

# Use of AFM in experimental surface geochemistry

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## Introduction

Atomic-force microscopy (AFM) was developed in the mid-1980s and is rapidly becoming one of the most widely used techniques for imaging mineral surfaces in air and aqueous solutions. Geochemical applications include determining the molecular- to atomic-scale structure of mineral surfaces (e.g., Ohnesorge and Binnig, 1993), probing forces at the mineral/water interface (Hartmann, 1992; Weisenhorn *et al.*, 1992), quantifying the role of surface heterogeneity in mineral growth (Dove and Hochella, 1993) and dissolution (Maurice-Johnsson *et al.*, 1994), measuring directly the kinetics of growth, dissolution, heterogeneous nucleation and redox reactions (Gratz *et al.*, 1993; Maurice-Johnsson, 1993; Maurice-Johnsson *et al.*, 1994), elucidating the effects of varying sorption mechanisms over the course of electrochemical reactions (Manne *et al.*, 1991), and measuring clay particle thicknesses (Blum, 1994). As a relatively new technique, the theory and applications of AFM are still in the development stage; as more laboratories join the AFM community, widespread critical review is needed.

Although AFM at first appears to be a simple technique, there are numerous potential pitfalls. This paper focuses on pitfalls and recommendations for 3 primary applications: (1) determining atomic-scale surface structure, (2) in-situ kinetic experiments, and (3) imaging particle morphology. The paper is not intended to be an extensive review but rather a catalyst for further discussion.

## Atomic-scale surface structure

The essential elements of AFM are the: tip, cantilever, detector (laser/cantilever/photodiode system), scanner, and sample. Each contributes its own set of limitations and artifacts (Barrett, 1991). This discussion focuses on tip/sample interactions as the most crucial element. *Forces in air and water.* AFM and the science of interfacial forces are evolving together, as theories of interfacial forces are used to explain imaging phenomena (Hartmann, 1992) while force spectroscopy is used to probe near-surface forces in various media (Weisenhorn *et al.*, 1992). The most important attractive forces are van der Waals

interactions (Hartmann, 1992) and capillary adhesion forces (Weisenhorn *et al.*, 1992). Capillary adhesion operates only in air (not solution), and results from formation of a meniscus made up of water and contaminants sorbed on the surface of the tip and the sample (Weisenhorn *et al.*, 1992). The primary repulsive force is the repulsive force that occurs between any two atoms or molecules at close approach, when their electron orbitals begin to overlap (Israelachvili, 1985); the effects on this force of factors such as surface-atomic relaxation remain in debate (Ohnesorge and Binnig, 1993). Repulsive forces also may arise from solvation or hydration forces (Israelachvili, 1985).

In aqueous solution, attractive or repulsive electrical double-layer forces may be present near tip and sample surfaces; these forces arise because surfaces in aqueous solution often are charged due to (Sposito, 1984): (1) permanent structural charge, (2) hydroxylation and ionization of surface functional groups, and/or (3) adsorption of ions from solution onto an otherwise uncharged surface.

*Importance of forces in atomic-scale imaging.* Since the advent of AFM, a controversy has raged regarding whether or not AFM can provide true atomic-scale resolution. The controversy revolves around the facts that (1) most published atomic-scale images show perfectly ordered periodic arrays, with none of the small-scale defects commonly present in STM images (e.g. Eggleston and Hochella, 1992); and (2) the heights of atomic corrugations often are inordinately large (Barrett, 1991).

Recently, Ohnesorge and Binnig (1993) demonstrated in a study of calcite structure that true atomic-scale resolution, including imaging of monoatomic steps, could be achieved only when the estimated net repulsive loading force was  $< 10^{-10}$  N. At higher forces, more than just the foremost tip atom may interact. Images with periodicity related to crystallographic structure can occur at higher forces, but the images do not show individual atoms, and high forces can distort relative atomic positions.

According to Ohnesorge and Binnig (1993), the 4 keys to atomic-scale resolution are: (1) using sharp tips, (2) imaging in solution, (3) systematically regulating forces, and (4) when possible,

imaging in the attractive-force regime. Previous work on molecular- to atomic-scale imaging of mineral surfaces (e.g. Hartman *et al.*, 1990; Johnsson *et al.*, 1991) should be improved upon using these guidelines.

Atomic-scale AFM analysis also should include: (5) imaging at numerous locations, on a number of samples or subsamples, with a variety of tips, in different media, and with systematic variation of imaging forces. Although atomic-scale imaging is difficult, such painstaking work is required. (6) publication of unfiltered images and transform plots. Although two-dimensional fast Fourier-transform filtering can be used to remove noise without introducing extra spots, unfiltered images are needed to evaluate the reliability of the data. Transform plots, while less glamorous than images, summarize data and are useful for determining artifacts such as drift and double-tip effects. (7) combination of AFM studies with STM, LEED, XPS, XRD, TEM, etc. Given mineral-surface heterogeneity and the potential for ambiguous structural data, combination of techniques is crucial.

#### Nanometer-scale imaging of surface reactions *in situ*

Important pitfalls of *in-situ* imaging over the course of reaction include: (1) accounting for surface heterogeneity, (2) linking macroscopic and microscopic data, and (3) ensuring that surface microtopography and reaction kinetics are not altered by the scan process. The first two require formulating statistical criteria, and a combination of geochemical techniques (Dove and Hochella, 1993; Maurice-Johnsson *et al.*, 1994). Although forces are minimized in solution, damage of the sample surface can occur, especially during small-region scans and when soft features are present; e.g. over the course of dissolution or during growth of an amorphous precipitate (Maurice-Johnsson, 1993). Small-region scan speed may be too fast to prevent the tip from abrading topographical features. Such damage often results in features that align with the scan direction and the image frame. Reaction rates may appear to vary from a small-scan (e.g. .5 microns) to a large-scan area (e.g. 16 microns). To evaluate scan-induced artifacts, *in-situ* reaction studies should include: (1) careful calibration and monitoring of forces, (2) systematic alteration of scan angle, (3) periodic y-dis-enablement, (4) periodic change in scan size, and when possible (5) occasional tip withdrawal and re-engagement.

#### Imaging particle morphology and thickness

An excellent review of particle morphology and thickness measurements is provided by Blum (1994), who discusses sample preparation and mounting procedures; characterization of substrate materials; and image collection, processing, and interpretation. In addition, this author has found polycarbonate membrane filters to be excellent substrates for many particles (Maurice-Johnsson *et al.*, 1994), and that Tapping-mode AFM often allows particles to be imaged more easily.

#### Conclusion

Although this review has only touched upon some of the many practices, procedures, and problems of AFM applications in geochemistry, it is hoped that further discussion will be generated. Like all new techniques, it will take some time to 'work out all of the bugs in the system', but with constructive criticism, the applicability to experimental geochemistry should continue to increase at a rapid rate.

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