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In situ hot-stage AFM study of the dissolution of the barite (001) surface in water at 30–55 °C

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Abstract

This paper reports in situ observations of the dissolution behavior of the barite (001) surface in pure water at 30–55 °C using hot-stage atomic force microscopy (AFM). The dissolution at 30 and 40 °C occurred in three stages; however, at 55 °C, the dissolution behavior observed at the former temperatures started immediately after injecting water into the AFM fluid cell. The first stage of the dissolution was characterized by the retreat of the initial steps and continued for about 60 min at 30 °C and about 10 min at 40 °C. The second stage of the dissolution was characterized by the splitting of the initial <*hk*0> one-layer step into two half-layer steps [fast ("f") and slow ("s") retreat steps] with different retreat rates and by the formation of etch pits. The large difference in the retreat rate of the "f" and "s" steps led to the formation of a new one-layer step, which showed slightly faster retreat rates than the "s" half-layer step at all temperatures. The splitting of the [010] one-layer step into two half-layer steps was observed only at 55 °C. During the third stage, the development of angular deep etch pits from an initial form with a curved outline differed at each temperature. The deep etch pits grew rapidly at higher temperature, but showed at least two different retreat rates for the (001) plane at each temperature, indicating the development of the pits along different dislocations (screw and edge dislocations).

The activation energies (62–74 kJ/mol) for the step and face retreats in this study were significantly higher than those reported in earlier studies. Recalculations performed using only data obtained under similar conditions in previous studies led to activation energies of 66–79 kJ/mol. These results and the earlier report showing that the form of the deep etch pits changed from angular to bow-shaped at about 60 °C may indicate that the activation energy of barite dissolution in water is higher at lower temperatures as compared with higher temperatures, thus changing the rate-limiting step. Whether the vertical and lateral retreat rates of the barite (001) plane differ in dependence of temperature remains unclear; however, the activation energies of the retreat of the (001) face in deep etch pits tended to be slightly higher than that of the lateral retreat rates of steps or other faces in deep etch pits.

Keywords: Barite, dissolution kinetics, hot-stage AFM, step retreat, etch pit