Visualization of two-dimensional distributions of pH and Ca^{2+} concentration around dissolving/forming $CaCO_3$ minerals

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To understand the mechanisms of mineral formation or dissolution, analyzing the local conditions of the solution around the dissolving or forming minerals is important. Recently, we succeeded in visualizing the distribution of pH around a calcium carbonate crystal dissolving in aqueous solution using a fluorescent probe [1]. However, the ionic concentration of Ca^{2+} is another important factor to describe the formation/dissolution reaction of calcium carbonate. In this study, we attempted to visualize the distribution of Ca^{2+} concentration along with the pH around (1) a dissolving calcium carbonate crystal in aqueous solution and (2) forming crystals synthesized by the counter-diffusion (CD) method [2] in gel media.

By simultaneously using HPTS (8-hydroxypyrene-1,3,6-trisul-fonic acid) and Rhod-FF as a fluorescent probe for the pH and Ca^{2+} concentration, respectively, their distributions around the dissolving calcium carbonate in an aqueous solution were successfully visualized. The pH was found to increase and saturate rapidly just above the surfaces, while the Ca^{2+} concentration changed more slowly and its 2D features were different from those of pH.

In the synthesis by CD method with the $CaCl_2$ and Na_2CO_3 solutions, the tiny particles were first precipitated at the center of the gel to form a crystallization band, followed by nucleation and growth of rhombohedral and spherical crystals on both sides of the band. The distributions of pH and Ca^{2+} concentration during the synthesis were visualized by using HPTS and calcein, respectively; no differences of local distributions were observed around their polymorphs and morphologies. The Ca^{2+}/CO_3^{2-} ratios discontinuously changed across the band, which may affect the growth mechanisms of the forming crystals.

These results suggest that the proposed visualization technique can provide new insights into the dissolution/formation mechanism of minerals.

[1] Kawano et al. (2019) Cryst. Growth Des., **19**, 4212-4217.

[2] Genovese et al. (2016) Cryst. Growth Des., **16**, 4173-4177.