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In situ AFM crystal growth and dissolution study of calcite in the presence of aqueous fluoride

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Fluoride is naturally abundant, encountered in rocks, soil and fresh and ocean water. Calcite crystals, during crystal growth may incorporate fluoride ions into their lattice *(Okumura et al., 1983). In situ* atomic force microscopy (AFM) has been used to study the growth and dissolution of calcite {10$\bar{1}$4} surfaces in aqueous solutions in the presence of fluoride, using a fluid cell in which the supersaturated and the understaturated solutions respectively, flow over a freshly cleaved calcite crystal. For growth experiments, supersaturation index (S.I.) with respect to calcite was equal to 0.89 and the initial solution pH 10.2. The crystal growth rates were measured from the closure of the rhombohedral etch pits along the [010] direction induced by an initial dissolution step using pure water. The spreading rate of 2-dimensional nuclei was also measured along the same direction. In the presence of low fluoride concentrations ($\leq$0.33 mM), the crystal growth rate of calcite was unaffected. At higher concentrations (up to 5 mM) growth rate decreased substantially to 50% of the rate in the absence of fluoride. Potential fluoride sorption over the calcite surface may ascribe the decrease of growth rates. Dissolution experiments were conducted at pH= 7.2 and dissolution rates of calcite were measured from the spreading of rhombohedral etch pits along both [010] and [42$\bar{1}$] directions. The presence of low concentrations of fluoride ($\leq$1.1 mM) in the undersaturated solutions enhanced the dissolution rate along the [42$\bar{1}$] direction by 50% in comparison with pure water. The morphology of rhombohedral etch pits changed to hexagonal in the presence of fluoride in the undersaturated solutions. The AFM dissolution experiments suggested that the fluoride ions adsorbed onto the calcite surface. Further increase of fluoride concentrations (up to 1.6 mM) resulted in the decrease of the calcite dissolution rate by 60% in both [010] and [42$\bar{1}$] directions.

Reference:

Okumura, M, Kitano, Y., Idogaki, M., 1983. Inorporation of fluoride ions into calcite – Effect of organic materials and magnesium ions in a parent solution. Geochemical Journal 17, 257-263.