Promotion of calcite dissolution in succinic acid and L-malic acid aqueous solution.

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Calcite is one of the polymorphs of calcium carbonate and is known as a poorly soluble mineral in water. When calcite is dissolved in pure water, the dissolution proceeds with forming rhombic etch pits on (104) plane. On the other hand, some organic additives containing carboxylic acid groups significantly alter the dissolution rate and the etch pits morphology [1]. Despite of numerous studies, the calcite dissolution mechanisms in the presence of additives still remain elusive. In this study we investigated the changes in etch pit morphology and step retreat velocity in succinic acid and L-malic acid aqueous solutions to elucidate the changes in dissolution processes by these additives, which have the same molecular geometry except for the presence of a hydroxylic group.

Single calcite crystals cleaved along the (104) plane were placed in a fluid cell and dissolved in aqueous solutions for 40 minutes at temperature of 25°C. The flow rate was controlled at 80 mL/min to achieve surface reaction rate-limiting. The concentration of di-carboxylic acids was varied from 0 to 0.25 M and the pH was adjusted to 6.5 by adding sodium hydroxide. In-situ observations were carried out by using differential interference contrast microscope and atomic force microscope.

In low concentration solutions of succinic acid (0 ~ 0.1 M), the morphology of the etch pits remained typical rhombus but the retreat velocities of $[48\bar{1}]$ and $[\bar{4}41]$ steps were drastically increased with the concentration. At higher concentrations (0.15 ~ 0.25 M), the morphology changed to hexagon by the appearance of $[42\bar{1}]$ steps. In contrast, the increase of L-malic acid concentration (0.1 ~ 0.25 M), resulted in the morphological changes to pentagon by the appearance of $[42\bar{1}]$ and [010] steps. These results indicate that the additives promote the dissolution of calcite and simultaneously inhibit the dissolution of the specific steps. The appearance of different steps between these additives is attributed to the matching of the molecular geometry and calcite surface geometry.

References

[1] T. Yoshino et al." Effects of L-Aspartic acid on the step retreat kinetics of calcite," J Cryst Growth. 2012;338:244-250.