Characterization of mica dissolution in the presence of bulk and confined solutions: Implications for natural weathering processes

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A significant portion of silicate weathering reactions taking place in soils and rocks occurs in the presence of thin films of water, for example within microcracks and micropores, and along grain boundaries. Here, the properties of aqueous solutions (e.g. atomic structure, solvent properties, viscosity, dielectric constant) can be quite different than they are in bulk solution, and the dominant transport mechanism shifts from advection to diffusion (Hochella and Banfield, 1995). It is unclear how these differences may influence dissolution and precipitation reactions. In this study we examine the characteristics and rates of mica dissolution at room temperature both in the presence of bulk solutions and thin, confined aqueous films. Mica minerals are ideally suited for this study because they can be cleaved to yield atomically smooth surfaces to produce films of uniform thickness.

Materials and methods

Phlogopite and muscovite samples were prepared by cutting approximately 1 cm^2 pieces with a scalpel and carefully removing thin sheets from both sides with tweezers. After cleaving, reactive sites were generated on the samples by brief exposure to dilute HF solution for periods ranging from 1 second to 10 minutes. Following exposure to HF, samples were thoroughly rinsed under a stream of membrane-filtered, deionized water for 15 minutes and blown dry with N_2.

Samples were imaged in air using a Digital Instruments Nanoscope III scanning force microscope (SFM) equipped with silicon nitride tips and cantilevers operating in contact mode. For bulk solution experiments, the samples were then placed in a well-stirred 2 L batch reactor containing membrane-filtered, deionized water equilibrated with atmospheric CO_2 and having a pH of ~5.7. For confined fluid experiments, the sample was wetted and clamped together with an unetched mica sheet and then placed in the same type of batch reactor. After reacting for periods of 24 to 48 hours in both the open and closed experiments, the samples were removed, thoroughly rinsed, and blown dry with N_2. The same regions of the sample were then reimaged using SFM. Several scans of each region were taken to ensure that observed changes were not caused by tip induced artifacts.

The thickness of fluid films formed between mica surfaces can accurately be measured over a range of a few nanometers to tens of micrometers with an optical interferometry technique known as FECO (fringes of equal chromatic order). Measurements using this technique have been made in our lab to measure film thicknesses between 800 nm and 25 µm, with an accuracy of ± 80 nm. Our implementation of the technique is currently being refined so that it will achieve sub-nanometer resolution down to film thicknesses in the nanometer range as previously demonstrated by Israelachvili (1973).

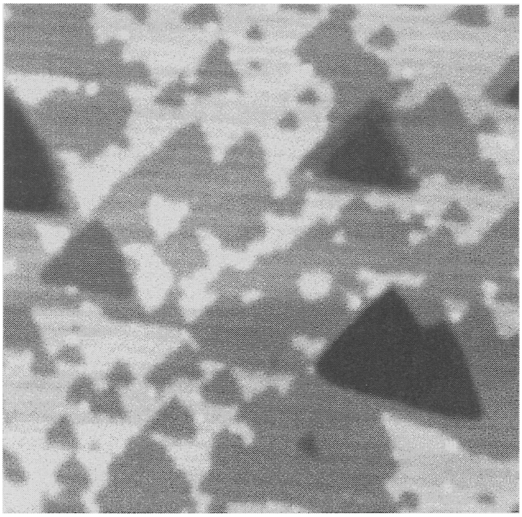

FIG. 1. SFM image of a phlogopite (001) surface after initial HF etching followed by 24 hours in DI water at pH 5.7. The image is 1.8 µm wide, and the total relief is 8 nm.

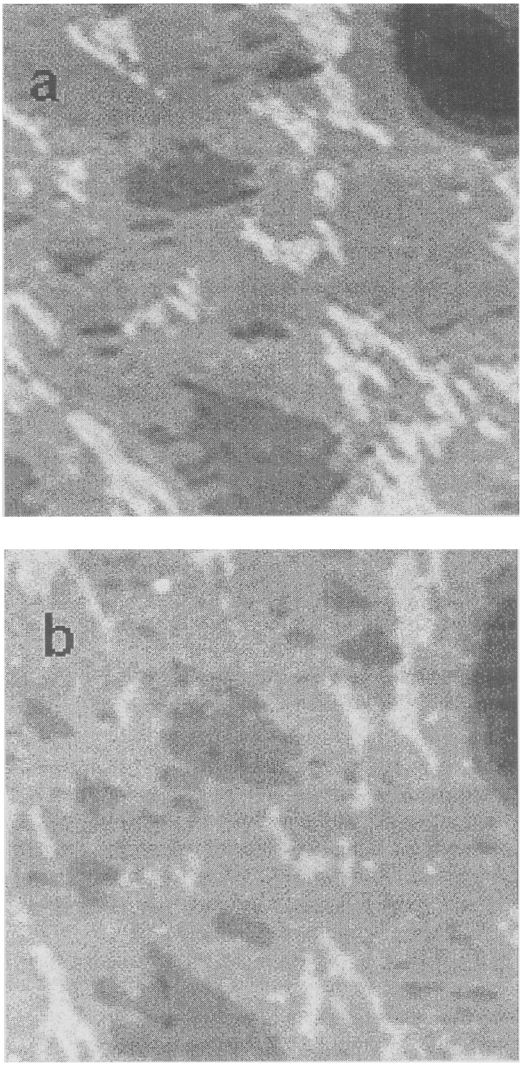

FIG. 2. Two SFM images of same region of muscovite (001) surface showing the same etch pits after initial HF etching (a), and followed by 48 hours reaction in DI water at pH 5.7 (b). Both images are 1.2 μm wide and the total relief is 5 nm. The images are slightly offset, and Fig. 2b is rotated by 21° CW relative to Fig. 2a.

Results and discussion

X-ray photoelectron spectroscopy and low energy electron diffraction analysis of both the phlogopite and muscovite (001) surfaces before and after HF etching indicate that no significant chemical or structural alteration is induced by this procedure. Most etch pits are 1 nm deep and commonly coalesce to form irregularly shaped terraces. Deeper etch pits are less abundant and range in depth from 2 to >30 nm. Phlogopite forms triangular pits (Fig. 1) while muscovite forms irregularly shaped pits (Fig. 2). Dissolution in the batch reactor proceeds by removal of material from step edges (Fig. 2a and b). While etch pits grow laterally during the course of dissolution, etch pits have not been observed to grow deeper.

Phlogopite (001) dissolution has been characterized by detailed analysis of SFM images of samples reacted in the presence of both bulk solution and a confined fluid film with an estimated thickness of ~40 μm. The volume of material removed from the edges of etch pits was determined by measuring the change in the lateral dimensions of the pits. Isolated, euhedral etch pits, such as the triangular etch pits shown in Fig. 1, were used for this analysis. Dissolution rates were normalized to the surface area of the steps forming pit edges. Dissolution rates for phlogopite determined in this way are $5.1 \pm 2.1 \times 10^{-10}$ mol m^{-2} sec^{-1} for the open case, and $1.1 \pm 0.6 \times 10^{-10}$ mol m^{-2} sec^{-1} for the confined fluid case. Rates are based on Si release, and (O,OH,F) = 24. These rates are valid only for the reactive surface area on phlogopite, and the difference between the open and confined case is most likely due to advective vs. diffusive transport of dissolved species away from the mineral-water interface. Dissolution data of this type will be invaluable in understanding dissolution rates obtained from field data, and in their comparison with laboratory data.

In our most recent approach, rates for both phlogopite and muscovite are being determined by the volume of material removed from pit edges as determined by isolating an individual feature and counting the change in the number of pixels occupying a specific topographic level before and after reaction. In order to calculate dissolution rates from this volume data, the reactive surface area of each feature must be determined by measuring the feature's perimeter using a pixel-edge counting routine. Preliminary dissolution rates measured this way for both muscovite and phlogopite range between 10^{-9} and 10^{-13} mol m^{-2} sec^{-1}. Note that the perimeter measurements are very sensitive to noise and image artifacts, and require high quality SFM images to yield quantitative results. These routines are currently being refined to provide more accurate perimeter measurements.