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In situ AFM study on crystal growth of barite

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Barite ($BaSO_4$) is the most abundant mineral of barium and occurs in a wide variety of geologic environments that span geologic time from the Early Archean to the present. Because of its low solubility ($K_{sp} = 10_{-9.99}$ at 25C) in water, the dissolution and precipitation of barite control the concentration and mobility of Ba in ground and surface water. Barite is also a common scale mineral, and its formation, with its low solubility in water, is almost inevitable in industrial water, oil, and gas-production systems. Because Ra^{2+} and Ba^{2+} are of similar ionic radius and electronegativity, some Ra^{2+} is incorporated into the barite crystal structure during its precipitation. Therefore, water including radioactive Ra ions produced from oil, gas, and geothermal wells or from U mine wastes, which contain an array of radioactive nuclides, including ^{226}Ra, may precipitate radioactive barite.

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, information on microscopic growth reactions of barite in aqueous solutions is sparse. Here we report the results of a preliminary experiment performed by in situ AFM observations of the growth behavior on the (001) surface of barite in supersaturated $BaSO_4$ solutions at 25C.

The barite sample was obtained from the Stonehem Barite Deposit in Colorado, USA in the form of a single optically clear crystal. The barite crystal was cleaved parallel to the (001) cleavage plane with a sharp knife blade immediately before the AFM observations. The $BaSO_4$ aqueous solution was prepared by mixing Na_2SO_4 and $Ba(NO_3)_2$ solutions consisting of analytical grade chemicals and deionized water immediately before the AFM observations. The degree of supersaturation and ionic strength were calculated using the program PHREEQC. In situ observations of the barite 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 barite crystals were first reacted with deionized water at 25C to ensure stable AFM scanning conditions and obtain reliable AFM images. We then replaced the water with $BaSO_4$ solution in the fluid cell and began observing the growth process on the barite (001) surface at 25C. Deionized water and BaSO4 solution flowed through the fluid cell at a constant rate of 0.6 ml/h, controlled by a syringe pump.

The growth behavior on the barite (001) surface at 25C appeared to begin with the advancement of the initial step edges and filling in of the etch pits formed in the water before the $BaSO_4$ solution was injected. The advancing fronts of the steps were not angular but rather irregular, wavy, or rounded. Under higher supersaturation conditions ($>$S = 13), circular sector-shaped two-dimensional (2D) nuclei were observed slightly later than the advancement of the initial step edges. These sector-shaped islands are defined by half-layer steps (3.6 A) parallel to [120], [1-20] and a curved step edge tangent to [010]. The advance rate of the curved step was approximately 5 times that of the [120] step.

Other growth behavior observed on the barite (001) surface included the formation of prismatic or bladed growth ledges and growth hillocks and spirals. The prismatic growth ledges were formed at kinks or faults at multi-layer steps and were elongated along the [010] direction with curved edges. The growth hillocks and spirals were also elongated along the [010] direction and displayed a bow-shaped form. The morphology of the growth hillocks and spirals was very similar to that of the deep etch pits formed in NaCl solutions at room temperature or in water at 60C, that is, under the conditions that promote barite dissolution.

Keywords: crystal growth, barite, atomic force microscopy, two-dimensional nucleus, spiral growth