High Yield of Vaterite Precipitation Induced by Trace Lanthanum Ion from a Supersaturated Solution of Calcium Carbonate at 50 °C

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The formation of calcium carbonate from a supersaturated solution doped with trace lanthanum was studied at various temperatures. At a temperature of around 50 °C, more than 80% of calcium carbonate precipitated from 5 μmol kg^{-1} $LaCl_3$, 15 mmol kg^{-1} $CaCl_2$-$NaHCO_3$ solution was vaterite while from a lanthanum-free solution calcium carbonate precipitated exclusively as calcite.

Calcium carbonate has three crystal forms (calcite, aragonite and vaterite) in natural minerals and organisms. Vaterite, the most labile phase of calcium carbonate at ambient P-T condition, is quite rare in natural minerals[1,2] presumably because of its instability.[3] Many organisms, however, produce it as a result of their biological activities.[4] In the laboratory, vaterite precipitates from supersaturated solutions as a metastable phase and is transformed into a more stable phase. Some surfactants are known to be effective inhibitors for the transformation of vaterite into calcite or aragonite even in trace amounts.[5,6] The presence of a large amount of barium ions comparable to Ca^{2+} resulted in vaterite formation,[7,8] but a highly effective cation for inducing the formation of vaterite has not been reported so far. Most recently, Tsuno et al. reported that the transformation of vaterite to calcite was inhibited by trace amount of lanthanum ion at room temperature and that the abundance of vaterite can stay constantly at 30% for a long period.[9] A further study demonstrated that the stabilization of vaterite was attributable to the inhibition of calcite growth.[10] In the present work, we have investigated the dependence of the temperature of the solution on the stability of vaterite and discuss the role of chemical substitution in the lattice.

The methods of synthesis of calcium carbonate have been described previously.[9] The experiments were conducted in a close system in a surface-silanized glass vessel in a thermostat-water bath. The amounts of precipitate and ion activity products (IAP) of calcium carbonate were calculated from the pH of the solutions on the assumption of chemical equilibrium among the ionic species in the solutions.[9,11] Starting solutions were mixtures of calcium chloride and sodium hydrogen carbonate solutions doped with a given amount of lanthanum chloride (see Table 1). After standing for 1 day, the precipitate was filtered with a membrane filter with a pore size of 0.45 μm (Millipore® HAWP 024 00), rinsed with milli-Q water and dried at 110 °C. The polymorphic composition of calcium carbonate was determined by a powder X-ray diffraction (XRD).[12] To determine the chemical composition, the samples were dissolved with 10 M nitric acid. The solution was then diluted to 0.2 M of nitric acid with milli-Q water. The concentrations of lanthanum and sodium in the solutions were analyzed by means of an inductively coupled plasma atomic emission spectrometer (ICP-AES, SPS1200, Seiko Instrument Inc.).

Table 1. The concentration of starting solutions and the results of $CaCO_3$ precipitation experiments

Exp. No.	Initial solution [ΣCO_2] /mmol kg^{-1}	[Ca] /mmol kg^{-1}	[La] /μmol kg^{-1}	Temp. /°C	log IAP[a]	Vaterite[b] /%
1	15.6	15.4	0	30	−8.4	0
2	15.4	14.9	0	40	−8.6	0
3	15.0	16.0	0	50	−8.6	0
4	15.2	15.0	0	70	−8.6	0
5	14.9	15.4	5.23	25	−7.9	28.9
6	15.3	15.1	5.16	30	−7.8	34.0
7	14.5	15.2	5.13	35	−7.8	39.3
8	15.0	15.0	5.21	40	−8.0	78.0
9	15.2	15.0	5.20	50	−8.1	83.4
10	15.2	15.0	5.03	70	−8.3	57.9
11	15.5	15.0	0.72	30	−8.1	4.8

[a]Calculated value assuming equilibrium. [b]Abundance of vaterite in the precipitate recovered at the end of reaction.

The pH changes during the experiments with and without lanthanum ion at various temperatures are shown in Figure 1. The decrease in pH was caused by the precipitation of calcium carbonate. In the case of the lanthanum-free system (Figure 1(A)), the pH change became sluggish after the initial quick change. During this transitional stage, the calcium carbonate was transformed from the initial precipitated vaterite to stable calcite.[9] Once most of the vaterite has been transformed to calcite, calcium carbonate precipitated quickly to reach an equilibrium. Equilibrated IAP of each experiment without lanthanum (Table 1) is close to the reported K_{SP} values of calcite at each temperature[13] ($\log K\text{sp}_{\text{calcite}}$: −8.509 at 30 °C; −8.579 at 40 °C; −8.661 at 50 °C; −8.866 at 70 °C). The polymorphic composition of the all La-free systems were pure calcite. The obtained values of IAP were consistent with a polymorphic composition determined by XRD (see Table 1). With increasing temperature, the pH values of the transitional stage decreased and the duration of the transitional stage shortened. At the beginning of transitional stage, the calculated IAP values were slightly higher than that of vaterite while, at the end of this stage, the IAP decreased to that of the solution saturated with vaterite. These values depended on the solubility of vaterite at each temperature.

When lanthanum ion was doped in the initial solutions, a remarkable difference was observed in the pH change at the various temperatures. When the temperature was relatively low (Figure 1(B) e), a distinct metastable stage was observed which had been described in our previous paper.[9] During the metastable stage, the

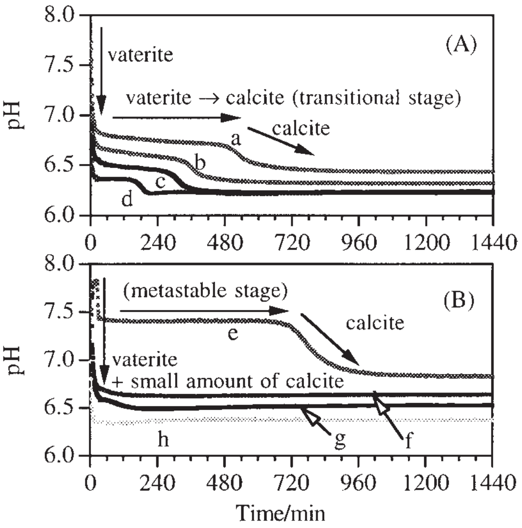

Figure 1. Plots of pH change with time during the crystallization in solutions without lanthanum (A; a: 30 °C, b: 40 °C, c: 50 °C and d: 70 °C) and solutions with lanthanum (B; e: 25 °C, f: 40 °C, g: 50 °C and h: 70 °C). Arrows show the precipitation or the transformation of polymorphism during those ranges.

abundance of polymorphs of calcium carbonate did not change. When the solution temperature was 40 °C or higher, the metastable stage was not observed (Figure 1(B) f, g and h). Calculated IAP after 1 day (see Table 1) was close to the reported values of vaterite at each temperature[13] ($\log K\mathrm{sp}_{\mathrm{vaterite}}$: −7.912 at 25 °C; −8.001 at 35 °C; −8.050 at 40 °C; −8.050 at 50 °C; −8.403 at 70 °C). According to XRD analysis, the relative amounts of vaterite increased with increasing temperature of the solutions (see Table 1). There was an abrupt increase of vaterite abundance at a temperature of between 35 and 40 °C. At 50 °C, the abundance of vaterite in the precipitate was at maximum (more than 80%). Kitano reported that the high concentration of sodium chloride (1.5–25 $\mathrm{g\,l^{-1}}$) in the mother solution (calcium hydrogen carbonate solution) favored predominantly vaterite formation at a high temperature, around boiling point, without stirring.[14] At 50 °C, 1.5 $\mathrm{g\,l^{-1}}$ sodium chloride precipitated 12% vaterite and predominantly aragonite and sodium-free solution precipitated approximately 40% vaterite without aragonite. Our results showed that lanthanum ion has a strong effect of inducing the formation of vaterite at temperatures lower than observed in Kitano's work and stabilization of vaterite with much lower concentration of impurity and stirring condition. The mechanism of calcite formation seemed to change around 40 °C as deduced from changes in the pH plots between 40 and 25 °C (see Figure 1(B)). When the temperature was 35 °C or lower, only a small amount of calcite (approximately 10%) formed at the initial stage and most of calcite in the final precipitate was transformed from vaterite.[9] In contrast, for starting solution at higher temperature (not less than 40 °C), the formation of vaterite was accelerated by higher precipitation rate at the beginning of reaction. Calcite precipitated directly at the initial formation stage and the quantity of calcite was not increased by the following transformation from vaterite later. It was accorded with the disappearance of metastable stage (Figure 1(B) f, g and h). Under this condition, vaterite formation seemed to be complete at the beginning of experiment (approximately 16–43% of total amount of $CaCO_3$).

In order to consider the mechanism of incorporation of lanthanum into calcium carbonate, the concentration of sodium in the precipitate which is a possible cation compensating the charge balance resulting from the incorporation of lanthanum ions, was investigated. For calcium carbonate formed from lanthanum-free solutions, sodium was not detected. In the precipitate from the lanthanum-doped solutions, considerable amounts of sodium were detected. Figure 2 shows plots of La/Ca vs Na/Ca. This figure suggested that La was incorporated into calcium carbonate with a constant La/Na ratio of approximately 1, which implies the substitution:

$$2Ca^{2+} \rightleftarrows Na^{+} + La^{3+}.$$

The concentrations of La and Na in the samples precipitated at the relatively high temperature fell along the 1 : 1 line. The Na/Ca ratios at lower temperature deviated systematically from the line (see Figure 2) suggesting that the maturation of the precipitate might have been poor at lower temperature or that the incorporation mechanism of lanthanum differ between calcite and vaterite.

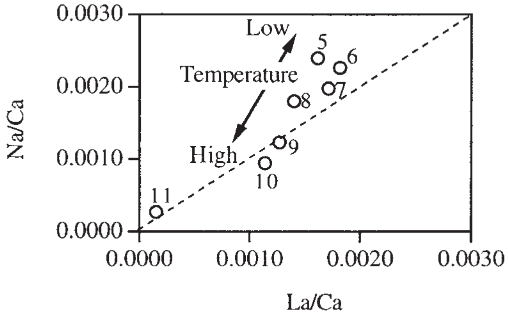

Figure 2. The plots of Na/Ca molar ratio against La/Ca molar ratio in the precipitate. Numbers beside the plots represent the respective experiment number in Table 1. The dashed line corresponds to La/Na = 1.

In conclusion, at around 50 °C vaterite formation and stabilization was strongly induced by lanthanum ion in the starting supersaturated solution and more than 80% of the calcium carbonate was vaterite for a long period. Coexisting calcite precipitated directly at the initial stage of calcium carbonate formation. Lanthanum completely inhibited the transformation of vaterite to calcite at higher temperatures.

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