Visualization of Chiral Molecules on Growing Calcite Surfaces Reveals Adsorption at Kinks

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http://www.ganko.tohoku.ac.jp/shigen/tsukamoto.html

Calcite is one of the most abundant minerals in the calcium carbonate group and crucial biomineral. The regulation of calcite crystal growth has been the subject of intense investigations. Recently, it was reported that chiral aminoacids asymmetrically affect the growth and dissolution of steps on calcite crystal surfaces1. Furthermore, it was shown that aspartic acid (Asp) and some other peptides at low concentrations promote the growth of steps on calcite surfaces, while at high concentrations of the same additives, growth inhibition was observed.2,3 Both of these observations, the unusual growth promotion and the more intuitive inhibition, were tested and confirmed in our laboratory.4 Understanding of the growth enhancement at low additive concentrations is crucial for understanding of the regulation of calcite crystallization and morphology. Towards such understanding, it was proposed that the additives destroy the structure of the water coating the kinks on the calcite surface. For critical tests of the proposed mechanism, it is necessary to establish the sites of adsorption of additive molecules on the calcite surfaces. Here, using direct visualization of fluorescently labeled L-aspartate molecules we show that L-Asp preferentially adsorbs to the kinks.

We employ a single-molecule visualization technique. The fluorophor tetramethylrhodamin (TR) was attached to L-Asp molecules and the product was purified using high performance liquid chromatography. The compound TR-L-Asp is chiral and its effects on calcite surfaces are also chiral. TR-L-Asp at concentration 0.1 nmol/l was added to equilibrium or supersaturated solutions of CaCO3. Cleaved calcite single crystals were etched in ultra-pure water to produce etch pits, which possess a regular pattern of steps and are suitable for observation. The crystal and solution were held in an observation cell custom designed for in-situ visualization single fluorescent molecules. The crystal surface was illuminated from the bottom of observation cell with a 532 nm laser, and the TR-L-Asps on the calcite surface were tracked at emission wavelength more than 580 nm.

At equilibrium between the crystals and the solution, when the steps are nearly motionless, the molecules of the additive were immobile at the step front. The residence times varied, with an average of 9.0 s. In contrast, in supersaturated solutions, less than 0.2 of all adsorbed molecules were immobile, while the rest diffused along the surface. The average residence time of fixed molecules was ˜1 s, considerably shorter than in the case of equilibrium. This surface diffusion of the mobile TR-L-Asp molecules was not constrained by the calcite steps. The trajectories of the moving molecules yield a diffusion coefficient of TR-L-Asp on calcite surfaces: $6.5*10^{-7}cm^2/s$, somewhat slower than the bulk diffusivity of 5-TRITC in water. Furthermore, we found that the number of adsorbed additive molecules increases smoothly as the supersaturation is increased. The counterposition between an entire population of immobile adsorbed molecules at equilibrium and significant fraction of mobile TR-L-Asp molecules on growing calcite surfaces suggests that the additive molecules are not adsorbed on terraces or macrosteps-these behave in an approximately identical way in supersaturated solutions and in equilibrium. The increasing number of adsorbed additive molecules at increasing supersaturation indicates that the adsorption sites are the kinks, rather than locations along the steps: since the steps are generated along the etchpit walls during the preparation of the surface, the step density does not change with supersaturation. However, calcite is a classical example of increasing kink density with supersaturation.

The set of observation reported here clearly demonstrates that the TR-L-Asp molecules adsorb at kinks, a major step in the mechanism of regulation of calcite crystallization by biological additives.