

In situ hot/cool-stage AFM study on crystal growth of barite at 10 - 40°C

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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. Many in situ and ex situ AFM studies on the dissolution reactions of the barite (001) surface have been conducted to elucidate the processes involved and problems mentioned above. However, to our knowledge, no in situ AFM study on mineral growth at low temperatures (below room temperature) has been reported. The dearth of low-temperature studies most likely owes to difficulties in constructing the AFM experimental system. Here we report the results of a experiment performed by in situ hot/cool-stage AFM observations of the growth behavior on the (001) surface of barite in supersaturated BaSO_4 solutions at 10 - 40°C.

The mechanism of crystal growth of barite was characterized by the spiral growth mechanism where rhombic growth spirals elongated along the [010] direction were formed and the two-dimensional (2D) nucleation mechanism in which circular sector-shaped two-dimensional (2D) nuclei were formed and developed. In addition, the adhesive growth mechanism was observed only at 10°C.

The kinetic laws of the crystal growth on the barite (001) surface differed among crystallographic directions and crystal growth mechanisms. The advance rates of the two steps of 2D nuclei were proportional to the S . In contrast, the advance rates of the parallel steps with extremely short step spacing on growth spirals were proportional to S^2 , indicating that the lateral growth rates of growth spirals were directly proportional to the step separations. This dependence of the advance rate of every step on the growth spirals on the step separations predicts that the growth rates along the [001] direction of the growth spirals were proportional to S for higher supersaturations. The nucleation and growth rates of the 2D nuclei increased sharply for higher supersaturations using exponential functions. Only at 10°C, these rates changed to be proportional to S for higher supersaturations, indicating a change in main crystal growth mechanism from the 2D nucleation to the adhesive growth one. Two critical supersaturation points corresponding to the changes in main crystal growth mechanisms from the spiral growth, via 2D nucleation, to adhesive growth tended to decrease with decreasing of solution temperature.

Keywords: Barite, Crystal Growth, AFM