

## Dissolution of baryte (001) observed by hydrothermal scanning force microscopy

G. Jordan  
S. R. Higgins  
C. M. Eggleston

Dept. of Geology and Geophysics, Univ. of Wyoming, Laramie,  
WY 82071-3006, USA

K. G. Knauss  
C. O. Boro

L-202, Earth Sci. Division, Lawrence Livermore Natl. Laboratory,  
Livermore, CA 94550, USA

Scanning force microscopy (SFM) provides *in situ* access to the microtopography of mineral surfaces and its kinematics during dissolution, with monolayer resolution. Information about not only the mechanism of dissolution, but also quantitative data such as the dissolution rate or activation energy can be acquired. However, the lower limit of dissolution rates that can be studied by SFM lies in the range of  $10^{-9}$  mol/m<sup>2</sup>s. Experiments at elevated temperatures (e.g. those requiring elevated pressure) were not possible using commercial microscopes. Therefore, SFM *in situ* studies were mainly limited to minerals with dissolution rates higher than  $10^{-9}$  mol/m<sup>2</sup>s at near-room temperature. In order to solve this problem, a pressurizable SFM was constructed (Higgins *et al.*, 1998) which allows examination of dissolution kinetics on mineral surfaces beyond the ambient boiling point of water.

Here we present kinetic data on the dissolution of baryte (001). Dissolution and growth of baryte is significant in regulating the abundance of solvated Ba in the hydrosphere and has relevance in baryte scale formation in offshore oil wells (Putnis *et al.*, 1995). In deionized water between 90°C and 125°C, baryte (001) dissolves by retreat of steps at (001) terraces. The orientation of the steps is parallel to <120> and [010]. The <120> steps occur such that, in alternating half layers (height:  $c/2$ ), only steps that retreat either in the positive or negative  $a$ -direction are stable. In the case that <120> steps retreat in the positive  $a$ -direction, the [010] steps are only stable retreating in the negative  $a$ -direction, and *vice versa*. Therefore, steps generated by pits form a triangle pointing in alternating half layers in the positive and negative  $a$ -directions alternately (Fig. 1a). This alternating pattern can be attributed to the  $2_1$  screw axis parallel to [001] (Putnis *et al.*, 1995). Between 90°C and 125°C, <120> steps retreat about twice as fast as [010] steps. Due to these different velocities and the alternating step pattern, etch pits, probably generated

by linear defects, have a six-sided shape elongated in [010] (Fig. 1b,c).

By measuring step velocities between 90°C and 125°C, the activation energy for step retreat ( $E_s$ ) can be determined. On baryte (001) we found  $E_s$  for retreat of <120> steps to be  $34 \pm 4$  kJ/mol and for [010] steps to be  $31 \pm 6$  kJ/mol. Due to the error ranges, different activation energies for different steps cannot be resolved. However, judging by the shape of etch pits at room temperature reported by Putnis *et al.* (1995), a higher activation energy for the retreat of <120> steps seems to be likely. Considering the step velocities and the slopes of the pit walls, the frequency of generating monolayer pits within deep etch pits can be calculated. By this frequency the dissolution rate of a surface consisting exclusively of pit walls can be determined (Jordan and Rammensee, 1998). At 90°C (125°C) this rate is about  $7 \times 10^{-7}$  mol/m<sup>2</sup>s ( $1 \times 10^{-6}$  mol/m<sup>2</sup>s). The rates reasonably agree with literature data determined by solution chemistry ( $1.12 \times 10^{-7}$  mol/m<sup>2</sup>s, 90°C, pH 5.7; Dove and Czank, 1995), bearing in mind that due to the flat bottoms of the etch pits, our rates must be regarded as maximum rates. Figure 1d shows the baryte (001) surface during dissolution on a large scale. Low dissolution rate areas cover at least 30% of the surface in this scan area. As in the case of the step velocities, it is possible to calculate the activation energy ( $E_p$ ) by the temperature dependence of the maximum rates (about 10 kJ/mol). However,  $E_p$  is primarily the activation energy for monolayer pit formation within etch pits. If step retreat does not contribute to the macroscopic activation energy for dissolution ( $E_m$ ), as observable e.g. in bulk experiments,  $E_p$  reflects  $E_m$ . However, the actual rate and, therefore, the macroscopic activation energy ( $E_m$ ) are determined by the rate of step formation and the step velocities (via the expansion of fast dissolving areas such as pit walls).

In comparison to room temperature (Putnis *et al.*,

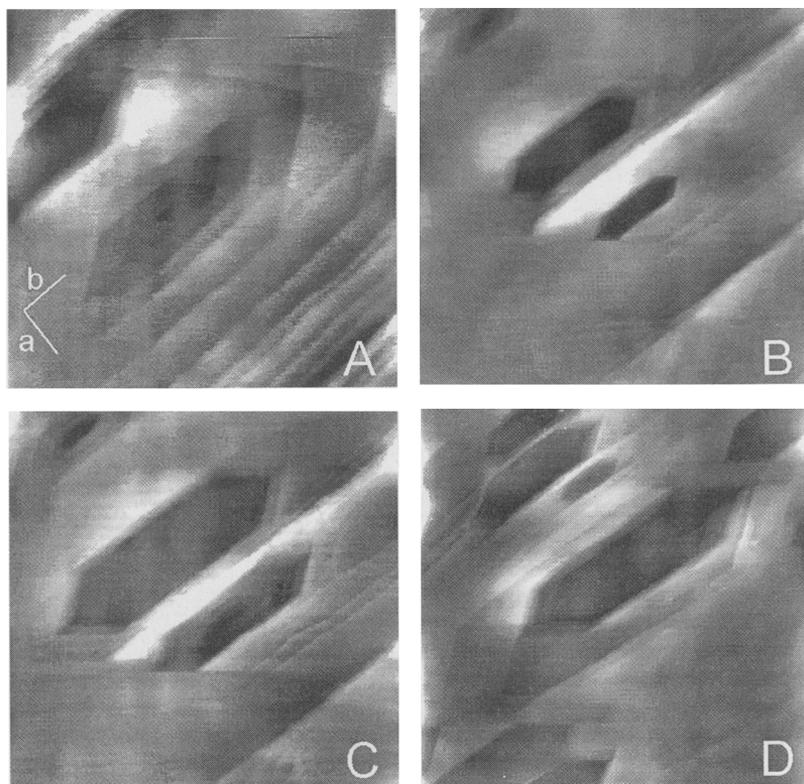


FIG. 1. Baryte (001) during dissolution in deionized water at 125°C and 700 kPa. (a) In each half layer ( $c/2$ ) steps generated by pits form a triangle. The triangles point in positive and negative  $a$ -directions in alternate layers (scan size:  $2 \times 2 \mu\text{m}^2$ ). (b)–(c) Steps parallel to  $\langle 120 \rangle$  (short sides of pit walls) retreat about two times faster than  $[010]$  steps (long sides of pit walls). Due to the alternating triangles and different step velocities, the shape of deep etch pits is six-sided and elongated in  $[010]$  (time between images: 216 s; scan size:  $10 \times 10 \mu\text{m}^2$ ). (d) Areas with a low dissolution rate (e.g. within the bottoms of deep etch pits) cover at least 30% of the surface (scan size:  $20 \times 20 \mu\text{m}^2$ ).

1995), baryte (001) dissolves with noticeable differences (e.g. pit geometry, step kinematics) at elevated temperatures. These differences show the importance in study dissolution of minerals by SFM in a wider range of temperature than possible in past times.

## References

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