

In situ AFM study on crystal growth and dissolution of calcite at a nano-level

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Calcite is one of useful indicator minerals for environmental changes and occurs in a wide variety of geologic environments. The processes and kinetics of dissolution and crystal growth of calcite easily change with slight variations of temperature and concentration of solutions. Most global-scale geochemical phenomena begin with atomic-scale growth and dissolution reactions at the mineral-water interface. In situ Atomic Force Microscopy (AFM) allows direct observation of the growth and dissolution processes at the mineral-water interface at the site or step level. Here we report the results of an experiment performed by in situ AFM observations of the dissolution and growth behaviors on the (10-14) surface of calcite in under- and supersaturated CaCO_3 solutions at 25°C.

The calcite sample was obtained from the Stoneham Barite Deposit in Colorado, USA in the form of a single optically clear crystal. The calcite crystal was cleaved parallel to the (10-14) cleavage plane with a sharp knife blade immediately before the AFM observations. The CaCO_3 aqueous solution ($\text{Ca}^{2+} : \text{CO}_3^{2-} = 1:1$) was prepared by mixing Na_2CO_3 and CaCl_2 solutions consisting of analytical grade chemicals and deionized water immediately before the AFM observations. The degree of super- (or under-) saturation (S) and ionic strength were calculated using the program PHREEQC. In situ observations of the calcite dissolution and growth were performed by a Nanoscope III with a Multimode SPM unit (Digital Instruments) operating in contact-mode AFM (CMAFM) on a vibration isolation platform in a temperature- and humidity-controlled room. The cleaved calcite crystals were first reacted with deionized water to ensure stable AFM scanning conditions and obtain reliable AFM images. We then replaced the water with CaCO_3 solution in the fluid cell and began observing the growth process on the calcite (10-14) surface at 25(±0.2)°C. Deionized water and CaCO_3 solution flowed through the fluid cell at a constant rate of 10 ml/h, controlled by a syringe pump.

In pure water and all undersaturated solutions, inverted pyramidal-shaped etch pits which were defined by [-441] and [48-1] steps were formed during the dissolution. However, a pair of [-441] and [48-1] steps of a quadrangular pyramid tended to curve with higher undersaturations. The two pairs of [-441] and [48-1] steps in etch pits showed the anisotropic retreat behavior, that is, the steps having higher retreat rates showed the higher effect of the undersaturation of the solution on the retreat rates. The retreat rate of the (10-14) plane was much slower than those of the [-441] and [48-1] steps in etch pits.

In supersaturated solutions, pyramidal-shaped growth spirals which were defined by [-441] and [48-1] steps were formed during the growth. The pyramidal-shaped growth spirals showed clear ridgelines. The [-441] and [48-1] steps on the growth spirals have a height of approximately 0.3 nm which corresponds to a monomolecular of CaCO_3 but showed mostly two layer periodicity. The advance rates of the steps during the growth tended to be faster than the retreat rates of those during the dissolution, while the growth rates of growth spirals toward the direction perpendicular to the (10-14) plane were slower than the retreat rates of (10-14) plane in etch pits.

Keywords: calcite, crystal growth, dissolution, AFM