In-situ observation of oxide and silicate mineral dissolution by hydrothermal scanning force microscopy: Initial results for hematite and albite

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The dissolution and growth of oxide and silicate minerals is of interest to the geochemical community in fields ranging from radioactive waste storage, enhanced oil recovery and the influence of weathering on global climate. Recently, application of scanning force microscopy (SFM) has revealed new details of dissolution and growth mechanisms for ionic solids such as calcite (Gratz *et al.*, 1993), but the dissolution rates of most oxide and silicate minerals are lower than the range accessible to *in situ* SFM imaging at room temperature (about 10^{-6} to 10^{-9} moles m^{-2} s^{-1}; Dove and Chermak, 1994, Stumm and Morgan, 1996).

The vapour pressure of water imposes a fundamental temperature limit on currently available SFM fluid cell temperatures. Here, we present initial results from an SFM of our design capable of imaging in aqueous solution up to 150°C. We report initial observations on the dissolution of hematite and albite in aqueous solution at 100°C−143°C and 6 bar. Albite dissolution is compared to the behaviour of periclase (MgO) at room temperature. Multicomponent oxides such as albite probably do not dissolve by a step-motion mechanism such as observed for calcite, gypsum, and brucite by SFM (e.g. Jordan and Rammensee, 1996). Rather, surface alteration and roughening occurs. Hydrothermal AFM provides real-time, *in situ* imaging access to reactions of silicate minerals with hydrothermal solutions.

Experimental

Our hydrothermal SFM consists of a stepper motor and piezoelectric tube scanner housed in a nitrogen-pressurized vessel. An inert membrane (Kalrez) separates the gas environment from a Ti fluid cell and optical window equipped with inlet, outlet and thermocouple ports. Flow is controlled by a mass flow controller. A 600 ml Ti bomb serves as a solution source. A Digital Instruments (DI) optical head was mounted on a custom base; electronics were developed to couple our SFM to a DI controller.

Results

Figure 1 shows a growth spiral on a hematite (0001) surface, imaged in pH 2 HCl (pH at 25°C) at 100 psi (N_2) and 135°C, flow rate = 330 µL/min. We estimate that the dissolution rate should be 2×10^{-9} mol $m^{-2}s^{-1}$ under these conditions, which for the step spacing in Fig. 1 corresponds to a step velocity of about 100 to 500 nm/hr. The fact that no clear evidence of step motion is found for this growth spiral after two hours indicates that the velocity of these steps is much slower than expected; the overall
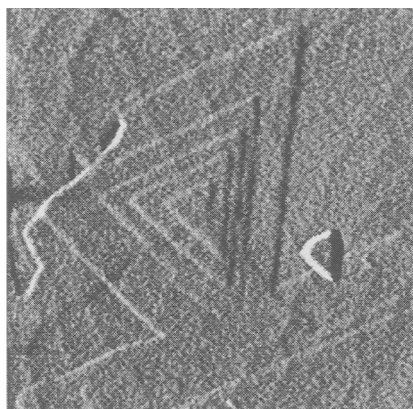

FIG. 1. A growth spiral on hematite (0001) imaged at 135°C *in situ*; image size is 4.0 × 4.0 µm. Steps surrounding growth spiral are single-layer steps.
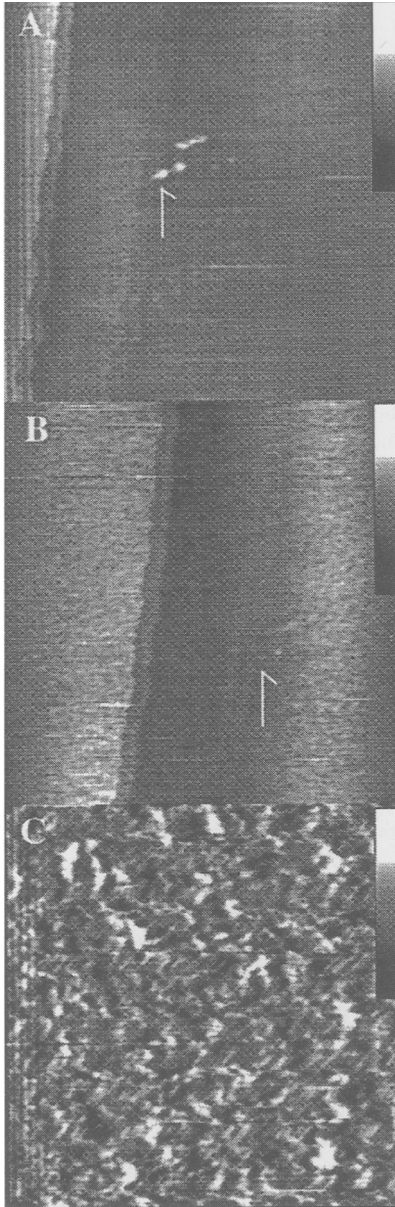
surface-area normalized rate must be dominated by areas of high step density, and probably by surfaces other than (0001).

Figure 2 shows a (001) cleavage surface of albite at 127°C in pH 1 HCl (100 psi N_2). There is no evidence of step motion during the 2 hours between Fig. 2a and 2b. However, we observe surface roughening between Fig. 2b and 2c; maximum roughness increases by about 8 nm within 4 hours. Under these conditions, the surface should be leached of Na and Al (Hellmann et al., 1990). The increase in maximum roughness is in approximate agreement with the expected thickness of a leached layer under these conditions. Arrows in Fig. 2a,b show the position of small protrusions (doubled by a tip artifact) that appear to dissolve. Steps are obscured by roughening (Fig. 2c).

The results for albite are similar to those for the 25°C dissolution of MgO (001) in pH 1.0 HCl. The MgO surface roughens rapidly as Mg^{2+} is exchanged out of the surface to form a (presumably) disordered hydroxide layer akin to brucite in composition. At steady-state, MgO surface roughness is constant, and the surface retreats by a rough-surface site-removal mechanism. We hypothesize that albite surfaces dissolving at low pH behave similarly, and Fig. 2 is an initial step in confirming this hypothesis.

These initial results from a new hydrothermal SFM are promising. In future, parallel SFM and wet-chemical (stoichiometric) experiments will further explore silicate and oxide mineral dissolution mechanisms. We will likely need to increase the temperature limits of the SFM before imaging of dissolution of more refractory silicate minerals becomes routine. Hydrothermal SFM will provide a unique window on dissolution and alteration mechanisms.

FIG. 2. Vertical greyscale in all images is 8 nm. (A) Albite (001) cleavage surface imaged at 127°C in pH 2 HCl. A double tip artifact produces double-images of all surface features. (B) Same surface as in (A), after 2 hours of dissolution. White arrows in (A) and (B) show the dissolution of protrusions. (C) Roughened albite surface after 4 hours of dissolution; original steps are no longer visible. Images (A) and (B) are $3.5 \times 3.5 \mu m$, image (C) is $5 \times 5 \mu m$.

References

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