACC

solubility of $K_{sp,ACC} = 10^{-6.4}$ is too high (Brečević and Nielsen, 1989). Ion activities were calculated using Geochemist's Workbench for each solution condition in order to quantify saturation state.

To prepare ACC, the syringe pump continuously injected the two solutions— NaHCO_3 and the MgCl_2 and CaCl_2 mixture—into the reactor, where they were stirred at ≈ 800 rpm. As the contents of the MFR became supersaturated with respect to the amorphous phase, ACC precipitated continuously (see Blue and Dove, 2015). All experiments prepared ACC using a 1-minute hydraulic residence time (τ):

$$\tau = . \quad (2)$$

For each experiment, the reactor operated for a minimum of three residence times to allow input solutions and ACC products within the reactor to reach steady-state conditions (Jensen, 2001). The time elapsed to steady state and the sample collection varied with solution chemistry. The output suspension from the top of the reactor unit was sampled by vacuum filtration. The ACC was collected on a SterliTech[®] polyethersulfone (PES) filter with a pore size of $0.03 \mu\text{m}$ and the effluent solution was retained in a vacuum flask. The steady state pH of the effluent solution was measured within one minute of the termination of the experiment in order to minimize re-equilibration from exposure to the atmosphere (**Appendix Table A1**). The produced ACC was rinsed with ethanol and dried in a class II biological safety cabinet for 20 minutes, then dried for an additional 10 minutes in a vacuum desiccator. Samples were subsequently weighed and stored in a 4°C refrigerator overnight prior to analysis.

2.2 ACC Transformation to Crystalline Products

To conduct the transformation experiments, additional slurry was collected from the MFR during the steady-state conditions of ACC production. Using a 100 mL glass vessel, the suspension was stirred at 250 rpm, with a 1-minute rest interval each hour before reversing the

rotation direction of the stir bar. All vessels were maintained at 25°C in a temperature monitored room or incubator throughout the transformation process. Given the dependence of transformation time on solutions composition (e.g. discussion in Section 3.2), the sampling intervals varied with solution composition from 30 minutes to 12 hours, where low Mg/Ca solutions were sampled the most frequently. Sampling continued until XRD and SEM analyses showed the initial transformation was complete.

At each sampling interval (**Appendix Table A1**), 6 ml of slurry was extracted from the vessel during stirring for their respective analysis. The pH of the slurry was measured using electrodes that were calibrated approximately every 2 hours using pH 7.0 and 10.1 buffer solutions at 25°C. The solids were captured by vacuum filtration on a 0.03 µm Nylon filter, rinsed from the filter with ethanol into a petri dish, and saved for analysis. The filtered solution was analyzed separately. The same transformation protocol was used for unstirred experiments, except that they were not stirred after collection from the MFR. Stirred and unstirred experiments were not run concurrently, and a new batch of ACC was prepared for each transformation experiment (listed in **Appendix Table A1**).

Throughout the transformation process, $[Mg]_{tot}$ and $[Ca]_{tot}$ were also measured. Total inorganic carbon concentration of the solution at a given time point was calculated by assuming that all Ca and Mg removed from solution was precipitated according to the following stoichiometry:

Thus, the moles of (Ca + Mg) removed from solution must equal the moles of carbonate removed from solution. Ion activities were calculated from the solution measurements using Geochemist's Workbench (**Appendix Table A1**).

2.3 Sample Characterization

2.3.1 SEM

All dried precipitates were placed on ultra smooth carbon tape and sputter-coated with ≈ 10 nm of gold-palladium. Analyses were performed on an FEI Quanta 600 FEG ESEM. Micrographs of the ACC and crystalline products were acquired using secondary electron (SE) scattering. All samples were examined for their morphology and particle size. SEM images of morphology and XRD analyses documented the formation of three anhydrous polymorphs (calcite, aragonite, and vaterite) and one hydrated polymorph of CaCO_3 (monohydrocalcite: $\text{CaCO}_3 \cdot \text{H}_2\text{O}$). Representative images are shown in **Figure 2**.

*** FIG. 2 ***

2.3.2 XRD

X-ray diffraction was used to confirm the mineralogy of each sample. The dried samples were prepared by pipetting 0.30 mL of an ethanol smear containing the filtered precipitate onto a zero background holder. Samples were then placed in a biological safety cabinet to allow the ethanol to completely evaporate at 25°C before analysis. All diffractograms were obtained using a Rigaku MiniFlex II, and data collected over 10° – 60° 2θ at a step width of 0.05° and a 5 s count time ($\lambda = 1.5405 \text{ \AA}$). Standard spectra were collected from calcite (var. Iceland Spar) and aragonite (Ward's Science, USA) prior to sample analyses. Representative XRD patterns for each phase identified in this study are shown (**Fig. 3**)

*** FIG. 3 ***

2.3.3 Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES)

The composition of all solid products and their corresponding solutions were characterized separately by ICP-AES. The ACC samples collected from the MFR remained on the PES filters and were rinsed in ethanol, dried, and then immersed in 0.5 N nitric acid to

dissolve the ACC. The products collected from the transformation experiments in the batch reactor were washed from the filter with ethanol into a petri dish, dried in air in a Class II Biological Safety Cabinet for 20 minutes, and dissolved using 0.5 N nitric acid. The resultant filtered solutions were also mixed with 0.5 N nitric acid and analyzed. Analyses were performed using a Spectro ARCOS SOP. An yttrium internal standard was added to each sample in an internal standard mixing chamber (Glass Expansion, Inc., USA). Each sample then passed through a cross-flow nebulizer into a modified Scott-style spray chamber. The sample uptake rate was 2 mL/min, with each sample analysis using 5 mL of solution. Calibration solutions for Ca and Mg were prepared from commercially available standards (Environmental Express, Inc.) by dilution in a matrix-matched solution of 0.067 N HNO₃. The second source check standards were obtained from Spex, Inc.

2.3.4 Thermogravimetric Analysis

Thermogravimetric analyses of the ACC prepared by the same flow-through synthesis methods showed that all amorphous calcium-magnesium carbonate (ACMC) products contain slightly more than one water molecule (1.42–1.63) per carbonate ion (Blue and Dove, 2015). This higher water contents was consistent with a previous report of ACMC formed at very high pH (Radha et al., 2012). The water content and structure of the Mg-free ACC (control) is consistent with TGA and NMR measurements (Schmidt et al., 2014). The analysis suggests water associated with larger proportions of the charge-dense Mg compared to Ca (e.g. Di Tommaso and de Leeuw, 2010; Rodriquez-Blanco et al., 2011; Cobourne et al., 2014). The complexity of the spectra at higher temperatures (e.g. Blue and Dove, 2015) suggests that the greater Mg content is correlated with differences in the hydroxyl content and structure. These data suggest a relationship between the Mg and water contents of ACMC, but Blue and Dove

(2015) did not measure a dependence for the conditions of that study. Clearly, a detailed structural investigation of ACCM is needed.

3. RESULTS

3.1 Characterization of ACC and Crystalline Products

Characterization of the initial ACC precipitates by scanning electron microscopy (SEM) showed a characteristic spherical morphology with a particle size distribution of ≈ 0.1 to $2.0 \mu\text{m}$ (**Fig. 2A**). The polymorphs that transform from ACC exhibit a polycrystalline texture with distinct morphologies. Calcite occurs as spherulites with surfaces that are increasingly rounded as the Mg content increases and surface facets become smaller (i.e. **Fig. 2B,C**). Aragonite exhibits clusters of needles (**Fig. 2D**), whereas monohydrocalcite generally assumes the twisted, branching structure indicative of low Mg content (Rodriguez et al., 2014) (**Fig. 2E**), and vaterite grows as spherical rosettes (**Fig. 2F**).

The initial ACC and the polymorphs associated with these morphologies were confirmed by powder x-ray diffraction. All ACC products were confirmed as amorphous, without Bragg peaks on the XRD pattern and only a broad peak displayed from 25° – 35° 2θ (**Fig. 3A**). Spectra for low-Mg calcite (**Fig. 3B**) nearly align with the pure calcite standard (Iceland Spar, Ward's Science, USA), whereas peaks become broader and shift to higher 2θ with increasing Mg content (**Fig. 3C**). Peak broadening may indicate the presence of small Mg-enhanced crystal domains (Lenders et al., 2011). Mg content is also correlated with a decrease in d-spacing for all reflections compared to the pure calcite standard (**Fig. 3C**). For example, the 2θ of the (104) reflection increases from 29.583° (pure calcite) to 29.727° for calcite with 20 mole % Mg, which corresponds to a reduction in d-spacing from $3.017 \text{ \AA}$ to $3.003 \text{ \AA}$. Peak broadening and smaller d-spacing result from Mg incorporation into the crystallites (Bischoff et al., 1983; Mackenzie et

al., 1983), which indicate that Mg^{2+} ions are located within the crystal structure rather than adsorbed on surfaces as free ions (Vegard, 1921; Denton and Ashcroft, 1991).

All aragonite diffraction patterns (**Fig. 3D**) match the published standard (Ward's Science, USA). Patterns for monohydrocalcite (**Fig. 3E**) and vaterite (**Fig. 3F**) are in good agreement with those from other synthesis studies (e.g. Sand et al., 2011; Hu et al., 2012; Kimura and Koga, 2011; Rodriguez-Blanco et al., 2014). Additional XRD data are provided and discussed later in **Appendix Figures A1 and A2**.

3.2 Initial Crystalline Polymorphs Correlate with Solution Composition

The transformation of ACC produces crystalline polymorphs that indicate a systematic relationship to solution composition. Recall that the ACC-aqueous slurries output from the MFR at steady-state conditions (e.g. Section 2.2) were allowed to transform under physically stirred or quiescent (unstirred) conditions. For the 34 experiments that transformed under stirred conditions, **Figure 4A** shows that the initial calcite or monohydrocalcite occurs in reproducible composition fields when plotted as a function of the $a\text{Mg}^{2+}/a\text{Ca}^{2+}$ and $a\text{CO}_3^{2-}/a\text{Ca}^{2+}$ of the solutions. This study did not specifically investigate the effect of pH but low values of $a\text{CO}_3^{2-}/a\text{Ca}^{2+}$ are roughly correlated with the lower steady-state pH that varied from 8.2 – 9.5 (see Methods).

*** FIG. 4AB***

As expected, ACC transforms to calcite in solutions with a low $a\text{Mg}^{2+}/a\text{Ca}^{2+}$ (zero to ≈ 4) and low $a\text{CO}_3^{2-}/a\text{Ca}^{2+}$ (below dashed line in **Fig. 4A**). For solutions with intermediate $a\text{Mg}^{2+}/a\text{Ca}^{2+}$ (4–8) and low $a\text{CO}_3^{2-}/a\text{Ca}^{2+}$ (< 0.5), ACC transforms to a mixture of aragonite and calcite. The calcite that forms under the stirred transformation conditions contains 0–15 mol% MgCO_3 for conditions where the solution Mg/Ca is less than ≈ 3.5 –4 (**Fig. 5A**). The

transformation process is complete within 4 hours, according to XRD and SEM characterization (**Fig. 5A**). Under these conditions, 15 mol% is the uppermost Mg content measured and Mg/Ca >6 lead to the formation of monohydrocalcite from ACC (e.g. **Fig. 4A**).

*** FIG. 5 ***

Only one experiment produced aragonite as the initial crystalline phase from ACC under the conditions investigated in this study. Our observations that aragonite typically forms only as a late stage product is consistent with the notion that aragonite nucleation is limited by slow kinetics in simple inorganic solutions (Loste et al., 2003; Wang et al., 2012). Pathways to primary aragonite likely do exist, however, as seen in anecdotal reports that aragonite forms directly from ACC in water-alcohol solutions (Sand et al., 2011) and during in-situ TEM observations (Nielsen et al., 2014). These observations suggest the factors that regulate aragonite formation are not yet fully established.

Similarly, one experiment produced vaterite at the lowest $a\text{Mg}^{2+}/a\text{Ca}^{2+}$ and lowest $a\text{CO}_3^{2-}/a\text{Ca}^{2+}$ —a result that could not be replicated. Vaterite formation at very low Mg levels and high precipitation rates is consistent with previous reports (e.g. Loste et al., 2003; Nishiyama et al., 2013; Niedermayr et al., 2013) and observations that substrate composition also stabilizes the formation of this relatively unstable polymorph (Smeets et al., 2015).

ACC transforms to monohydrocalcite under a broad range of conditions when the solutions are stirred and the compositions have high $a\text{Mg}^{2+}/a\text{Ca}^{2+}$ and $a\text{CO}_3^{2-}/a\text{Ca}^{2+}$ (**Fig. 4A**). This result is consistent with reports of monohydrocalcite formation in Mg-rich solutions (>0.01 M) and high solution $a\text{CO}_3^{2-}/a\text{Ca}^{2+}$ (>1.0) (Loste et al., 2003; Kimura and Koga, 2011; Nishiyama et al., 2013; Rodriguez-Blanco et al., 2014). The separate $a\text{Mg}^{2+}/a\text{Ca}^{2+}$ and $a\text{CO}_3^{2-}/a\text{Ca}^{2+}$ solution fields that lead to calcite versus monohydrocalcite highlight the sensitivity of

polymorph formation to chemical conditions—in this case through $a\text{Mg}^{2+}$ and $a\text{CO}_3^{2-}$. The solution pH is also a possible influential factor, primarily through controls on the $\text{CO}_3^{2-}:\text{HCO}_3^-$ ratio.

Although this study focused on the *initial* polymorph that forms upon ACC transformation, additional measurements and observations show that many of the initial products eventually transform again into a tertiary solid phase. For example, most of the Mg-calcite is consumed to produce aragonite, a transformation that is accompanied by small increases in pH (**Appendix Table A1**). Similarly, monohydrocalcite persists for only a few hours before transforming to aragonite, minor nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), and possibly hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) (**Appendix Fig. A2**). These observations concur with reports that monohydrocalcite appears as a metastable intermediate between the precipitation of ACC and late-stage formation of aragonite (Munemoto and Fukusi, 2008; Fukushi et al., 2011; Zhang et al., 2012; Rodriguez-Blanco et al., 2014) and emphasize the point that monohydrocalcite formation can be easily missed en route to final products.

The measurements also show the time required for ACC to transform to initial crystalline products increases with the $\text{Mg}_{\text{tot}}/\text{Ca}_{\text{tot}}$ of the initial solution (**Fig. 4B**). For example, ACC transforms to vaterite within 10 minutes at the lowest Mg/Ca conditions (compare **Fig. 4A** and **4B**). At higher $\text{Mg}_{\text{tot}}/\text{Ca}_{\text{tot}}$, calcite typically forms within one hour; whereas aragonite or the calcite-aragonite mixtures form in <3–12 hours. These measurements are consistent with reports that Mg increases the lifetime of ACC (Loste et al., 2003; Wang et al., 2009, 2012; Rodriguez-Blanco et al., 2012; Han et al., 2013), likely owing to the stronger hydration of Mg compared to calcium (Burgess, 1988; Politi et al., 2010). At the highest Mg/Ca levels that correspond to ACC compositions of >15 mol% Mg, ACC transforms slowly to monohydrocalcite—sometimes

requiring up to 50 hours for the conditions of these experiments (**Fig. 4B**). Measurements for monohydrocalcite transformation show significant variability and may be caused by 1) high metastability of monohydrocalcite in solutions with $a\text{Mg}^{2+}/a\text{Ca}^{2+}$ greater than 6.0 (Nishiyama et al., 2013; Rodriquez-Blanco et al., 2014); 2) experimental and analytical error in accurately estimating the longer transformation times; and 3) variable CO_3^{2-} activity whereby higher levels influence the rate of monohydrocalcite formation (compare **Fig. 4A** and **Fig. 4B**) (Kimura and Koga, 2011; Nishiyama et al., 2013). Relationships in **Fig. 4B** further suggest the role of solution composition in directing the initial polymorphs that form from ACC.

3.3 Quiescent Conditions Open Pathway to Very High Mg Calcite?

In contrast to stirred conditions, the ACC to crystalline transformation under unstirred conditions expands the range of Mg/Ca conditions that produce calcite. Although the transformation is slow, requiring up to 40 hours (**Fig. 5B**), transformation experiments conducted under quiescent conditions produce calcite when solution Mg/Ca are as high as 10. The Mg content of this calcite is extremely high (up to 26 mol% MgCO_3) without evidence of monohydrocalcite (**Fig. 5B, Appendix Table A1**). Characterization of these products by XRD confirms that these are high Mg calcite and lack the (015) reflection that is characteristic of dolomite.

4. DISCUSSION

4.1 Polymorph-Specific Evolution of Solution Chemistry during Transformation

Our measurements show that solution compositions exhibit a polymorph-specific evolution of pH and solution Mg_{tot}/Ca_{tot} . These patterns can be used to predict the polymorph into which ACC transforms and provide insight about the reaction stoichiometry.

4.1.1 Calcite

The onset of calcite formation is accompanied by an abrupt decrease in pH of approximately one unit, followed by an increase to relatively constant values (**Fig. 6A**). Calcites with a higher Mg content are associated with a slower transformation rate and thus slower a decrease in pH (**Fig. 6A, exp. #11**). The ACC to calcite transformation is also accompanied by an approximately linear increase in Mg_{tot}/Ca_{tot} (**Fig. 6B**). This presumably occurs as the calcite consumes calcium relative to magnesium from solution and the additional drawdown of reactant concentration with the precipitation of this lower solubility phase.

*** FIG. 6***

There are two explanations for the changes in solution composition (**Fig. 4A** and **Fig. 6AB**) that accompany the ACC to calcite transformation. First, the onset of calcite formation would further decrease reactant concentration to approach the lower solubility of this phase while releasing protons to solution. An additional contribution to a lower pH could come from dissociation of bicarbonate in the ACC structure by the overall transformation reaction:

This stoichiometry assumes: 1) Mg is conserved in the ACC to calcite transformation (**Section 4.2**) and 2) the ACC begins as a carbonate-bicarbonate solid solution.

Although this second explanation is more speculative, three lines of evidence suggest bicarbonate could be expected in ACC and may be significant in some settings. First, recall that ACC in this study was synthesized at mild pH conditions that approximate HCO_3^- -dominated environments of biogenic CaCO_3 precipitation and most natural waters. Thus, the amorphous polymorph may contain HCO_3^- ions. There is no structural or chemical basis to exclude the presence of this species. Second, a recent NMR study detected minor HCO_3^- as intracrystalline defects in calcites that transformed from ACC despite its synthesis in a very high pH solution (Kababya et al., 2015). Third, a titration and NMR study of carbonate formation via a metastable liquid carbonate phase indicate the presence of a Ca-bound bicarbonate species for experiments conducted under similar pH conditions (Bewernitz et al., 2012). Thus, some component of the original ACC formed in these mild conditions may contain bicarbonate suggesting further study is warranted.

4.1.2 Aragonite

A similar evolution in pH was measured when ACC transformed to aragonite (**Appendix Table A1, exp. #3**) or vaterite (**Appendix Table A1, exp. #21**). For the one experiment that transformed to aragonite, solution $\text{Mg}_{\text{tot}}/\text{Ca}_{\text{tot}}$ also increases approximately linearly but the ratio becomes much larger (to 57), likely because Mg is preferentially excluded from the aragonite structure.

4.1.3 Monohydrocalcite

The transformation of ACC to monohydrocalcite (MHC) occurs without a significant change in the solution pH (**Fig. 6C**). This different type of pattern from the other polymorphs is consistent with very small shifts reported by Rodriguez-Blanco et al. (2014). Nevertheless, the onset of the transformation occurs with a sharp increase in solution $\text{Mg}_{\text{tot}}/\text{Ca}_{\text{tot}}$ to values

approaching 80 to >160 (**Fig. 6D**). This behavior may explain the multi stage evolution of ACC to a lower Mg MHC that is described by Rodriguez-Blanco et al. (2014). By monitoring the formation of MHC from ACC using x-ray scattering methods, they found that ACC transforms to high Mg MHC, to low Mg MHC and finally to aragonite/calcite. Data in our study supports their multistage model with measurements showing that: 1) MHC formation is coincident with a sharp increase in solution Mg_{tot}/Ca_{tot} (**Fig. 6D**); and 2) For experiments where we monitored solution composition and polymorph after the transformation, all MHC and most calcite was consumed and eventually transformed to aragonite (data not shown).

To better understand the ACC to MHC transformation, recall that MHC arises from ACC that forms in solutions with high aCO_3^{2-}/aCa^{2+} (>1.0) and/or high aMg^{2+}/aCa^{2+} (>6.0) (**Fig. 4A**). Furthermore, the minor amounts of nesquehonite and hydromagnesite observed in a few experiments (**Appendix Fig. A2**) leads us to speculate that some $MgCO_3^\circ$ may form during the transformation. Accordingly, we can write the balanced reaction:

Comparisons of the trends in **Figure 6** are consistent with the stoichiometries of Reactions (4,5) which show: 1) A sharp decrease in solution pH indicates ACC is transforming to calcite whereas a marked increase in solution Mg_{tot}/Ca_{tot} indicates the onset of MHC. The data show that calcite formation is generally associated with lower alkalinity solutions, hence their lower pH buffering capacity. 2) Under the conditions investigated in this study, however, initial pH cannot be used to predict initial polymorph. **Figures 6A,C** show that ACC can transform to calcite or MHC from similar pH solutions. 3) Monohydrocalcite formation and its associated textures can be missed if pH alone is monitored. Temporal sampling of cation concentration and solids is necessary to detect the appearance of this phase.

4.1.4 Insights for ACC structure and composition?

The polymorph-specific evolution of solutions during the transformation raises the question of whether 1) the initial ACC is formed with inherent structural and/or chemical differences at the time of synthesis, or 2) the polymorphs are determined by conditions at the time of ACC to crystal transformation. **Figure 4A** suggests the latter process is predominant with fields of polymorphs correlated with output solution composition. The isotope tracer study of the ACC to calcite transformation is consistent with this interpretation (Giuffrè et al., 2015). Indeed, previous studies propose that ACC can display structural or chemical differences with a ‘polyamorphism’ that sets the stage for transformation to different crystalline polymorphs (Gebauer et al., 2010; Cartwright et al., 2012). While speculative, our measurements of a polymorph-dependent evolution of solution chemistry may support to this idea. The incipient ACC may have distinct composition differences that include a carbonate-bicarbonate solid solution. Also, **Appendix Figure A3** shows the initial ACC synthesis conditions provide a rough indication of the crystalline polymorphs into which it transforms (i.e., within the fields similar to those in **Figure 4A**). Nevertheless, the comparison is inconclusive because the compositions of the input solutions are correlated with the transformation solutions. It is also possible that solution composition at the time of transformation biases the barriers to the evolution of ACC to distinct crystalline products. The data do provide, however, a basis for designing future structure and composition studies of ACC.

4.2 Effects of an ACC Pathway on Calcite Composition

The measurements in this study allow us to quantify the relationship between ACC composition and the composition that is recorded in incipient calcite. By comparing the Mg content of ACC and the resulting calcite, we find a 1:1 relationship (**Fig. 7**). Acknowledging

some scatter in the data with offsets of $\approx 1\text{--}3$ mole % MgCO_3 (see **Appendix Table A2**), the approximately linear dependence appears general to calcites that form in stirred and unstirred conditions. For calcites that form under mixed and quiescent conditions, respectively, the relationship extends to $\approx 14\%$ and almost 30 mol% MgCO_3 . Recall that the upper end of the calcite range is limited for stirred conditions because MHC is produced (e.g. **Fig. 4A** and **Fig. 5A**).

*** FIG. 7 ***

Our finding of a simple 1:1 dependence suggests Mg signatures in calcite are determined at the time of ACC precipitation. Thus, Mg partitioning into calcite to produce high mol% Mg must be controlled by local re-equilibration of solutions and solids at the time of transformation for the conditions of these experiments. This interpretation is consistent with an isotope tracer study of the ACC to calcite transformation (Giuffrè et al., 2015) that concluded that the transformation is dominated by a dissolution-reprecipitation process in the presence of bulk solution. Hence, the Mg content of the ambient/parental solution is recorded in the subsequent growth of calcite during the transformation. Additional investigations report a similar dependence on the Mg content of ACC and calcite (Wang et al., 2012; Han et al., 2013), but they show the 1:1 dependence breaks down at very high solution Mg/Ca levels (up to 80 and 16, respectively) such that the amount of Mg in calcite reaches a plateau at about 35–40 mol % MgCO_3 .

Detailed structural analyses during the transformation will be necessary to decipher the processes by which physical mixing influence the resulting polymorphs and their compositions. We hypothesize that quiescent conditions create a diffusion-limited environment that allows local solution Mg/Ca to increase to extreme levels as the calcite begins to precipitate. Because

Mg is a strong inhibitor to calcite growth (Lippman, 1973; Folk, 1974; Morse, 1983; Davis et al., 2000; Stephenson et al., 2008), the transformation must proceed by reducing the free energy (supersaturation) through nucleation, i.e. the ACC spherulites relax to produce a Mg-rich calcite (Wang et al., 2012; De Yoreo et al., 2015). The comparable size of the high-Mg calcite spherulites and the original ACC particles support this explanation (compare **Fig. 2A, B, C**).

4.3 Dependence of Calcite Composition on ACC versus Classical Pathway

The measurements in this study also present an opportunity to compare the Mg content of calcites formed via transformation of ACC versus a classical growth process. Both processes are active in biological and geological systems, but environmental proxy models that investigate calcite composition make the implicit assumption that signatures are independent of crystallization process. To explore this question, we compare the Mg content of calcites grown by two pathways relative to their initial parental solution composition: 1) non-classical two-step process via ACC (this study) and 2) direct growth from solution by classical step propagation in simple Mg-Ca-CO₃ solutions and synthetic seawater.

To compare the measurements in this study with previous investigations that report the composition of calcite that grew by step propagation, we compiled data using three criteria: 1) provide direct evidence for growth by step propagation or make direct claim of classical crystal growth; 2) report Mg content of the resulting calcite; and 3) provide sufficient information to determine the parental solution Mg/Ca. To our knowledge, only five other studies meet all of these criteria. The AFM studies of calcite step growth (Davis et al., 2000; Stephenson et al., 2008) assume the input/output compositions of these high flow rate experiments are approximately equal. Seeded growth measurements conducted in synthetic seawater were also included in our comparisons using data compiled in Mucci and Morse (1990) from three

previous studies (Mucci and Morse, 1983; Mucci et al., 1985; Mucci, 1987). Note that some of the 25°C data points were interpolated from 5°C and 40°C data. All data are summarized in **Appendix Table A3**.

The resulting trend in **Figure 8** indicates the Mg content of calcite grown by an ACC or classical step growth pathway is correlated with solution Mg_{tot}/Ca_{tot} at the time of initial precipitation. Data from this study reports the x-axis using the composition of the output solution that was separated from the ACC-solution slurry. Fitting a linear function to the 34 measurements reporting calcite formation in simple solutions gives:

$$\text{mol\% MgCO}_3 \text{ (calcite)} = (3.08 \pm 0.15) [Mg_{tot}/Ca_{tot}] \quad (6)$$

where $R^2 = 0.89$. The $\approx 3:1$ relationship is general to calcite growth where bulk water is present, and the correlation exists whether the solution is mixed or quiescent during growth by a step propagation process or via an ACC intermediate.

For comparison, the Mg content of calcites grown in synthetic seawater using a seeded growth method are also shown using data summarized in Mucci and Morse (1990) from three previous studies. These measurements also produce a linear trend:

$$\text{mol\% MgCO}_3 \text{ (calcite)} = (1.16 \pm 0.05) [Mg_{tot}/Ca_{tot}] \quad (7)$$

where $R^2 = 0.92$. Thus, the relationship for synthetic seawater shows a lower slope with a $\approx 1:1$ dependence. This study cannot deduce the physical basis for the different dependences in Eq (6) and (7), the lower slope associated with synthetic seawater is consistent with laboratory measurements showing that synthetic seawater suppresses the Mg content of calcite (Zhong and Mucci, 1989)—a result that was explained by competition from sulfate ion. For further discussion of this and other studies that investigated the effect of ionic strength on calcite composition, see Stephenson et al. (2011) and Table 1 therein.

*** FIG. 8 ***

Returning to **Fig. 8**, the data set that yields Eq (6) provides the only direct comparison of calcite compositions produced by multiple pathways (to our knowledge). Nevertheless, we recognize that the data set is limited and Eq (6) should be interpreted with caution. The number of available data is relatively small, and span of values determined from the AFM studies are limited to very low Mg concentrations because step propagation becomes immeasurably slower at higher levels (Davis et al., 2000; Stephenson et al., 2008). Finally, the low supersaturation conditions associated with step growth do not have significant overlap with the high supersaturations associated with a transformation from ACC, as a consequence of the different growth methods. In spite of these differences, 34 data points from multiple studies conducted over a range of supersaturation values show a correlation that reiterates the primary control on Mg content of calcite is the Mg:Ca ratio of the initial mineralizing solution. More importantly, in the presence of bulk solutions, the relationship suggests the process by which calcite forms is secondary.

5. CONCLUSIONS AND IMPLICATIONS

5.1. Transformation as an Interplay of Chemical and Physical Conditions

This inorganic study used a mixed-flow reactor to synthesize ACC under quantified chemical conditions and monitor the evolution of ACC to crystalline products within the bulk solution. For the conditions of this study, the measurements show three variables are important in determining the crystalline polymorph that forms—two chemical and one physical. First, the data reiterate the importance of Mg/Ca as a master variable in carbonate mineralization. High ratios increase the lifetime of ACC and influence the type of crystalline polymorph that forms as the initial and the long-term product. The data suggest that $\text{CO}_3^{2-}/\text{Ca}^{2+}$ may be an important,

second, master variable (**Fig. 4AB**). Indeed, previous laboratory and field studies report anecdotal evidence that the CO_3^{2-} concentration and $\text{CO}_3^{2-}/\text{Ca}^{2+}$ are significant variables in polymorph selection (Sandberg, 1983; Mackenzie and Pigott, 1981; Given and Wilkinson, 1985; Wilkinson and Given, 1986; Rodriguez-Blanco et al., 2014).

As a third variable, physical mixing further influences the initial polymorph that forms from ACC. Stirred solutions produce MHC as a metastable intermediate over a wide range of conditions. In contrast, quiescent conditions slow the rate of ACC transformation and enlarge the range of solution compositions ($a\text{Mg}^{2+}/a\text{Ca}^{2+} > 12$) that produce calcite. This combination of composition and mixing opens a pathway to the formation of very high Mg calcites (up to 26 mol% MgCO_3). Neither organic molecules nor extreme pH is required.

This interplay of chemical and physical conditions provides a framework for reconciling apparent inconsistencies (e.g. discussion of **Table 1**) between previous studies that investigated ACC and the crystalline polymorphs it transformed into. Returning to **Table 1**, seven studies report that stirred conditions produce calcites with relatively lower Mg contents. Although three different experimental methods are used, they consistently show that ACC transforms to calcites with 0–8 mol% MgCO_3 with stirring. In contrast, eight studies that investigated the ACC transformation in the absence of stirring produced very high-Mg calcite. Reports that some products contain 30–40 mol% Mg are consistent with our finding (e.g. **Table 1**).

5.2 Monohydrocalcite: An Overlooked Polymorph?

Our observations that ACC transforms to monohydrocalcite as the initial phase for a broad range of solution compositions suggests MHC may be an often overlooked polymorph. This metastability of MHC is consistent with sparse occurrences in natural settings. As a biomineral, MHC is limited to highly specific environments such as the calcareous corpuscles of

tapeworms (Señorale-Pose et al., 2008), the guinea pig bladder stone (Catherine et al., 1977), some bacterial cultures (Rivadeneyra et al., 2004), skeletal products in some mollusks (Lowenstam, 1981), vertebrate otoliths (Carlström, 1963), and as a decay product of the Saguaro cactus (Garvie, 2003). In geologic settings, MHC is associated with extreme environments that contain significant magnesium and other ions that apparently inhibit the formation of calcite and aragonite. Good examples are found in the sediments of saline alkaline lakes (Stoffers and Fischbeck, 1974; Taylor, 1975; Swainson, 2008; Last et al., 2010; Nishiyama et al., 2013), saline spring waters (Ito, 1993), the speleothems of limestone (Fischbeck and Müller, 1971) and basaltic caves (Léveillé et al., 2000), as well as polar systems (Bird et al., 1991; Dahl and Buchardt, 2006). In these environments, MHC is typically associated with calcite, aragonite, dolomite ($\text{Ca,Mg}(\text{CO}_3)_2$), hydromagnesite, and nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) (Fischbeck and Müller, 1971; Nishiyama et al., 2013).

Despite limited occurrences of MHC in natural systems, there is potential for its widespread formation as a metastable phase. The findings in this study lead us to concur with the conclusion that some calcite and aragonite deposits may have secondary origins (Rodriguez-Blanco et al., 2014). The role of MHC as an intermediate phase is demonstrated by the absence of a pH shift during the ACC transformation (**Fig. 6B**) in contrast to the marked decrease in pH that signals the onset of calcite formation (compare **Fig. 4A**). In the lab, these findings call for careful monitoring (solution Mg/Ca levels) and repeated analysis of solids to obtain a more accurate picture of transformation processes. In the field, long-standing assumptions regarding calcification should consider multi-step pathways to mineral formation that may include MHC.

5.3 Consequences of an Amorphous Pathway for Calcite Composition

The quantitative design of this study allows us to explore the consequences of an amorphous pathway on Mg signatures in calcite. First, we find a 1:1 relationship between the Mg content of ACC and the subsequent calcite that forms. The trend is general to calcites that transform under both stirred (limited range) and unstirred conditions over compositions of 0–26 mol% MgCO_3 . This finding is consistent with evidence that the ACC to crystal transformation process occurs by dissolution-reprecipitation when water is present (Giuffrè, et al., 2015). The ACC pathway extends the amount of Mg that can be incorporated into the calcite products. For example, calcite that forms via a simple step growth process and cannot incorporate more than 4% MgCO_3 (Davis et al., 2000) while we show that calcite with up to 26% MgCO_3 becomes possible. Here, reprecipitation likely involves nucleation and aggregation of Mg-rich calcite particles.

We further find a $\approx 3:1$ relationship between the solution ratio of $\text{Mg}_{\text{tot}}/\text{Ca}_{\text{tot}}$ and the mole % MgCO_3 of the resulting calcite. Although the number of measurements is limited, the data from experiments that were conducted in bulk solutions indicate the Mg content of the final calcite could be independent of formation by a classical versus ACC pathway.

The single composition trend that emerges for both pathways raises the question of whether most calcite compositions are far from equilibrium. The 1:1 dependence between the Mg content of initial ACC and the composition of the resulting calcite (**Fig 7**) shows the ACC transforms without excluding Mg to give a final product that is far from equilibrium in terms of Mg content. Yet, the compositions of the calcites originating from ACC fall along a similar trend to those produced by a classical step growth process (**Fig. 8**). The logical conclusion from

the findings is that all of these laboratory-formed calcites, regardless of mineralization process, are recording nonequilibrium compositions.

5.4 Traditional Picture of Carbonate Formation Needs to be Revisited.

Insights from our study suggest the traditional picture of controls on CaCO_3 polymorph selection needs to be revisited. Most early investigations assumed the sequential appearance of crystalline polymorphs is governed by the Ostwald step rule (as noted later) and the role of kinetics was debated. For example, the appearance of aragonite instead of calcite at sufficiently high Mg^{2+} concentrations was attributed to the reversal of the order of the apparent solubility of Mg -calcite relative to aragonite, but the observation that aragonite is the only polymorph to spontaneously form from supersaturated seawater could also argue for the role of kinetic factors (see discussions in Carlson, 1983 and Morse, 1983). Yet, other studies recognized kinetics could determine the initial polymorph to form and influence composition (Matthews, 1968; Given and Wilkinson, 1985). For these relatively simple solution compositions, we show that, even at Mg^{2+} concentrations where aragonite will eventually dominate, the initial precipitate is calcite.

In that regard, the sequence of calcite-to-aragonite is analogous to initial ACC formation followed by transformation to MHC, calcite, or aragonite. It is an example of the heuristic known as the Ostwald-Lussac rule of stages—also called the Ostwald step rule—wherein a metastable phase, whose appearance would not be predicted based on thermodynamic stability, appears initially for kinetic reasons and is replaced over time by progressively more thermodynamically stable phases (De Yoreo et al., 2015). This behavior, though often called non-classical, may be completely consistent with the expectations of classical nucleation theory. Our previous analysis shows that creating a classical nucleation barrier small enough to permit nucleation of the stable CaCO_3 phase on a reasonable timescale, requires a supersaturation that is

sufficiently high to render all other phases potential metastable intermediates (Hu et al., 2012). Because the nucleation barrier scales with the cube of the interfacial energy and the latter scales inversely with solubility (De Yoreo and Vekilov, 2003), as aragonite becomes less soluble than calcite at greater Mg concentrations, the nucleation barrier is thus expected to exceed that of calcite at sufficiently high supersaturation, leading to the observed order of appearance.

This reaffirms the point that some calcite and aragonite deposits may have formed under conditions that allowed alternative pathways and thus could be of secondary origin (e.g. Rodriguez-Blanco et al., 2014). For example, high-Mg calcite and monohydrocalcite transform to aragonite over long periods, but early studies (Berner, 1975; Mucci and Morse, 1983; Bischoff et al., 1987) may not have had the temporal resolution to identify intermediate phases and recognize a sequential process. As seen in this study, early phases influence local solution composition and the morphology/texture of the early stage products. Similarly, the ability of organisms to precisely control local alkalinity, pH, and thus supersaturation during calcification could also enable precipitation of metastable phases (Dupraz et al., 2009; Gagnon et al., 2013). Macromolecules impose an additional level of control.

Other aspects of the traditional picture may also be incomplete. To our knowledge, physical mixing is not widely recognized as a control on polymorph selection in geologic settings. Exceptions are seen in reports that chemical/physical mixing zones influence dolomite formation and low- versus high-energy settings (Folk and Land, 1975; Hardie, 1987). Also, Duguid et al. (2010) consider the influence of wave energy on ooid structure and composition. As a mechanism-based picture of calcification begins to emerge, we may find alternate pathways are the missing link to interpreting the unusual calcite compositions and textures that occur in geological and biological systems but unexplained by traditional crystal growth models.

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Captions only.

Fig. 1. Schematic of the mixed flow reactor system used in this study (after Blue et al., 2013). Arrows indicate the direction of flow. Star denotes the location of the filter.

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Fig. 4. The solution composition associated with ACC formation produces fields of crystalline polymorphs when quantified as $a\text{Mg}^{2+}/a\text{Ca}^{2+}$ and the $a\text{CO}_3^{2-}/a\text{Ca}^{2+}$. **(A)** When the ACC-solution slurry is stirred during the transformation, monohydrocalcite (MHC) is formed for a broad range of conditions. MHC eventually transforms to aragonite (for all conditions), nesquehonite, and possibly hydromagnesite (at the highest Mg levels). **(B)** The time required for ACC to transform into the initial crystalline polymorph correlates with solution Mg/Ca. Calcite forms in low to moderate Mg/Ca (0–4) and transforms between within three hours. Aragonite occurs when Mg/Ca is moderately high (~5) and transformation requires up to 10 hours. MHC is formed when solutions begin with higher Mg/Ca (>4) and the transformation is generally slow, sometimes up to 45 hours.

Fig. 5. The time required for ACC to transform to calcite increases with the steady state solution Mg:Ca ratio for **A)** stirred and **B)** unstirred conditions. For a given ratio of Mg:Ca in solution, the resulting calcites produce similar compositions and transformation times. However, in the absence of stirring, the Mg content of calcites that can transform is almost doubled to 26 mole%. At higher Mg/Ca levels, for stirred and unstirred conditions, the transformation produces MHC.

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Table 1. Experimental studies of ACC transformation into crystalline polymorphs with calcite compositions.

Study	Synthesis method	Temp (°C)	Initial [Mg]:[Ca]	Initial [CO ₃ ²⁻] (M)	Phases reported ¹	Calcite mol% Mg
<i>Stirring during ACC transformation</i>						
Sand et al., 2011	Batch reactor with Na ₂ CO ₃ ²	24	n/a	0.025	ACC; Calc.; Arag.; Vat.	n/a
Nishiyama et al., 2012	Batch reactor with Na ₂ CO ₃	25	0–2:1	0.03-1.0	ACC; MHC; Calc.; Vat.	0–8
Rodriguez-Blanco et al., 2012	Batch reactor with Na ₂ CO ₃	10-25	0; 9:1	1.0	ACC; Calc.; Vat.	10
Zhang et al., 2012	Batch reactor with Dimethyl carbonate ³	30	0–5:1	0.06	ACC; MHC; Calc.; Arag.	not reported
Niedermayr et al., 2013	CO ₂ diffusion	6-40	0–5:1	variable	ACC; Vat.; Arag.; Calc.	0–4
Rodriguez-Blanco et al., 2014	Batch reactor with Na ₂ CO ₃	21	7:3	1.0	ACC; MHC ⁴ ; Calc.	3–7
<i>This study</i>	<i>Mixed flow reactor with NaHCO₃</i>	25	<i>0.4:1–6:1</i>	<i>0.05–0.20</i>	<i>ACC; Vat.; Calc.; Arag.; MHC</i>	<i>4–13</i>
<i>No stirring during ACC transformation</i>						
Towe and Malone, 1970	(NH ₄) ₂ CO ₃ diffusion	23–25	5:1	not reported	ACC; MHC; Nesq.; Arag.; H-Mg calc.	3–32
Raz et al., 2000	(NH ₄) ₂ CO ₃ diffusion	25	4:1	not reported	ACC; Arag.; H-Mg calc.	11–14
Loste et al., 2003	Batch reactor with NaHCO ₃ (open to air)	25	0–10:1	0.54	ACC; MHC; Arag.; Vat.; H-Mg calc.	0–22 (top & bottom samples)
Ajikumar et al., 2005	(NH ₄) ₂ CO ₃ diffusion	4; 25	1:9–1:3	not reported	ACC; Calc.	“low Mg”
Lam et al., 2007	(NH ₄) ₂ CO ₃ diffusion	25	2:1–9:1	not reported	ACC; Nesq.; MHC	n/a
Wang et al., 2012	(NH ₄) ₂ CO ₃ diffusion	25	0-6:1	5.2	ACC; H-Mg calc. ; Arag	0–40
Han et al., 2013	Batch reactor with NaHCO ₃	25	0.5:1–10:1	0.20	ACC; H-Mg calc.	10–30
<i>This study</i>	<i>Mixed flow reactor with NaHCO₃</i>	25	<i>0.4:1–6.5:1</i>	<i>0.07–0.20</i>	<i>ACC; MHC; H-Mg calc.</i>	<i>7–28</i>

¹ACC = amorphous calcium carbonate; Calc = Calcite; Arag. = Aragonite; Vat. = Vaterite; MHC = Monohydrocalcite; H-Mg = High-Mg; Nesq. = Nesquehonite (MgCO₃•3H₂O). ²Stirring was gentle versus vigorous. ³Stirring by shaking.

⁴Produced high Mg MHC that subsequently transformed to low Mg MHC.

Chemical and physical controls on the transformation of amorphous calcium carbonate into crystalline CaCO_3 polymorphs

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FIGURES WITH CAPTIONS

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