ATOMIC FORCE MICROSCOPY OF MICA SURFACE AFTER ION REPLACEMENT

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Atomic Force Microscope (AFM)\(^1\), is the newest, and potentially most powerful of the scanning probe microscopes. The (AFM) is capable of resolutions approaching atomic dimensions on ideal surfaces. One of the favorite such surfaces is that of mica. Muscovite mica has a plate-like structure consisting of an octahedral alumina sheet sandwiched by two tetrahedral silicate sheets. As a result of this structure, mica cleaves readily along a plane leaving a molecularly smooth surface. Because of the isomorphous substitution of the tetravalent silicon by trivalent aluminium, mica has an excess negative surface charge.\(^2\)

This negative surface charge of \(2.1 \times 10^{14}\) charges per cm\(^2\) is neutralized by an equal number of positive monovalent ions, mainly potassium ions. The ion-exchangeable surface ions of mica, in aqueous solution, can be readily replaced by other monovalent or multivalent ions. This ion exchange alters the surface of the mica. We then follow these changes by imaging with the AFM in air.

The AFM, which records the interatomic forces between the tip of a microfabricated cantilever and a sample, is used here to examine mica after the monovalent K\(^+\) ions have been replaced. Figure 1 shows AFM images of the structure of untreated mica imaged in air. The 7x7 nm (a) image is raw data. The 3x3 nm (b) image has been filtered and illustrates the typical hexagonal lattice structure of the mica surface. Dark areas correspond to lower areas, that is below the average surface height. The vertical distance from inside the lattice to the surface of the untreated mica measures about 0.10 nm. Figure 2 shows unfiltered (a) and filtered (b) AFM images of the mica surface after treatment with 0.01 N HCl solution for about 2 hours. Oxinium (H\(_3\)O\(^+\)) ions readily displace potassium ions on the mica, and are generally believed to penetrate the mica lattice and bind much more tightly than the potassium to the hydroxyl groups closest to the surface. The replacement of K\(^+\) by H\(_3\)O\(^+\) is energetically favorable. The vertical distance from inside the lattice to the surface measures 0.08 nm. The bright spots are interpreted as the H\(_3\)O\(^+\) ions occupying the center of the hexagonal lattice. Figure 3 shows the mica surface after the mica was treated with 0.1 M AlCl\(_3\). The vertical distance from inside this lattice to the surface is 0.25 nm. There is no evidence of the hexagonal mica lattice. Al\(^3+\) also binds strongly to mica and results in a net + charge on the surface. This is reflected in a stronger repulsive force between the AFM tip and the surface, and hence a larger apparent height.

These initial AFM results indicate that AFM images are directly related to the molecular structure of the sample surface. By chemically altering the mica surface in known ways, we have shown that the AFM image accurately reflects the expected changes in the mica surface. As mica is the substrate of choice for many AFM experiments, it is important to understand the effects of common chemical treatments on its surface. Such images are important to understand as we examine biologically relevant surfaces such as biomembranes or DNA on mica substrates.\(^4\)

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Figure 1  Untreated mica. Hexagonal lattices are evident in both 7x7 and 3x3 images.
Figure 2  HCl treated mica, (a) unfiltered 7x7 nm and (b) filtered 3x3nm.
Figure 3  AlCl3 treated mica (a) unfiltered 7x7 nm and (b) filtered 3x3nm.