Inhibiting Effects of Trace Amounts of Lanthanum Ion on the Dissolution of Calcite: A Comparative Study on Calcium Carbonate Polymorphs

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A significant inhibiting effect was observed on the dissolution of calcite by addition of 5 μM lanthanum ion to the solution, whereas no inhibition was observed both for aragonite and vaterite under the same conditions. In situ AFM (atomic force microscopy) images suggested that micro-precipitates depositing at the step site of calcite inhibited the dissolution in the lanthanum-doped solution. The solubility-calculation for the given solution was consistent with lanthanum carbonate being the micro-precipitate.

Crystal growth and dissolution of calcium carbonate are crucial for understanding global carbon cycling. Calcium carbonate exhibits three polymorphs: calcite, aragonite and vaterite in order of the thermodynamic stability at atmospheric pressure and temperature.[1,2] The effects of various trace elements on the nucleation and the growth of calcite have been widely reported.[3–5] It is also known that the metastable phases of calcium carbonate at ambient conditions, aragonite and vaterite can be precipitated and remain stable in solution when a trace amount of impurity is added to a starting supersaturated solution: for example, magnesium ion can induce the precipitation of aragonite.[6] Trace amount of rare earth elements can give rise to a significant effect in solutions of calcium carbonate. For example, Akagi and Kono reported an increase in the solubility of calcium carbonate with an addition of 1 μM lanthanum ion into the solution.[7] Tsuno et al. reported the stabilization of vaterite, the most labile phase of calcium carbonate, by adding 5 μM lanthanum ion in the starting solution.[8] Vaterite precipitates initially from a supersaturated solution of calcium carbonate and then dissolves during calcite formation in the lanthanum-free system. On the other hand, for the lanthanum-doped system, the amount of vaterite remained constant even after the precipitation of calcite. From these two reports, it is obvious that trace amounts of lanthanum ion can affect the precipitation of calcium carbonate significantly. The purpose of this study is to clarify the effect of lanthanum ion on the dissolution of calcium carbonate by making a comparison of dissolution rates among the three polymorphs and considering the surface processes.

Calcium carbonate samples used for this study were as follows. Single crystals of calcite were approximately 7 mm × 3 mm × 2 mm cleaved fragments of a mineral specimen from Brazil. Single crystals of aragonite were approximately 5 mm × 5 mm × 5 mm fragments of a mineral specimen from Fukuoka, Japan. The powder sample of calcite was the analytical-grade chemical reagent (Wako Co.) with an average grain size of 13 μm. Vaterite powder was prepared from the initial precipitation (5 min.) from the mixture of 30 mM sodium hydrogen carbonate solution and 30 mM calcium chloride solution.[8] The grain size of vaterite was in the range of 5–10 μm.

Dissolution experiments for the powder samples were performed in a glass vessel open to the atmosphere. Single-crystal experiments, on the other hand, were performed a closed in a Teflon® vessel in order to avoid the selective adsorption of lanthanum ion on the wall of glass vessel. The excess amounts of calcium carbonate, twice as much as the solubility of calcite, were placed into 500 mL of milli-Q® water or of 5 μM lanthanum chloride solution at 30 °C whilst stirring. The increase in the pH with the dissolution of calcium carbonate was monitored using a pH meter (In Lab 410 and MA 235, Mettler Toledo).

Figure 1 shows the plots of pH vs. time during the dissolution of calcium carbonate for the three polymorphs with and without 5 μM lanthanum ion. The increase in pH corresponds to the release of hydroxide ion resulting in the dissolution of calcium carbonate. Figure 1(a) shows the changes of pH in the dissolution of a single crystal of calcite. The increase in pH at the beginning of dissolution was commonly observed in both experiments with

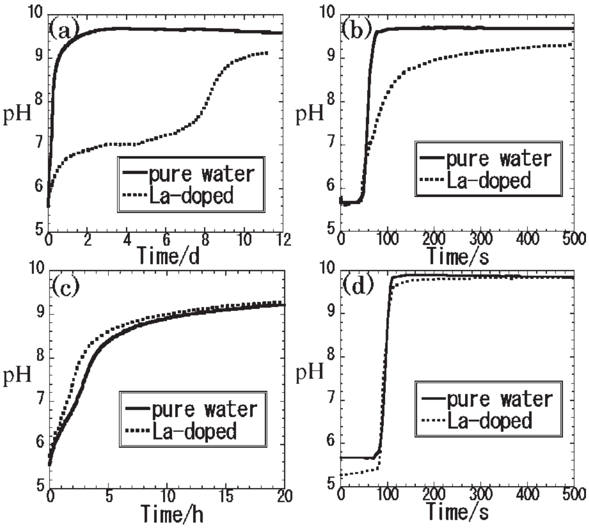

Figure 1. Plot of pH vs time in the dissolution of calcium carbonate comparing between in pure milli-Q® water and in 5 μM lanthanum-doped water: (a) a single crystal of calcite, (b) powder of calcite, (c) a single crystal of aragonite, (d) powder of vaterite. Inhibiting effect on the dissolution of calcium carbonate was observed exclusively for calcite. No such effect was observed for aragonite and vaterite.

and without lanthanum ion. The pH change then became sluggish for 4–5 days exclusively for the lanthanum-doped solution. This observation clearly demonstrates the significant decrease in the dissolution rate of crystal calcite in the lanthanum-doped system. The decrease in the dissolution rate was also observed for the powder sample of calcite in the lanthanum-doped solution (Figure 1(b)). The inhibition on the dissolution of calcite by lanthanum ion was effective even on the powder sample with a large surface area, which potentially has a large dissolution rate. On the other hand, no inhibiting effect on the dissolution was observed for the fragment sample of aragonite (Figure 1(c)) and the powder sample of vaterite (Figure 1(d)). The data for aragonite and vaterite revealed no decrease in the dissolution rate on addition of the lanthanum ion. These data suggested that the surface reactivity of calcium carbonate was different for the three polymorphs.

In conclusion, substantial inhibition was observed on the dissolution of calcite by the addition of 5 μM lanthanum ion to the solution, whereas no inhibition was observed for the dissolution of aragonite and vaterite under the same conditions. This result throws light on the mechanism of stabilization of the metastable phase of calcium carbonate. The increased stability of the vaterite induced by the trace amounts of lanthanum ion (Tsuno et al., 2001) could be the result of at least two mechanisms; the inhibition of dissolution of vaterite or the inhibition of calcite growth. The present experimental results exclude the first possibility.

For the purpose of clarifying the surface process resulting in the inhibiting effect of the lanthanum ion on the dissolution of calcite, we obtained in situ AFM images of calcite during dissolution. The AFM observation was carried out for a single crystal of calcite which had been placed on the bottom of a fluid cell, to which was added 1 mL of milli-Q® water followed by dropping 10 μL of 5×10^2 μM lanthanum chloride solution. In situ AFM images of calcite were taken with a contact mode and a scanning frequency of 3 Hz using a Shimadzu Inc. SPM-9500.[9,10] Collection of one image takes approximately 1.5 min and each observation continued at least for 90 minutes.

Figure 2(a) shows an AFM image of a $(10\bar{1}4)$ cleaved surface of calcite which was taken under solution immediately (in less than one minute) after the addition of the lanthanum ion. Well-defined flat terraces with steps were observed. Step height was 0.24–0.28 nm corresponding to one monolayer of calcite.[11] Figure 2(b) shows an AFM image taken 5 minutes after the observation of Figure 2(a) at the same location. It was found that the micro-precipitates deposited at the step site of calcite. Figure 2(c) was taken 15 minutes later. No propagation of steps was observed where the micro-precipitates appeared, whereas the generation and enlargement of etch pits were found out. No micro-precipitate was observed on the boundary of the evolving etch pits. These AFM images suggest that the micro-precipitates covering the step site, where crystal dissolution occurs actively in the absence of lanthanum ion, may cause the inhibition of dissolution for calcite. The size of micro-precipitates on the steps increased from 0.5 nm (5 minutes later) to 1.1 nm (15 minutes later) in height.

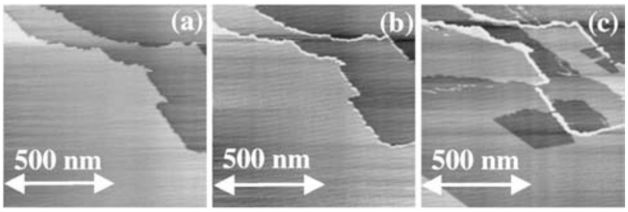

Figure 2. In-situ AFM image of a cleaved surface of calcite taken under the 5 μM lanthanum-doped solution: (a) immediately after the addition of the lanthanum chloride, (b) 5 minutes later, (c) 15 minutes later.

In order to characterize the precipitates deposited on the step-sites, the ion activity product (IAP) was calculated along with the chemical equilibrium equations described in Tsuno et al.[8] In the present calculation, the dissociation reactions of carbonic acids and ion-pairing reactions were considered on the assumption that calcite was in equilibrium with the 5 μM lanthanum chloride solution. The obtained IAP for $La_2(CO_3)_3$ was 1.08×10^{-30} which is comparable to a K_{sp} value of $La_2(CO_3)_3$, (1.23×10^{-30})[12] but is much larger than another reported K_{sp} value (4×10^{-34})[13]. This calculation suggests that the precipitate observed in the AFM images is presumably lanthanum carbonate. We have not applied a similar calculation to aragonite and vaterite, but these polymorphs should result in a higher $CO_3{}^{2-}$ concentration because they are more soluble than calcite.

It is suggested that the surface reactivity of calcium carbonate with lanthanum ion differs among the three polymorphs. More intensive studies on the surface mechanism of dissolution for all the polymorphs will be necessary to clarify the behavior of lanthanum ion.

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