Effects of Aspartic Acid on Calcite Dissolution Rate and Solubility

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The dissolution rate and solubility of calcite, a polymorph of $CaCO_3$, were determined in aspartic acid (Asp) solutions: Asp inhibited the surface reaction of calcite dissolution but accelerated the transport process. The crossover of these contrastive effects caused a local maximum of the dissolution rate constant and the transition of rate-determining processes. The calcite solubility increased with increasing Asp concentration, which may reflect its association with the change of the calcite surface structure derived from the addition of Asp.

Interactions between some amino acids and crystals of calcium carbonate have been investigated to elucidate the biomineralization mechanism. Among amino acids, aspartic acid (Asp) particularly demands attention because, during the process of biomineralization, some Asp-rich peptides are known to control the polymorphism and structure of calcium carbonate.[1] Most previous papers have reported the effect of Asp on the calcite surface morphology during crystal growth and dissolution.[2] By contrast, few studies have investigated the kinetics and the solubility of calcite in an aqueous amino-acid system. To our knowledge, the only study of dissolution kinetics determined using the pH-stat method indicated that amino acids (L-arginine, glycine, L-phenyl alanine, and L-alanine) inhibited calcite dissolution.[3] For the present study, we used the free-drift method to investigate the kinetics of calcite dissolution in the Asp solution without controlling the solution composition, aside from the initial condition. The free-drift method is quite often used for examination of dissolution kinetics.[4] In the free-drift method, a dissolution rate of calcite can be determined from a change of pH or Ca concentration in the dissolution reaction. In this study, we estimated the dissolution rate of calcite from the change of Ca concentration in the dissolution reaction. The solubility of calcite in the Asp solutions was inferred from the Ca concentration and the pH of the solution at equilibrium.

The dissolution rate and solubility were determined independently from two experiments. The dissolution rate measurements were performed in a closed Pyrex® glass vessel containing 720 mL of solution for 10 min at 0, 10, 25, 40, and 50 °C. Solubility was measured in a 500-mL closed polypropylene vessel for 15–16 h at 25 °C. The solutions were stirred at the same rate in all runs. For this study, all solutions were prepared using Milli-Q® water and were bubbled with N_2 gas to remove dissolved CO_2 gas. Therefore, for calculations, it can be assumed that the initial carbonate concentration in solution was negligible. The additive solution was prepared from reagent grade powder L-Asp with concentrations of 0–0.1 M. The ionic strength was adjusted to $I = 0.1$ M using reagent grade NaCl. The initial pH was adjusted to pH 8.00 (±0.05) using aqueous solutions of reagent grade NaOH and HCl. An analytical-grade chemical reagent with an average grain size of 13 µm was used as the calcium carbonate (calcite) powder sample. The $CaCO_3$ powder surface area, as measured using BET method, was $0.89\,m^2\,g^{-1}$. The amounts of $CaCO_3$ powder used were 0.05 and 1.00 g for each run, respectively, for measurements of the dissolution rate and the solubility. All reagents were obtained from Wako.

Sjöberg (1976) reported that the dissolution rate (R) of calcite estimated by free-drift method could be expressed as the following equation

$$R = k\left(1 - \Omega^{\frac{1}{2}}\right) \qquad (1)$$

where k is the apparent dissolution rate constant and Ω ($= \mathrm{IAP}/K_{sp}$) is the saturation state.[4b] The IAP is ionic activity product. At the beginning of dissolution experiments in this study, where $\Omega = 0$, the dissolution rate is equivalent to k, which was estimated from the initial time derivative of $[Ca^{2+}]$ measured using ICP-MS (ELAN DRCII; Perkin-Elmer Inc.) In addition, k is constant at pH value higher than ca. 5.[5] From these reasons, we assumed that k was independent on pH in this study.

Additionally, k can be expressed as

$$k = \frac{k_S k_T}{k_S + k_T} \qquad (2)$$

where k_S is the surface reaction rate constant and k_T is the transport rate constant.[5a]

The IAP of calcite at equilibrium was calculated from mass balances and equilibriums of acid–bases (carbonate and Asp species), ionic-pairings ($CaHCO_3{}^+$, $CaCO_3{}^0$, $NaHCO_3{}^0$, and $NaCO_3{}^-$), and a complex (Ca–Asp), with pH measured using a glass electrode (InLab411; Mettler Toledo International Inc.) and the measured Ca concentration.[6] For this calculation, we used the Davies equation to correct activities.[7]

Figure 1 presents plots of the apparent dissolution rate

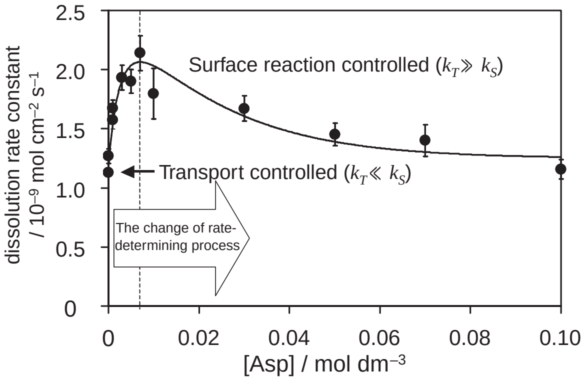

Figure 1. Plots of apparent dissolution rate constant vs. Asp concentration and fitting curves of dissolution rate constant in the calcite dissolution at 25 °C. The dotted line represents the transition of the rate-determining process.

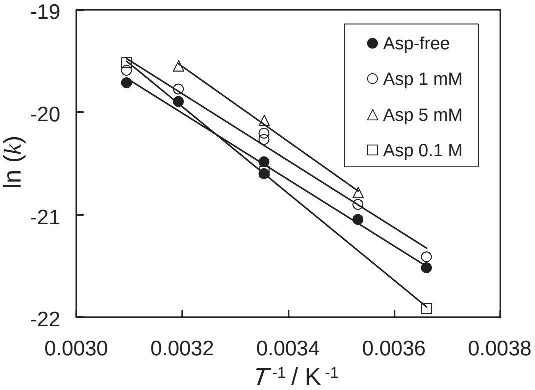

Figure 2. Arrhenius plots for apparent activation energy calculations for temperatures of 0–50 °C.

constant (k) vs. Asp concentration at 25 °C. A significant increase in the rate constant by the addition of Asp was found in the overall concentration range we studied. The k value increased with increasing Asp concentration at concentrations lower than 7 mM. In contrast, it decreased at concentrations higher than 7 mM, which implies a transition of the rate-determining process during dissolution.

The apparent activation energy for the overall dissolution reaction was calculated from the Arrhenius equation to confirm the transition of rate-determining process (Figure 2). The obtained apparent activation energies were 27 ± 2, 27 ± 2, 30 ± 2, and 35 ± 1 kJ mol^{-1}, respectively, in the Asp-free, 1.0×10^{-3} M Asp, 5.0×10^{-3} M Asp, and 0.10 M Asp solutions. The transport process is known to have less temperature dependence than that of surface reaction process.[4b,5] For example, Sjöberg and Rickard (1984) reported that activation energies of transport rate constant and surface reaction rate constant were 27 ± 2 and 46 ± 4 kJ mol^{-1}, respectively.[5a] The activation energy of k in the Asp-free condition coincided with the literature value of k_T, and the ones in the Asp additive condition were between k_T and k_S. The observed increase in the activation energies with increasing Asp concentration indicates the transition of the rate-determining process from the transport process ($k_T \ll k_S$) to surface reaction process ($k_T \gg k_S$). In other words, Asp inhibits the surface reaction process and accelerates the transport process in calcite dissolution. The crossover of these contrastive effects caused a local maximum of k value and the transition of rate determining processes. By contrast, Hamdona et al. (1995) indicated that amino acids decreased the rate constant of calcite dissolution. The contrast of their results to ours is presumably attributable to their experimental conditions, which were near equilibrium ($\Omega = 0.8$).[3] The rate-determining process at the near equilibrium condition tends to be surface reaction process because k_S decreases with approaching the equilibrium condition. Their results represented effect of amino acids on surface reaction during calcite dissolution.

Figure 3 shows plots of log (IAP) for calcite vs. the Asp concentration at 25 °C after 15–16 h reaction. The value of IAP in the Asp-free solution coincided with a value reported in the literature, $10^{-8.480 \pm 0.020}$.[6c] In Asp additive solutions, IAP increased with Asp concentration. Actually, IAP became higher than the K_{sp} value of aragonite for Asp concentrations higher than 0.05 M, but polymorphs of calcium carbonate other than calcite were not detected with powder X-ray diffraction. Actually, Asp is known to change the morphology of etch pit on the calcite cleavage surface from a rhombus to a triangular shape in a 0.1 M Asp condition.[2a] Furthermore, the solubility of calcite determined from step propagation kinetics reportedly depends on the crystallographic direction.[8] Taking these results into account, we infer that the increase of calcite solubility observed in this study was derived from morphological changes in the calcite surface structure. More detailed studies of in situ observations of surface structure are necessary to confirm this hypothesis.

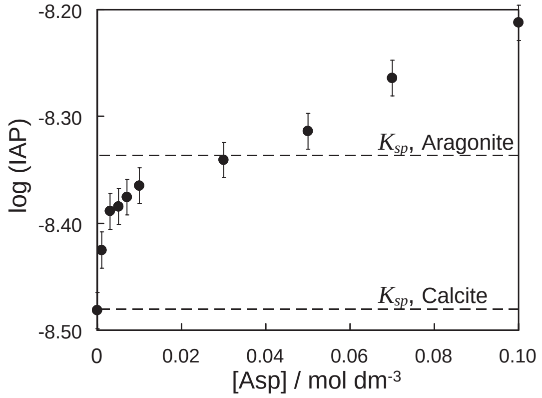

Figure 3. Plot of log (IAP) vs. Asp concentration at 25 °C. The K_{sp} values of calcite and aragonite are from Plummer and Busenberg (1982).[6c]

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