

Relation between dissolution rate and etch pit morphology of calcite in aspartic acid solution

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Some amino acids are known to strongly interact with surface of calcium carbonate and affect the kinetics and surface morphology during the crystal growth and dissolution. An atomic force microscopy (AFM) study showed that addition of aspartic acid (Asp) during the dissolution of calcite induced transition of etch-pit morphologies of calcite {10-14} faces from rhombus to triangular (e.g., Teng and Dove, 1997). Dissolution rate measured by pH-stat method indicated that amino acids played a role of inhibitor during dissolution of calcite (Hamdona et al., 1995). A new method using AFM fluid reaction cell can determine dissolution rate from measurement of solution composition as observing surface of the sample by AFM (Shiraki et al., 2000). However, no simultaneous measurement of changing of surface morphology and dissolution rate response has been carried out in the impurity bearing system. In this study, a system to observe the impurity effect of calcite was developed by using AFM fluid reaction cell. In the Asp doped aqueous solutions, we determined dissolution rate of calcite by measuring Ca concentration with ICP-MS (ELAN DRCII, PerkinElmer) and observing etch-pit morphology of calcite {10-14} faces by AFM (SPM-9500, Shimadzu Inc.), simultaneously.

Calcite samples were obtained from a single large crystal optical-quality Iceland spar from Mexico. We prepared {10-14} cleavage for each experiment. Input solution was prepared by dissolving aspartic acid reagent (Wako Co.) in MilliQ water, whose pH value was adjusted to 8.0 by adding sodium hydroxide solution (Wako Co.). The concentrations of Asp in the prepared solution were 1 mM, 0.01 M, and 0.1 M. All experiments were conducted at room temperature.

Dissolution rate, R_{diss} was calculated by equation (1), where C_{input} and C_{output} are Ca concentrations in the input and output solution, respectively, and A is surface area of the sample. F is flow rate of solution. By Measuring C_{input} and C_{output} with ICP-MS, we can determine R_{diss} (Shiraki et al., 2000).

$$R_{diss} = (C_{output} - C_{input}) * F / A \quad (1)$$

In situ AFM observations were carried out using a fluid reaction cell and with the contact mode. The reaction solution was injected to the cell by a syringe pump and pumped out by a peristaltic pump with the same flow rate of 0.5 ml min^{-1} for 2 hr. Scan rate was 2 Hz with 512 sampling points per scan line; a capture of image took 4.5 min.

Results of AFM observations indicated two kinds of etch pits with different depths (shallow and deep), which derived from point defect and dislocation, respectively. The shallow etch pit was difficult to detect after about 1 hr because of the wide depth range, except for the 1 mM Asp solution, and the density of deep etch pit increased with the increase of Asp concentration. Triangular etch pits appeared as well as Teng and Dove (1997) in the 0.1 M Asp solution. In the 0.01 M Asp solution, we also observed the uniaxially elongated variation of the etch pit morphology.

Results of measurements of dissolution rate indicated that the addition of aspartic acid in the solutions increased dissolution rate of calcite. It was consistent with the increase of etch pit density confirmed by the AFM observations, but different from the result of pH-stat method (Hamdona et al., 1995). In general, the pH-stat method determines dissolution rate of calcite from amount of acid added for maintaining pH constant. In the amino acid dominant solution, the increase of pH with dissolution of calcite is buffered by amino acid. Even if the more calcite had dissolved in the amino acid solution, the dissolution rate may be evaluated lower than the case without amino acid. Therefore, calcium concentration in the solution has to be measured for determining dissolution rate for precise discussion of dissolution kinetics of calcite, as shown as in the present study.