

Investigation of amorphous calcium carbonate's formation under high concentration of magnesium: The prenucleation cluster pathway

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ABSTRACT

This paper investigates the formation of amorphous calcium carbonate under high magnesium concentration ($Mg/Ca = 6$) via several novel methods. While feeding calcium chloride solution into the mixed solution of magnesium chloride and sodium carbonate, a large amount of calcium ions (>0.13 mol/L) stably coexisted with the amorphous calcium carbonate in the solution. The calcium concentration detected by the calcium ion selective electrode was proportional to the calcium concentration added. Surprisingly, the ratio of magnesium to calcium in the amorphous calcium carbonate was just 0.07, and the concentration of calcium continued to increase in the solution after the formation of the amorphous calcium carbonate. We propose that stable prenucleation cluster formed in the solution, which stably coexisted with the amorphous calcium carbonate because of the incorporation of hydrated magnesium ions. The high dehydration free energy barrier of magnesium ions led to its slow dehydration. Also, the hydroxide ion helped to bypass the high dehydration free energy barrier. This research indicates the possible significant role of prenucleation cluster pathway in the calcium carbonate crystallization.

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1. Introduction

Calcium carbonate precipitation plays a vital role in nature, for example, in the formation of biomineralizing organisms' shells and spines [1]. It also influences human activities, particularly scaling in water pipes and desalination facilities. Although calcium carbonate crystallization is ubiquitous to our everyday lives and carbon circulation of earth, its crystallization mechanism remains unclear.

Amorphous calcium carbonate (ACC) is unstable. However, it can be prepared in the presence of impurities (magnesium), or under low temperature [2–4]. Multistep crystallization of calcium carbonate via $ACC \rightarrow$ vaterite \rightarrow calcite has been observed and studied by in situ small- and wide-angle X-ray scattering (SAXS/WAXS) technology [5]. Moreover, other transformation pathways also have been discovered, such as the transformation of ACC to aragonite, and the formation of aragonite via ACC or vaterite [6,7]. After mixing calcium chloride solution and sodium carbonate solution, it is believed that calcium carbonate crystallization follows an energetically downhill sequence: disordered hydrated $ACC \rightarrow$ less ordered and hydrated $ACC \rightarrow$ anhydrous $ACC \rightarrow$ vaterite \rightarrow aragonite \rightarrow calcite [8], which is by the Ostwald step rule [9].

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Prenucleation cluster (<1 nm), which appears similar to ACC and other more stable polymorphs, has been detected by cryo-TEM. It was also proposed that ACC could be formed by aggregation of these clusters [10]. In addition, prenucleation clusters play an essential role in crystallization of calcium phosphate [11]. Computer molecular dynamic simulations also gave evidence of prenucleation cluster existence. Contrary to classical theory that predicts the cluster is unstable in solution for their high surface energy, the calcium carbonate cluster can exist in the solution. Based on computer simulation results, the size of these clusters varies from several to hundreds of ions [12]. Furthermore, these clusters can be treated as a new liquid phase that separates from the mother solution [7].

Non-classical calcium carbonate crystallization which has been observed by researchers can be mainly attributed to the stable existence of clusters [11]. Thus magnesium ions can be incorporated into ACC because of the similar chemical properties of calcium and magnesium. [2,13]. High concentration of magnesium can alter the morphology of calcium carbonate crystal, and determine the final polymorph form of calcium carbonate (Aragonite, vaterite, calcite, etc.) [3,14,15]. In addition, some unstable and uncommon calcium carbonate crystals in nature can be prepared under the influence of magnesium, such as monohydrocalcite and dolomite [16,17].

Prenucleation cluster is the key to the understanding non-classical or multistep crystallization mechanism of calcium carbonate. However, it is difficult to observe the formation and evolution of prenucleation cluster due to its disordered structure and fast transformation to stable polymorphs. Because magnesium can stabilize prenucleation cluster, the formation and transformation of the cluster can be observed and investigated in our experiments. This paper aims to study the formation of prenucleation cluster and ACC under the condition of high concentration of magnesium.

2. Materials and methods

2.1. Formation of ACC while feeding calcium chloride solution

The 50 mL calcium chloride solutions (0.2 mol/L) were slowly fed into the 500 mL mixed solutions (MgCl_2 0.12 mol/L, Na_2CO_3 0.02 mol/L) at constant feeding rates via a peristaltic pump (BT100S, LEADFLUID, China) (Fig. 1). The mixed solutions of magnesium chloride and sodium carbonate were supersaturated and metastable. The pH of the mixed solutions was kept at 9.25 by hydrochloric acid (pH 0.05) and sodium hydroxide solution (pH 14). The temperature of the solution in the reactor was controlled at 30 °C via a water bath. Several experiments were carried out at different feeding rates. The 50 mL calcium chloride solutions were fed within 10 min, 15 min, 30 min or 45 min separately. pH was monitored by a pH meter (PHSJ-3F, Lei Ci, China).

2.2. Formation of ACC while feeding sodium carbonate solution

As the first series of experiments above, the 50 mL sodium carbonate solutions (0.2 mol/L) were slowly injected into the 500 mL mixed solutions (MgCl_2 0.12 mol/L, CaCl_2 0.02 mol/L) at different pH (pH 9.00, 9.25 and 9.50). All sodium carbonate solutions were fed within 30 min at a constant rate.

During above experiments, the calcium concentration in the solution was detected by a calcium ion selective electrode (DX 240-Ca) that was coupled with a reference electrode (InLab® Reference Plus). Calcium selective electrode detects the calcium activity in the solution. Based on calcium activity, information about calcium concentration, the formation of ACC and the the prenucleation cluster can be obtained. Data were collected by the LabX direct pH 3.3 software 30 times per minute. The calcium selective electrode was calibrated by a set of calcium standard solutions (0, 0.001, 0.002, 0.005, 0.010, and 0.015 mol/L) before each set of experiments. The standard calcium solutions were prepared with magnesium chloride, calcium chloride, and deionized water.

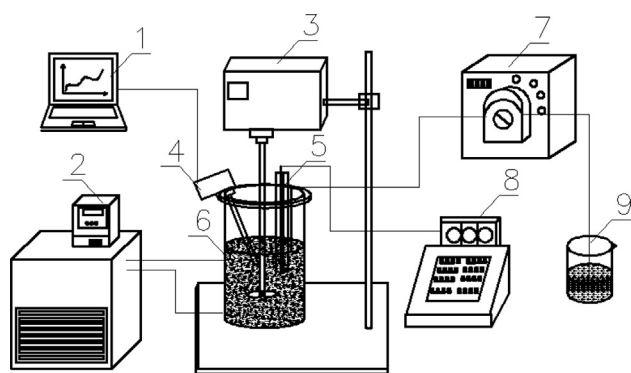


Fig. 1. Schematic of the experimental setup in this study. 1-Computer; 2-Water bath; 3-Stirrer; 4-FBRM probe; 5-Calcium selective electrode or pH electrode; 6-Mixed solution; 7-Peristaltic pump; 8- SevenMulti S40; 9-Solution.

Magnesium chloride solution (0.12 mol/L) was added to each standard calcium solution to eliminate interference of magnesium, and the change of magnesium concentration was small during experiments. The particle number in the solution was measured by the Focused Beam Reflectance Measurement (FBRM, Lasentec S400A, Mettler Toledo, USA) at the same time. FBRM monitored the particle size distribution in real time and in process. Thus, the formation of ACC could be detected by FBRM. The reagents used in our experiments, such as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , and Na_2CO_3 , were all AR grade and bought from Sinopharm group CO. LTD, China.

2.3. ACC preparation under lower concentration

In this series of experiments, the ACC was prepared by feeding the sodium carbonate solutions into the mixed solutions of calcium chloride and magnesium chloride. During studying influences of the sodium carbonate solution feeding rate, the 20 mL sodium carbonate solutions (0.2 mol/L) were injected into the 400 mL mixed solutions (MgCl_2 0.06 mol/L, CaCl_2 0.01 mol/L) at different constant feeding rates via a peristaltic pump. It took 0 s, 15.0 s, 37.5 s, 2.5 min and 10.0 min of time to pump all the sodium carbonate solutions in. Time equals to 0 s means that the sodium carbonate solution was poured in.

While analyzing the impact of sodium carbonate solution's volume or dilution, the sodium carbonate solutions were prepared by diluting 5 mL sodium carbonate solutions (0.8 mol/L) to 10 mL, 15 mL, 20 mL and 25 mL separately. These solutions were poured into the 400 mL mixed solution (MgCl_2 0.06 mol/L, CaCl_2 0.01 mol/L). If unspecified, the reactor was controlled at 30 °C and under 300 r/min stirring. In addition, pH was uncontrolled variable in this series of experiments.

2.4. ACC characterization

After reagents' mixing as described in the sections above, the mixed solution was centrifuged at 5000 rpm. Then, the ACC was collected by the micro-filtrate membrane. Before drying the ACC at 50 °C in vacuum, it was washed by isopropanol to get rid of the mother liquor. The ACC was also analyzed via the Thermogravimetry (TG, SDT Q600, METTLER TOLEDO, US), which adopted nitrogen as carrier gas. Moreover, the contents of Mass 44 (carbon dioxide) and mass 18 (water) in the carrier gas were monitored via the Mass Spectrometry (MS, TA Discovery, METTLER TOLEDO, US) that was connected after the TG. The ACC was also characterized via X-ray Polycrystalline Diffractometer (XRD, D8 Advance, Bruker AXS, Germany) and UHRFE-SEM (NOVA Nano SEM450, FEI, US).

3. Results

3.1. ACC formation when feeding the calcium chloride solutions into the mixed solutions of magnesium chloride and sodium carbonate

As shown in the Fig. 2, both the FBRM and calcium selective electrode could detect the formation of ACC, when 50 mL calcium chloride solutions (0.2 mol/L) were pumped into 500 mL mixed solutions (MgCl_2 0.12 mol/L, Na_2CO_3 0.02 mol/L) via a peristaltic pump at different constant feeding rates. 10 min, 15 min, 30 and 45 min were the time it took to pump all the calcium chloride solutions in. pH of the mixed solution was controlled at 9.25. Before the formation of ACC, the calcium concentration detected by the calcium selective electrode was proportional to the calcium concentration that had been added. Following the formation of the ACC, the rate of change of the concentration of calcium as a function of time suddenly decreased (Fig. 2a). FBRM results also gave evidence of the formation of ACC. The detected particle number in

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