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Direct observation of pH distribution during the formation of calcium carbonate polymorphs in gel media

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Direct observation of the local behavior of ions around growing or dissolving crystals would provide a detailed understanding of the crystal growth/dissolution process. Recently, we succeeded in visualizing the distribution of pH and Ca^{2+} ion concentration around a calcium carbonate crystal dissolving in an aqueous solution using a fluorescent probe [1]. In this study, we applied this technique to the formation of calcium carbonate in gel matrix, which has recently attracted attention as a method to mimic in vivo conditions. Genovese et al. have also visualized the pH of gels during the calcium carbonate formation using a fluorescent probe [2], while in the present study, we used laser confocal microscopy to focus more on the observation of the local pH condition around forming crystals and to analyze the formation environment of calcium carbonate polymorphs.

Here, calcium carbonate was synthesized in 0.3 M $CaCl_2$ and $NaHCO_3$ solutions in a counter-diffusion system using agar gels. As a fluorescent probe, HPTS (8-hydroxypyrene-1,3,6-trisulfonic acid) was included in all solutions and gels used to visualize the pH distribution during the process of diffusion of the solution and the formation of crystals. In the experiment with 1 wt% agar gel, rhombohedral and otoconia-like calcite crystals formed first and followed by the formation of dumbbell-shaped aragonite crystals. Visualization of pH distribution shows these deferent polymorphs formed in environments with different trends in pH change. Furthermore, it was observed that the pH just around the formed calcite crystals was about 0.1 lower than the surrounding pH. However, such local heterogeneity was not observed around aragonite crystals. These differences in trend may have influenced the formation of different calcium carbonate polymorphs.

[1] Kawano et al. (2019) Cryst. Growth Des., 19, 4212-4217.
[2] Genovese et al. (2016) Cryst. Growth Des., 16, 4173-4177.