

## Influence of Temperature on Calcium Carbonate Polymorph formed from Ammonium Carbonate and Calcium Acetate

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### Abstract

This research used ammonium carbonate and calcium acetate in the preparation of various calcium carbonate polymorphs for biomimetic composite applications. Biominerals were synthesized at temperatures ranging from 25 to 80°C to investigate the effect of synthesis temperature on the abundance of vaterite, aragonite, and calcite, delineating regions that are favorable for the formation of these different calcium carbonate polymorphs. In particular, it was observed that lower temperatures of 25-30°C were favorable for vaterite formation with increasing crystallite size at the higher temperature. Calcite was the preferred polymorph formed at temperatures of approximately 50°C. Although a trace of aragonite was observed at 70°C, it was not observed at the highest temperature investigated (80°C). The absence of aragonite formation at elevated temperatures may be a function of the lower pH (~8.4) in the ammonium carbonate/calcium acetate system compared to ~9.9 for the sodium carbonate/calcium acetate system that promotes the formation of vaterite over aragonite. These results are important when developing biomimetic materials incorporating calcium carbonate with different polymorphs and crystal sizes.

### Introduction

The syntheses of composites for protection or support that include both inorganic and organic components such as bones, shells, and teeth are an inspiration for bio-inspired materials' design[1,2]. Structurally, these materials typically are composites made from organic molecules as the matrix/binding phase and very often are present in various polymorphs of calcium carbonate. Nature has evolved mechanisms to control crystal growth and morphology, thereby producing mineralized structures that have engineering properties that far surpass the biomaterial calcium carbonate. These unique properties derive from the natural polymorphs and morphology of CaCO<sub>3</sub>. As such, the development of new strategies to produce these materials with an eye toward controlling the polymorph formed, and the size of the crystallites becomes extremely important. These CaCO<sub>3</sub> polymorphs with unusual morphologies can potentially be promising candidates for advanced materials due to the importance of shape and

texture in determining properties of materials. The precipitation of the polymorphs of calcium carbonate is critical to the formation of biomimetic materials[2,3]. Careful control of the critical variables in the process determines the shape and crystal structure of the calcium carbonate[3]. Research on calcium carbonate crystal precipitation from solution has demonstrated that the final product that forms during this reaction includes the polymorphs aragonite, vaterite, and calcite[4-15]. Although calcite is the most thermodynamically stable phase under ambient conditions, many authors have shown that it may take hours or longer for the transformation from the other polymorphs to calcite[5]. Previous research pointed out that many factors affect the yield of a specific type of polymorph such as magnesium to calcium ion ratios, phosphate and sulfate ions, organic compounds, and acids (change in pH), but among the most important are the carbonate ion controlled kinetics[11], metal ions[9], and temperature[3]. One author used a constant composition method to produce calcite, aragonite, and vaterite[4] and found that, from the controlled variables that they tested, which included solution pH, temperature, supersaturation[10], concentration ratio of the components, and concentration of additives,

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solution pH and temperature were the most important factors in determining the polymorphs of  $\text{CaCO}_3$  formed. Furthermore, they found that at room temperature, solution pH is the most significant factor, and high-yield polymorphs are present at different pH values. At a high temperature, aragonite becomes the major product at a pH below [12]. The temperature and pH values affect the kinetics of crystal formation, which favors certain polymorphs of calcium carbonate over the others. It was similarly found that aragonite was the predominant phase at temperatures over  $50^\circ\text{C}$  and was virtually the only phase present at temperatures above  $70^\circ\text{C}$  [5]. Another author used a novel method for production of calcium carbonate through the use of ammonium carbamate and calcium acetate that showed vaterite formed at low temperatures and calcite was formed at  $50^\circ\text{C}$ , although their research did not attempt crystallization at higher temperatures than  $50^\circ\text{C}$  [6]. This study examined the effect of temperature on calcium carbonate polymorphism with synthesis being performed using a different system of ammonium carbonate and calcium acetate. The study also extends the range of temperatures studied up to  $80^\circ\text{C}$ . Morphology and structure were investigated using Scanning Electron Microscopy (SEM) and x-ray diffraction (XRD). The following sections present details on the methods utilized and the results of the investigation.

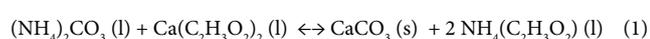
## Materials and Methods

### Materials

Calcium acetate with a molecular weight of 158.17 g/mol ( $\geq 99\%$ , Reagent Plus) was obtained from Sigma-Aldrich. Ammonium carbonate at 90.07 g/mol (Certified ACS,  $> 99\%$ ) was purchased from Fisher Scientific. A digital stirring hot plate and thermometer were utilized to control and monitor the temperature of the solutions.

### In-solution synthesis of calcium carbonate

The crystallization experiments to produce  $\text{CaCO}_3$  were performed by preparing 0.5 M solutions of ammonium carbonate  $(\text{NH}_4)_2\text{CO}_3$  and calcium acetate  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  followed by mixing at temperatures of 25, 30, 40, 50, 60, 70, and  $80^\circ\text{C}$ . The initial solutions were preheated at the desired temperature and stabilized for 30 min. Ammonium carbonate solutions were tightly sealed with parafilm paper (American National Can) to minimize the loss of ammonia and the introduction of carbon dioxide from the atmosphere. All solutions were stirred moderately until the reactants were completely dissolved. The pH of the solutions was measured before and subsequent to mixing. The measured pH values were 8.39 for the ammonium carbonate solution and 8.26 for the calcium acetate solution. After mixing the two solutions together, the pH equilibrated to 8.36. The ammonium carbonate was poured into beakers containing calcium acetate solution while being stirred, producing calcium carbonate following the net reaction (1).



The precipitated calcium carbonate slurry was filtered using filter paper (Whatman Ashless 9.0 cm) mounted inside a fil-

tration system operated under vacuum. Immediately after the precipitate was recovered, it was rinsed in deionized water and dried in a furnace at  $105^\circ\text{C}$ . The resulting precipitated powder was stored in a desiccator for further characterization using SEM and XRD analysis.

### Methods

X-ray Diffraction patterns, to be used for semi-quantitative phase identification and phase fraction analysis, were obtained using an X'Pert Pro Materials Research Diffractometer (Panalytical, Inc.) equipped with a  $\text{Co-K}\alpha$  X-ray source operated at 45 KV and 40 mA. Diffraction patterns were obtained from  $2.5$  to  $70^\circ 2\theta$  with a step size of  $0.016^\circ 2\theta$  with a total scan time of 2 hr. Phase identification was performed using MDI Jade 2010 analysis software for qualitative phase identification with ICSD powder diffraction file (PDF) reference databases and semi-quantitative phase fraction analysis using whole pattern fitting techniques.

SEM imaging was performed using a Nova NanoSEM 630 (FEI, Inc.) field-emission SEM, capable of high-resolution imaging on non-conductive materials. Imaging was performed in low-vacuum mode at pressures of 0.1 mbar and an accelerating voltage of 15 kV. All images were acquired using a backscattered electron detector to improve phase contrast. Samples for SEM imaging were prepared by depositing approximately 5 mg of material onto double-sided carbon tape followed by light dusting with clean compressed air to remove free particles.

## Results and Discussion

### X-ray Diffraction Analysis of $\text{CaCO}_3$ Polymorphism

XRD analysis was used to determine the phase compositions produced at the various temperatures. The predominant phase present for crystals precipitated at  $25^\circ\text{C}$  and  $80^\circ\text{C}$  was vaterite, while at  $50^\circ\text{C}$  the pattern showed clearly that the phase present was calcite (Figure 1). The presence of less than  $\sim 5\%$  aragonite was observed in one sample made at  $70^\circ\text{C}$ .

The temperature control was crucial during precipitation reactions as demonstrated by the results presented herein and is one of the most critical factors during calcium carbonate crystal growth. Based on the results from experiments performed by preheating the solutions at  $25^\circ\text{C}$  through  $80^\circ\text{C}$ , a distribution of the fraction of calcium carbonate polymorphs is presented in Figure 2. The polymorph vaterite was the predominant phase at both low and high temperatures with calcite being the dominant phase at the intermediate temperature of  $50^\circ\text{C}$ . The percentages of calcium carbonate crystals that were precipitated for this particular system from the samples produced are given in Table 1.

Ogino et al. [5] indicated a quite different assemblage at temperatures above  $50^\circ\text{C}$  for the sodium carbonate/calcium acetate system, whereby the stable phase was aragonite and not vaterite or calcite. One possible explanation is that the elevated

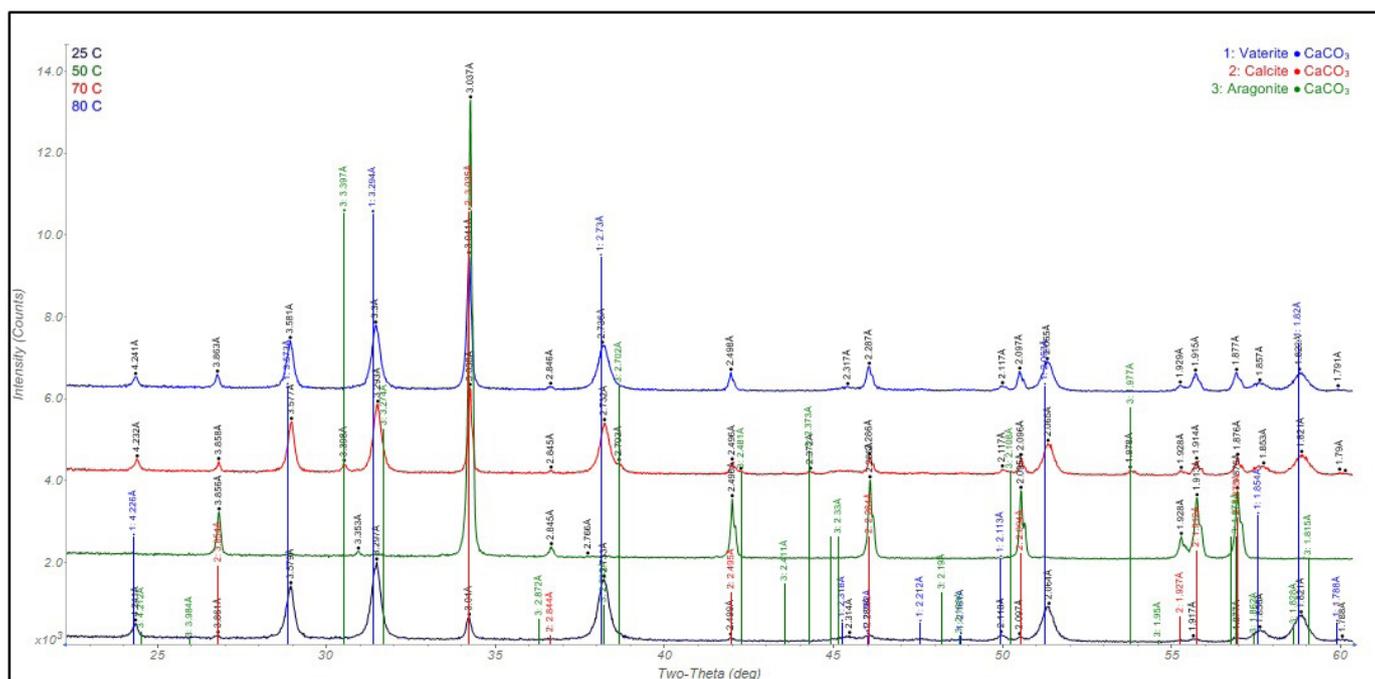


Figure 1. X-ray diffraction patterns for  $\text{CaCO}_3$  crystals precipitated at 25, 50, 70, and 80 °C.

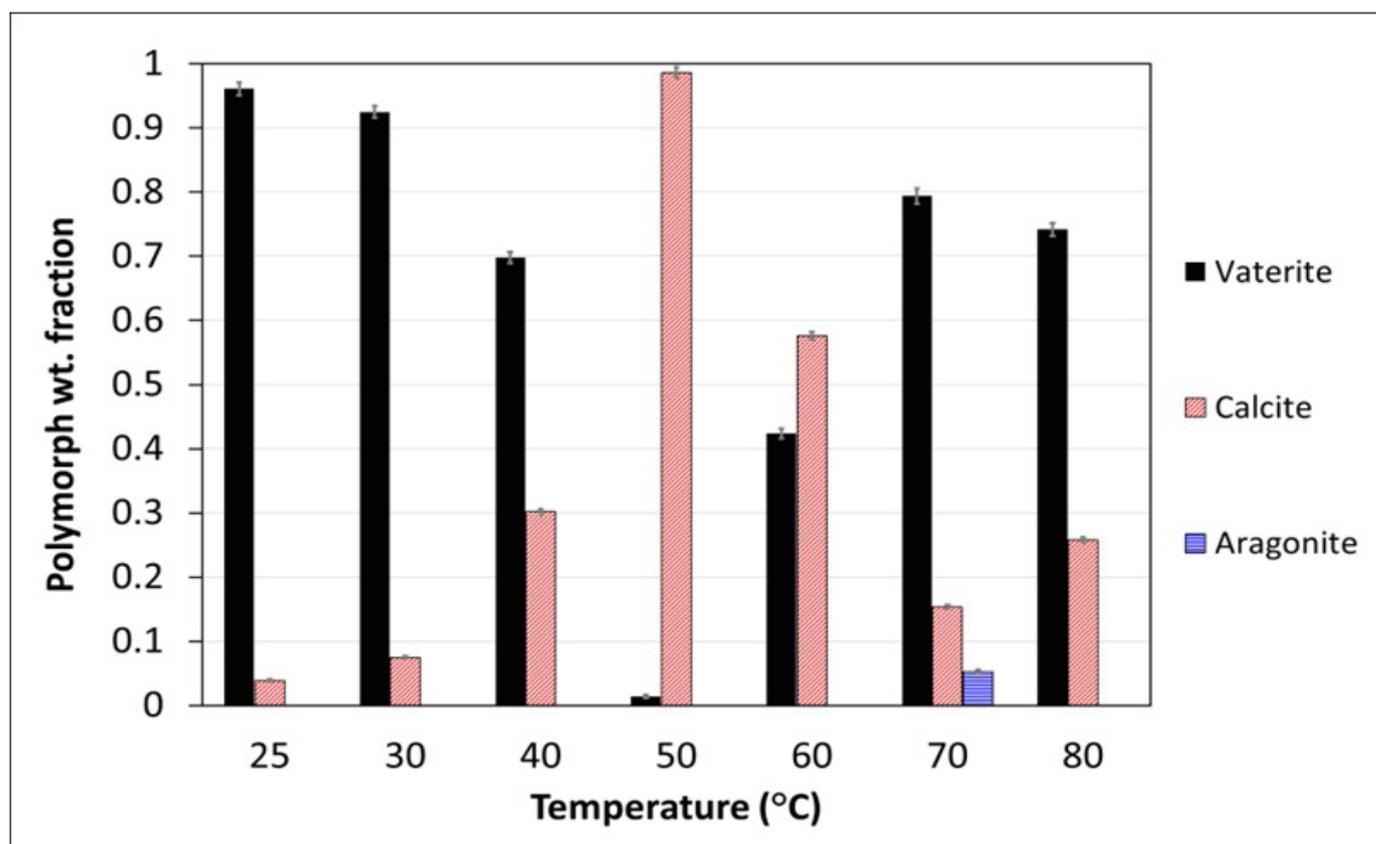
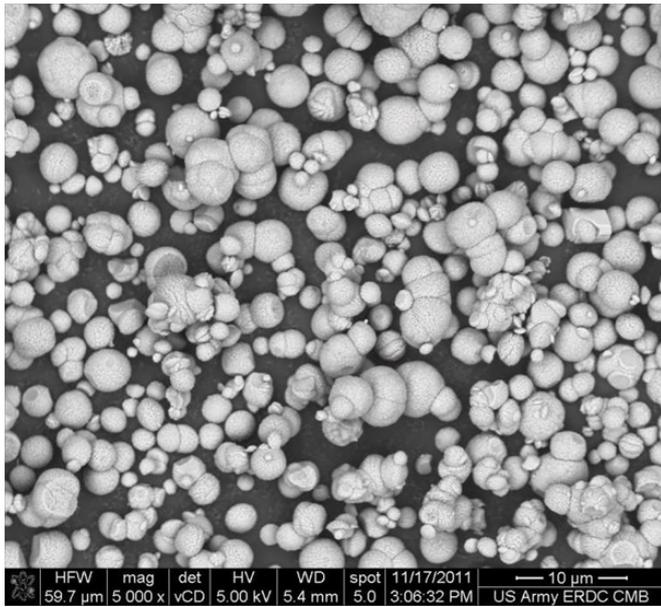


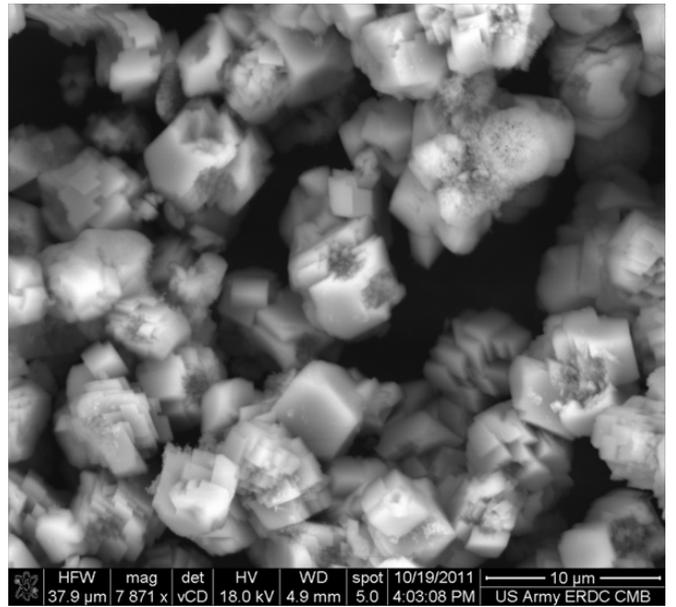
Figure 2. Bar chart of different polymorphs fractions by mass obtained at the synthesis temperatures (25-80 °C).

Temperature (°C)	25	30	40	50	60	70	80
Vaterite	0.961	0.925	0.698	0.014	0.424	0.794	0.742
Calcite	0.039	0.075	0.302	0.986	0.576	0.154	0.258
Aragonite	0	0	0	0	0	0.053	0

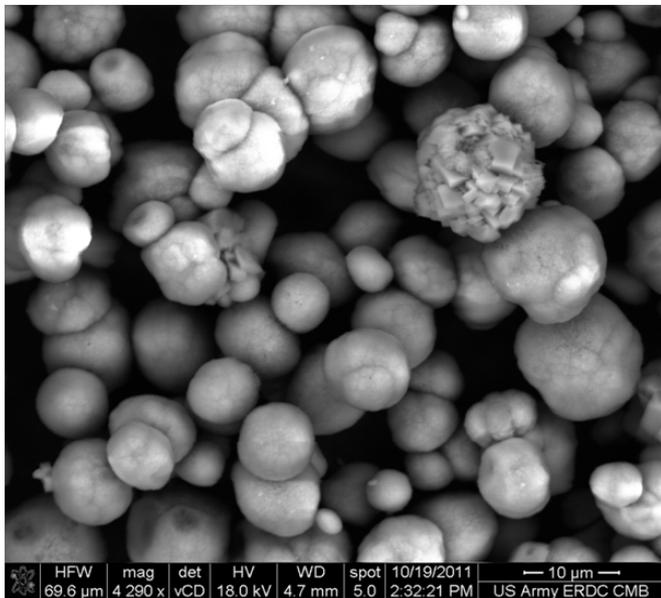
Table 1. Fractions of various polymorphs of calcium carbonate formed at each temperature (25-80 °C).



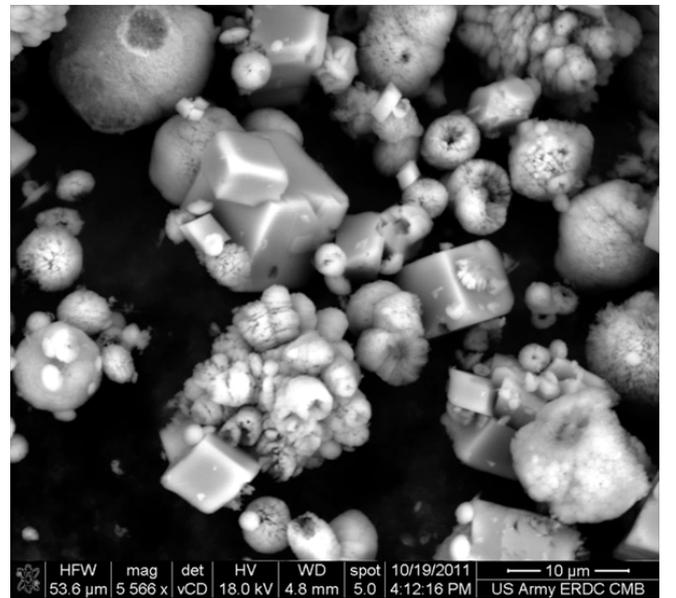
(a)



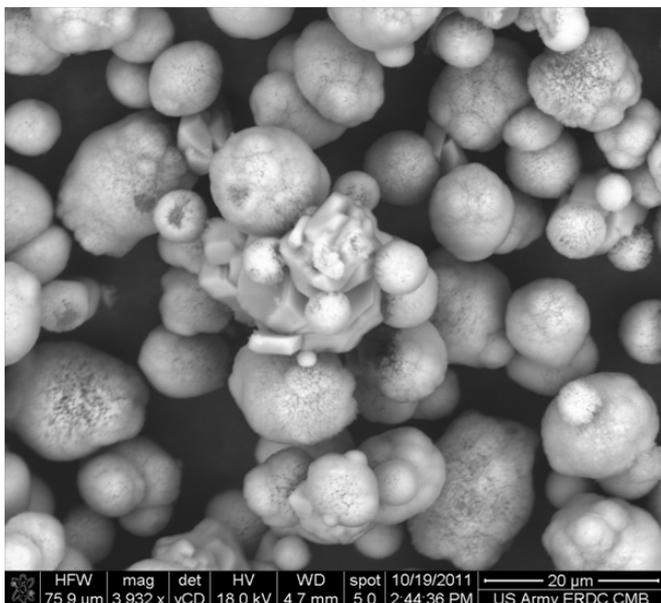
(d)



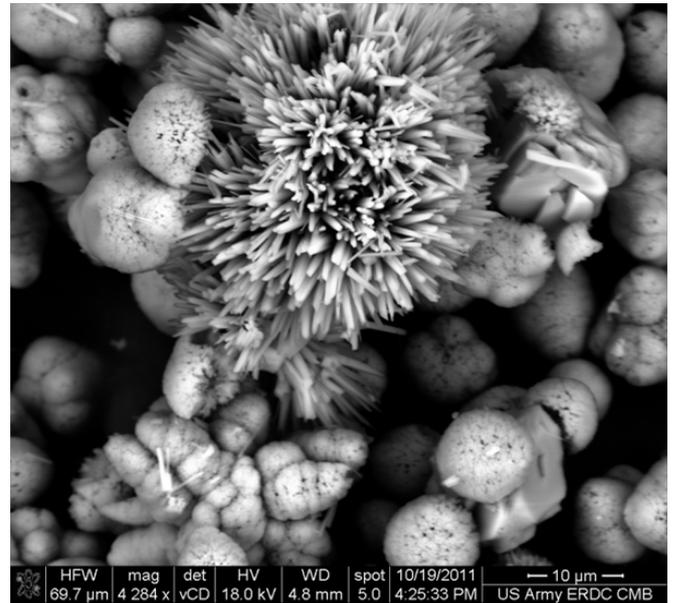
(b)



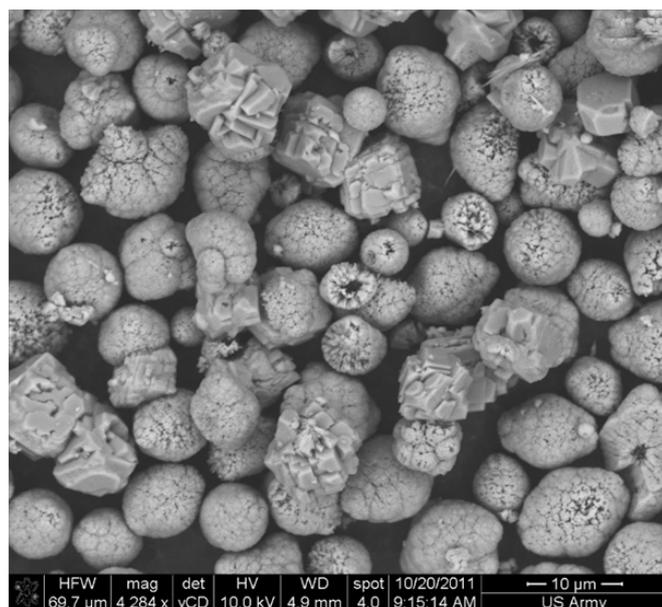
(e)



(c)



(f)



(g)

Figure 3. SEM images of calcium carbonate crystals precipitated at (a) 25 °C, (b) 30 °C, (c) 40 °C, (d) 50 °C, (e) 60 °C, (f) 70 °C, and (g) 80 °C.

pH present in the sodium carbonate/calcium acetate system changed the equilibrium assemblage. Investigations into determination of the effect of pH on the resultant calcium carbonate polymorph began by comparing the sodium carbonate system to the ammonium carbonate system. As indicated previously, the measured pHs were 8.39 for the ammonium carbonate solution and 8.26 for the calcium acetate solution with the resultant pH of the mixture at 8.36. Reactions of sodium carbonate (pH=11.28) and calcium acetate (pH=8.25) mixed together result in an equilibrium pH of 9.93. Rodriguez-Blanco et al. (1982) found that, at a neutral (~7) starting pH during mixing, the formation of calcite from amorphous calcium carbonate via a dissolution/reprecipitation mechanism was promoted, whereas, when starting from a solution at a high initial pH (~11.5), the transformation to calcite occurred via metastable vaterite, which formed via a spherulitic growth mechanism [16]. Furthermore they ascribe that these crystallization pathways are a function of the pH-dependence on composition, local structure, stability, and dissolution rates of the precursor phases. Friedman [17] attributed the lack of aragonite at depth in deep sea sediments to the dissolution of aragonite. One hypothesis is that the stability of aragonite may be promoted in the systems that have higher pH values. Rodriguez-Blanco et al. [16] indicate that, at lower pH values, there is a higher  $\text{CaCO}_3$  supersaturation that promotes the formation of vaterite. As such the production of aragonite at higher temperatures may be precluded due to the lower pH in the system using ammonium carbonate.

### Microscopic Investigation of Crystal Morphology

The morphology of the three polymorphs of  $\text{CaCO}_3$ , i.e., vaterite, aragonite, and calcite, were determined through SEM. Images of samples prepared at temperatures from 25 to 80 °C are shown in Figure 3. It was evident from previous work, as well as current results, that each of the phases formed a very different morphology [2,7]. Vaterite formed as spheroidal-shaped

crystallites, whereas calcite formed in a rhombohedral shape, and aragonite formed as acicular-shaped crystallites. The SEM image shows the spherical shape of the vaterite obtained at 25 °C (Figure 3a). At this temperature, the yield of vaterite is higher than for any other temperature, with a fraction of 0.961, for the system under study. It is also noted that at this temperature the smallest crystallites (about 1-2  $\mu\text{m}$ ) were formed. At 30 and 40 °C, which was only 5 °C higher in temperature than the sample depicted in Figure 3a, the coarsening of the vaterite crystallites was observed with crystallites size approaching 10  $\mu\text{m}$  (Figure 3b, 3c). Further crystallization of calcite is evident at 40 °C (Figure 3c). At 50 °C, there is a marked change in the polymorphs that formed (Figure 3d). In this sample, vaterite is virtually gone, and abundant calcite (crystallites about 1-2  $\mu\text{m}$ ) is observed in the sample. At 60 °C, calcite diminishes in abundance, and the presence of small vaterite crystallites (about 1-5  $\mu\text{m}$ ) are observed (Figure 3e). At 70 °C, large crystallites of vaterite (some crystallites up to 10  $\mu\text{m}$ ) are most abundant, but the presence of calcite and aragonite are also observed. Aragonite crystals are evident in the upper right corner of Figure 3f as the acicular, needle-shaped crystal structures. At 80 °C, all trace of aragonite is gone with only calcite and vaterite present in the sample. The results of the SEM investigations further support the XRD findings and indicate that temperature along with the reagents used for synthesis have a significant impact on the  $\text{CaCO}_3$  polymorph formed.

### Conclusions

The study presented herein utilized a synthesis technique with ammonium carbonate and calcium acetate for the preparation of various polymorphs of calcium carbonate at various temperature levels. XRD analysis of crystal structure and multi-phase composition of the precipitated carbonate indicated that temperature had a significant impact on the  $\text{CaCO}_3$  polymorph that was formed. Vaterite was predominantly formed at low and high temperatures along with calcite. Aragonite was only observed when materials were synthesized at 70 °C. These results are somewhat different from what has been reported by other researchers who have used a different series of reactants, which shifts the pH to either more acidic or basic levels. SEM investigations of crystallite size and morphology also indicated significant differences in crystal crystallite shape (spheroidal vaterite, acicular aragonite, and rhombohedral calcite) and size depending on the synthesis temperature used for synthesis, further supporting the findings of the XRD studies of mineralogy. These results provide additional guidance for techniques to control the polymorphism of  $\text{CaCO}_3$ , which is an important bio-compatible mineral phase present in many structural bio-materials. Such information is also useful for the synthesis of biomimetic and bio-inspired materials wherein biomineral phases such as  $\text{CaCO}_3$  and hydroxylapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) act as an inorganic phase in a hierarchical composite material.

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