

Direct tracking of selective adsorption of chiral molecules on calcite surface

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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 surfaces (Orme et al., 2001). 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 (Elhadj et al., 2006a; 2006b). Both of these observations, the unusual growth promotion and the more intuitive inhibition, were tested and confirmed in our laboratory (Maruyama et al., 2009). 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-aspartic acid molecules (F-LAsp) we show that F-LAsp preferentially adsorbs to the kinks and step-front.

We employ a single-molecule visualization technique. The fluorophor tetramethylrhodamin was attached to L-Asp molecules and the product was purified using high performance liquid chromatography. The compound F-LAsp is chiral and its effects on calcite surfaces are also chiral. F-LAsp at concentration 0.2 nmol/l was added to equilibrium or supersaturated solutions of CaCO_3 . 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.

F-LAsp stays on calcite surface from 0.1 to few seconds, and goes back to solution after the short stay on calcite surface. Permanent adsorption of F-LAsp on calcite surface was not observed in this experiment. From the plot of stay time vs. logarithm of number density, average stay time at each supersaturation was determined. Preferable positions of adsorption of F-LAsp were step-front and kinks. The average stay time of F-LAsp on step-front is 0.32 seconds. The most preferable position of F-LAsp is the kinks. The stay time of F-LAsp at kink is more than 1.2 seconds. Selective adsorptions of F-LAsp on step-front and at kink were also observed. In the case of step-front, considering acute steps, the stay time of F-LAsp on [48-1]- direction is 20% longer than that of [-441]- direction. Likewise, considering obtuse steps, F-LAsp prefer to stay [48-1]+ direction rather than [-441]+ direction. In the case of kinks, F-LAsp prefer to get adsorbed at a kink composed from acute-riser and obtuse-riser, which exist in the [-441]- step and [48-1]+ step.

The number of adsorbed additive molecules linearly increased with increasing supersaturation from 0 to 1.13, and exponentially increased at higher supersaturation than 1.13. At supersaturation from 0 to 1.13, the number of F-LAsp corresponds to adsorption at step-front: since step velocity strongly depends on supersaturation, relative number of molecules that can encounter step-front increases. At supersaturation higher than 1.13, the exponential increase of the number of F-LAsp should correspond to kink density: since calcite is a classical example of increasing kink density with supersaturation.