USING ATOMIC FORCE MICROSCOPY TO STUDY SOIL MINERAL REACTIONS

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I. INTRODUCTION

Within the realm of modern science, many of the most challenging fields of endeavor involve *interfaces*. Not only are interfaces highly complex environments in and of themselves, they also require interdisciplinary research in a time of increased specialization. Soils are the quintessential interfaces at the earth's surface, for they are the links connecting the atmosphere, the hydrosphere, the geosphere, and the biosphere. Soil particles, with their high surface-area-to-volume ratios, present practically infinite environments for interaction. Yet, the structures, chemical compositions, and chemical reactivities of soil mineral surfaces remain but poorly understood.

Over the past few decades, new techniques and approaches have evolved to probe the complex natures of mineral surfaces and surficial interactions. Sophisticated surface-sensitive technologies, such as X-ray photoelectron spectroscopy (XPS), secondary-ion mass spectroscopy (SIMS), low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES), become even more complex when they are applied not to pristine single crystals but to the "dirty" real world of soil environments. Whenever a new technique is applied to problems of soilmineral reactivity, it is essential for the soil science community to conduct critical evaluations focused on the unique requirements of actual soils.

One of the most exciting new interface techniques applied by soil scientists is atomic force microscopy (AFM; also called scanning force microscopy, SFM). AFM was developed in 1985 (Binnig *et al.*, 1986), and applications by geochemists and soil chemists began to appear in the literature by the early 1990s (e.g., Hartman *et al.*, 1990; Hochella *et al.*, 1990; Gratz *et al.*, 1991; Johnsson *et al.*, 1991). Briefly, AFM works by rastering a sample underneath a sharp tip that is attached to or part of a cantilever. A variety of forces, as described in Section I.B, cause the tip to deflect as different surface features pass beneath it. By monitoring this deflection, a three-dimensional map of the sample surface can be constructed. Although the tip may be used to map out a variety of surficial properties, the most commonly used modes of AFM result in a map of surface microtopography.

A number of factors make AFM uniquely applicable to studies of soil surface structure and reactivity: (1) when used properly, AFM is for the most part non-destructive; (2) under most operating conditions, micron- to nanometer-scale resolution is easily attainable; (3) under ideal operating conditions, molecular- to atomic-scale resolution may be achieved; (4) surfaces may be imaged in air or immersed in liquids, including aqueous solutions (vacuum AFMs are also available); (5) a nanometer- to micron-scale portion of the surface may be imaged repeatedly such that reaction progress can be monitored; and (6) sample preparation is generally minimal.

In most early work, AFM did not appear to produce true atomic-scale images of complex mineral surfaces. However, in 1993, Ohnesorge and Binnig demonstrated that AFM could provide true atomic-scale resolution on the mineral calcite, using small attractive forces on the order of 10^{-11} N. In addition to atomic-scale imaging, AFM has been used successfully to probe forces at the mineral–water interface (Ducker *et al.*, 1991, 1992; Weisenhorn *et al.*, 1992); to measure directly the kinetics of growth, dissolution, heterogeneous nucleation, and redox processes (e.g., Hillner *et al.*, 1992a,b; Dove and Hochella, 1993; Gratz *et al.*, 1993; Manne *et al.*, 1994; Maurice *et al.*, 1995; Junta-Rosso and Hochella, 1996; Jordan and Rammensee, 1996); to visualize sorption of macromolecular organic substances and hemimicelles (Manne *et al.*, 1994); to image soil aggregates (Maurice, 1996); and to determine clay particle thicknesses and morphology of clay-sized particles (Lindgreen *et al.*, 1991; Maurice *et al.*, 1995; Friedbacher *et al.*, 1991; Blum and Eberl, 1992; Blum, 1994; Nagy, 1994; Zhou *et al.*, manuscript under preparation). Many additional avenues of research certainly remain to be explored.

The goal of this chapter is to present a critical review of the state-of-the-art of AFM as applied to research on the structure, chemical composition, and chemical

reactivity of soil particle surfaces. First, basic operating principles are reviewed. Second, tip-sample interactions are discussed, including forces between the tip and the sample, special considerations in the new tapping-mode AFM (TMAFM), and tip shape considerations. A variety of common artifacts are discussed, with the dual purpose of alerting new users to potential pitfalls and of enabling nonusers to evaluate more fully AFM results. Third, examples of applications to studies of soil chemistry—particularly soil *particle* chemistry—are presented. Finally, several "new frontiers" in AFM research are discussed. The goal is to provide the reader with a sense of the ever-increasing capabilities of AFM and to point out some of the potential problems and limitations that need to be recognized, addressed, and eventually overcome.

II. FUNDAMENTALS OF AFM

A. BASIC OPERATING PRINCIPLES

We work primarily with commercial atomic-force microscopes manufactured by Digital Instruments (DI; Nanoscope II and Nanoscope III). The discussion that follows therefore is biased toward the Digital Instruments machines. The discussion should be applicable to most commercial AFMs, although some of the details and terminology may vary, depending on the manufacturer.

Detailed reviews of the basic operating principles of AFM were provided by Hochella (1990, 1995), Eggleston (1994), and Maurice (1996). A brief review of the basic operating principles is provided here as background for further discussion of image collection and interpretation.

AFM design is elegantly simple (Fig. 1). A sample is mounted on a piezoelectric tube, which allows the sample to be precisely scanned under a sharp tip that is attached to or part of a cantilever. Stable motion on a scale of less than 1.0 Å is possible with a well-built piezoelectric scanner. Deflection of the cantilever as the sample is scanned under it can be monitored by a variety of mechanisms, the most common of which is via an "optical lever" consisting of laser light reflected off the end of the cantilever toward a photodiode detector (Fig. 1). AFM imaging may be conducted in either the constant-force mode (also known as "height" mode), in which a feedback loop is used to adjust the height of the sample to keep the cantilever deflection constant during sample scanning, or the so-called constantheight mode (also known as "force" mode), in which the response of the z-piezo is more sluggish so that the height of the sample remains more nearly constant, and the cantilever changes its deflection as the sample is scanned under it. The constant-height mode is not appropriate for surfaces with a large amount of topographic relief, because the sample surface may be damaged as the z-piezo fails to



Figure 1 Schematic illustration of the atomic force microscope, showing that the essential elements are the tip, the cantilever, the detector (laser-cantilever-photodiode system), the piezoelectric scanner, the computer control, and the sample.

compensate for large changes in relief and the tip drags against relatively large topographic features.

As the surface is scanned, the computer keeps track of the position of the x-y scanner, controllable to the Ångström level and integrates these data with either the z-piezo movement (height mode or constant-force mode) or the cantilever deflection (force mode or constant-height mode). Individual scan lines are compiled into an image. The number of scan lines may vary with machine and application but is commonly 512. Since each scan line contains 512 points, a complete image consists of a grid of 512 points on a side. Each point represents a unique set of xyz coordinates. One area of the sample surface may be scanned repeatedly, providing a sequential series of images.

Scan speed must be varied as a function primarily of image size. In general, larger images (greater than 1 micron on a side) require slower scan speeds (less than 10 Hz) so that the tip may properly track large-scale surface features. Too fast a scan speed may result in smeared-out edges in the scan direction; an example is shown in Fig. 2. Smaller images (less than 1 micron) require increasingly faster scan speeds, primarily to account for thermal and piezoelectric drift. A 1 μ m- (or



Figure 2 Scanning too fast over sharp features (in this case, submicron-scale hematite particles) can result in "tail of the comet" type structures in the direction of scan. In essence, the signal is smeared by a scan speed that is too fast, resulting in a tip that cannot properly track features. Scan direction from right to left. Image by J. Forsythe (Kent State Univ.). Scan area = $2.00 \,\mu$ m on a side.

larger) scale image often takes approximately 1 to 3 minutes to complete; a nanometer-scale image can be completed in less than a minute. We have found that good TMAFM images of particles (discussed later) take much longer to complete than do contact-mode images. We routinely run micron-scale images at less than or equal to 1 Hz, so that a single image frame can take 10 minutes or longer to complete.

Depending upon the size of the particular scan head used, the microscopist may move from one area to another within a small region of space (e.g., a common scan head permits imaging anywhere within an area 16 microns on a side). The microscopist also may zoom in to an area of interest, although thermal and piezoelectric drift and piezoelectric nolinearity may limit precise "zoom" capabilities. This zoom capability does not merely blow up the area of interest; rather, the zoom area is imaged with higher resolution.

The computer control must go through a variety of data-processing procedures to compile an image that is true to sample structure and interpretable to the human eye. Blum (1994) discusses in detail planefit corrections for sample tilt (slope) and flattening procedures that are required for proper interpretation of rough surfaces. A variety of real-time high and low pass filters also may be applied. Such filters often are needed to remove vibrational noise during molecular- to atomic-scale imaging in air or solution. However, they need to be used with extreme caution because they do remove some portion of the overall signal (Blum, 1994). Use of real-time filters, and of postprocessing filters, as well, should be reported in publications, and images with and without filtering should be compared. For microtopographic images, we recommend that real-time filters not be used, since they seldom are needed at larger scales and the fact that they remove a portion of the overall signal means that resulting images cannot be used for precise measurements. If real-time filters appear to be needed, the AFM probably needs to be moved to a quieter room or placed in an isolation chamber. Postprocessing application of low-pass filters, of planefit filters to account for sample tilt, and of flatten filters to correct for problems associated with variable topography are common practice but should always be reported.

In general, we have found that AFMs work best if they are placed in a room located on bedrock, without windows, far removed from other equipment, and with temperature and humidity control. Basement closets often work well, if they are not too damp. Frequently encountered problems include too much traffic in and around the room; noisy heating and air conditioning; telephone noises; and poor humidity control, which can lead to the tip "sticking" to the surface because of thick layers of adsorbed water or to buildup of static electricity. Room temperatures of approximately 68°C tend to work well; warmer temperatures seem to result in increased thermal drift, whereas cooler temperatures can be uncomfortable when the microscopist sits still for hours on end. Vibrational noise, which can be a major problem for atomic-scale imaging, generally can be corrected for by placing the AFM on a cement block suspended from elastic cords. A variety of isolation boxes also are available from the manufacturer. Eggleston (1994) showed how a ringing telephone can ruin a high-resolution image. We use a telephone with a blinking light and turn the ringer off.

B. TIP-SAMPLE INTERACTIONS

1. Forces between the Tip and the Sample

Because AFM works by mechanical interaction between the tip and the sample, it is important to understand the nature and magnitude of tip-sample interaction forces. An excellent review of tip-sample interaction forces was provided by Eggleston (1994); a brief review is provided here.

Most AFM imaging to date has been conducted in the so-called repulsive mode, also known as the contact mode, wherein repulsive forces between the tip and the sample dominate. The main repulsive force is responsible for the original name of the instrument. This is the so-called atomic force that occurs between any two given atoms (e.g., on the tip and sample surfaces) when the electron clouds of the atoms begin to overlap. These repulsive forces have often been called Pauli-exclusion forces. Repulsive forces also may arise from solvation or hydration forces that occur because water near hydrophilic surfaces is structured (Israelachvili, 1992). When the tip and the sample are brought into close contact during atomic-force microscopy, resistance occurs; hence apparent repulsion arises as the structured water molecules on the surfaces of the tip and the sample are pushed away. Van der Waals (VdW) interaction forces also need to be considered. As described by Eggleston (1994), VdW forces are long-range, relatively weak forces that are generally attractive but can become repulsive in some media. Repulsive or attractive electrostatic forces also may come into play. As described in Section III.B, surface scientists are using AFM as a probe of double-layer forces by systematically varying tip and sample materials and solution conditions.

During imaging in air, capillary adhesion, which is a relatively strong attractive force, can become important. This capillary force results from formation of a meniscus made up of water and adventitious organic contaminants sorbed on the surface of the tip and the sample (Weisenhorn *et al.*, 1992). The capillary force is large and has been estimated to be on the order of 10^{-7} N or greater (Weisenhorn *et al.*, 1989). When the tip and the sample are completely immersed in water or another liquid, a meniscus does not form and hence the capillary forces are absent. Due to limitations imposed by the capillary forces, the minimum force that can be achieved by AFM in air tends to be on the order of 10^{-7} N. By working in solution, the overall tracking forces can be reduced by two to three orders of magnitude. Weihs *et al.* (1991) noted that the adhesive force between the tip and the sample decreased with decreasing tip radius. Capillary forces were reduced for samples in vacuum or in low-humidity environments (Thundat, 1993).

Lateral frictional forces also must be taken into account as the sample is rastered beneath the tip. Frictional forces have been shown to vary on an atomic scale and with temperature, scan velocity, relative humidity, and tip and sample materials (Delawski and Parkinson, 1992; Overney *et al.*, 1992). Scan direction also can be important. Frictional forces tend to be greatest when scanning parallel to the long axis of the tip-cantilever system (0° on Nanoscopes), due to flexure of the cantilever. Rotating scan direction to be perpendicular to the long axis (90°) often reduces lateral frictional forces and can be helpful in imaging particles that otherwise tend to be plucked from substrate surfaces.

As opposed to contact-mode, TMAFM (DI, 1995; Zhong *et al.*, 1993; Prater *et al.*, 1995) is a relatively new technique that allows high-resolution topographic imaging of soft, adhesive, or fragile samples because it overcomes problems associated with friction, adhesion, and electrostatic forces (Prater *et al.*, 1995). In TMAFM, a piezoelectric driver is used to excite the cantilever into resonance oscillation. The tip is thus caused to vibrate and to contact the sample surface numerous times for each data point. When imaging in air, the cantilever oscillation

is damped when the tip contacts the water layer and the sample surface, but the large vibration amplitude gives the cantilever sufficient energy to overcome the surface tension of the adsorbed water layer. TMAFM uses the root-mean-squared (RMS) of the cantilever deflection feedback symbol to keep the cantilever vibration amplitude constant by adjusting the piezo height. The change of voltage applied to the z piezo reflects the topography of the sample (Digital Instruments AFM Manual, 1993). The force between tip and sample is only 10^{-10} to 10^{-9} N. TMAFM has a large, linear operating range that makes for highly stable vertical feedback, allowing routine reproducible sample measurements (Prater *et al.*, 1995). Although originally TMAFM could not be performed in solution, a new TMAFM fluid cell has been developed. TMAFM does not appear to be capable of producing atomic-scale images on most surfaces. However, TMAFM is the technique of choice for imaging rough and/or easily deformable surfaces at scan sizes on the order of a few tens of nanometers and larger.

2. Tip Size and Shape Considerations

Finite tip size and shape are responsible for many of the major artifacts in AFM images. To a certain degree, the resolution of an image is dependent on the quality of the tip. Blum (1994) and Maurice (1996) have reviewed imaging artifacts caused by different tip shapes in imaging environmental particles. Eggleston (1994) summarized tip-sample interactions and resulting artifacts on nm-scale images.

Typical contact-mode imaging, including atomic-resolution imaging, is generally conducted using standard silicon nitride (Si_3N_4) probes that are integrated tips-cantilevers. These probes may also be used for TMAFM in solution, although we have found that specialized force modulation etched silicon probes tend to work better. As supplied (from DI), each Si_3N_4 probe contains two cantilever lengths and two widths, which are usually referred to as thick- and thin-legged. Thus, four different cantilever geometries result, with four different possible force (spring) constants. Different geometries may work better for atomic-scale versus micron-scale imaging or for different surfaces. Hence, it is worthwhile to try different cantilever geometries and see which works best for a particular application. A fall, 1996, DI Web page (http://www.di.com) gives the following specifications for standard Si_3N_4 probes:

Force (or spring) constants: 0.58, 0.32, 0.12, 0.06 N/m* Nominal tip radius of curvature: 20–60 nm Cantilever lengths: 100 and 200 μ m Cantilever configuration: V-shaped Reflective coating: gold Shape of tip: square pyramidal Tip half angle: 35° (*Actual values can vary substantially.) For tapping mode, etched silicon probes generally are used. Each probe contains only one integrated tip-cantilever. DI reports the following specifications for etched silicon tapping-mode probes:

Force (or spring) constants: 20-100 N/mResonant frequency: 200-400 kHzNominal tip radius of curvature: 5-10 nmCantilever length: $125 \mu \text{m}$ Cantilever configuration: single beam Reflective coating: uncoated Tip half angle: 17° side, 25° front, 10° back

Barrón *et al.* (1997, in press) report that these probes have a solid angle of between 20 and 50°, but that this solid angle decreases to about 20° within 200 nms of the end of the probe.

Blum (1994) reported that for vertical features less than ~ 30 nm, such as low-relief steps, the radius of curvature of the tip limits the resolution. This problem can make low-relief features and small particles either appear to be too broad or cause them to disappear altogether (Barrett, 1991; Griffith and Grigg, 1993). Wilson *et al.* (1996) demonstrated that contact-mode AFM images of biomolecules and other structures on the order of 10s of nanometers in height often are enlarged by as much as 25% due to the finite size of the tip. Note that the nominal radius of curvature for Si₃N₄ tips is greater than for etched silicon tapping-mode tips. These are "nominal" radii, because the radius of curvature may vary depending upon defects in manufacturing, and because tips tend to abrade with use. Although the nominal radius is less for tapping-mode tips, this does not result in higher resolution at the near-atomic scale. At present, the tapping procedure itself appears to limit resolution to the scale of 10s to 100s of nanometers.

Blum (1994) also reported that for imaging larger-scale features (vertical features greater than \sim 30 nm), it is the shape of the tip (tip half angle) that limits resolution. For large-scale features, tip shape can "convolve" with surface features, often producing misleading results (the quotation marks are used because this is not a true convolution, since it is nonlinear). When the tip rides over a sharp feature on a sample surface, the sides of the tip often contact the edges of features before the apex of the tip comes into contact. The solid angle (pyramidal) of a standard Si₃N₄ tip is ~55°, and according to Blum (1994), the steepest vertical features that can be accurately imaged are ~62.5°. Note that tapping-mode tips have asymmetrical tip half angles. Hence, different scan angles may result in notably different resolution on topographic features. Typical tapping-mode tips are sharper overall than contact-mode tips, and we have found that resolution of microtopographic features and submicron-scale particles tends to be better using tapping mode.

Often, tip-related artifacts can be difficult to identify as such; hence, the expe-

rience of the microscopist becomes invaluable. Excellent reviews, such as Griffith and Grigg (1993), are helping to alert microscopists to problems, limitations, and potential solutions. Once a particular artifact, such as a reverse-tip image (discussed later), is properly identified, the microscopist is alerted that similar structures imaged on other samples may also be artifacts.

In the extreme case of very sharp features on sample surfaces, a reverse image of the tip may result (Oden *et al.*, 1992). The process controlling such reverse-tip images is illustrated in Fig. 3(a). Such reverse-tip images show structures related to the tip shape, primarily pyramidal features with triangular facets. Convolution may result in an entire reverse-tip image, or more in subtle effects along step or particle edges, or wherever a sample surface feature is steeper than the tip structure. This problem can be particularly frustrating in the imaging of particles, as shown in Figs. 3(b) and 3(c). Figure 3(b) shows "convolution" along the termination of a needle of hydroxypyromorphite (HPY). Apparently, the end of the nee-

(a) (b)
Tip-cantilever
Sample



(c)



Figure 3 (a) Schematic illustration of how tip shape can "convolve" with sample shape if surface features are sharper than the tip. (b) An example of tip-sample "convolution." Here, the end of a hydroxypyromorphite (HPY) needle is probably oriented perpendicular to the substrate, resulting in convolution with the tip (see arrow). Scan area = 1.20 μ m on a side. (c) Reverse-tip images that occurred upon imaging submicronsized particles of hydroxylapatite (HAP). Numerous reverse-tip images are scattered across the image. Scan area = 3.21 μ m on a side. TMAFM images. dle was sticking up from the surface. Figure 3(c) occurred while imaging submicron-size particles of hydroxylapatite (HAP) and contains reverse-tip images. In Figs. 4(a) and 4(b), AFM images of hematite particles (a) are compared with TEM images of the same sample (b). Convolution with tip shape tends to obscure the



(a)



(b)

Figure 4 TMAFM images in air of hematite particles deposited on pc membrane filters (a) are compared with a TEM image of a different subsample from the same sample (b). The left-hand image in (a) shows height data; the right-hand image shows amplitude data. Pores are apparent on the filter-paper substrate in the AFM images. Scan area of each image is $2.35 \,\mu$ m on a side. Length of scale bar in (b) is 100 nm.

"Convolution" of sample and AFM tip shape tends to obscure the hexagonal-to-rhombohedral shapes of the particles, which are apparent in the TEM image. Such tip-sample convolution artifacts are common during imaging of particle aggregates, which tend to have rough surfaces. TEM image courtesy S. Traina, Ohio State University.

hexagonal to rhombohedral shapes of the particles, which are apparent in the TEM image. Such tip-sample convolution artifacts are extremely common during imaging of particle aggregates, which tend to have rough surfaces.

Tip-sample convolution also can lead to more subtle artifacts, such as sloping step and particle edges. For example, Fig. 5 (cross section) shows a distorted kaolinite edge surface caused by convolution of the tip shape with the vertical kaolinite edge (Zhou *et al.*, manuscript in preparation). The kaolinite crystal should have a vertical edge. Due to convolution, the edge of the kaolinite particle is a reverse mirror half-tip shape. Note that no distortion occurs on the basal-plane surface (001). This type of artifact does not affect the measurement of particle thickness; particle diameter can be measured from the top of the particle, but not from the bottom.

Kepler and Gewirth (1994) noted that different types of tips will result in different shapes of artifacts; for example, they found square pyramidal tip-sample convolution artifacts with a Digital Instruments Nanoscope tip-cantilever but triangular artifacts with a Park Scientific Ultralever tip-cantilever. The Nanoscope Si_3N_4 tips ideally have rectangular pyramidal shapes, whereas the Park Scientific Ultralever tips ideally have a triangular shape. Finally, frictional forces between tip and sample may result in frictional tip-sample convolution artifacts; such artifacts generally have a roughly L-shaped outline as the tip drags across a sharp surface feature.

Tip dimensions also can limit the ability of the tip to image narrow, deep features, such as steep-sided pits. In such a case, the pit will appear to be V-shaped, since the edges of the tip meet the sides of the pit before the tip reaches the bottom. If pit depth exceeds maximum z (height) range, the pit may appear to be too shallow and flat bottomed (off-scale).

In attempts to circumvent tip-shape artifacts, tips have been developed with high aspect ratios or smaller radii of curvature (Kado *et al.*, 1992; Keller *et al.*, 1992). Unfortunately, sharp tips tend to be fragile. As an alternative, a number of researchers have proposed methods and algorithms for improving images using deconvolution procedures. As pointed out by Griffith and Grigg (1993), the term *deconvolution* is not strictly correct because the tip and sample interact in a non-linear fashion; nevertheless, the term will be used here for simplicity. Some researchers have relied on purely mathematical treatments in which the geometry is assumed to be an idealized shape, such as spherical; however, more precise methods are possible. Markiewicz and Goh (1994) back-calculated the tip shape by imaging samples (polybead-amino microspheres) of known size and geometry, recognizing that the AFM image will be a convolution of tip and samples. Wilson *et al.* (1996) used 14-nm gold spheres in a similar procedure and found good agreement between back-calculated or "restored" tip shapes and actual SEM images of



Figure 5 TMAFM image in air of a kaolinite particle on muscovite mica. Cross section shows how the particle edges are distorted due to tip-sample convolution; however, accurate particle diameter and thickness data can be obtained. Vertical distance AB (15.9 nm) is the thickness of the particle; horizontal distance, CD (112.5 nm), is the diameter; vertical distance EF (0.22 nm), is the height difference on the mica substrate at points E and F. From Zhou *et al.*, manuscript in preparation.



Figure 6 TMAFM image in air of a hydroxylapatite (HAP) surface. The three-pronged "birds-foot-like" features that appear scattered on the surface, all with the same orientation, are not real surface features but rather the result of a "dirty" or imperfect tip. Scan area is 5.00 µm on a side.

tips. Deconvolution procedures such as these need to be calibrated and standardized and necessary algorithms incorporated into AFM software.

Irregular tip shapes can pose additional problems. On the atomic scale, multiple (more than single-atom) tips can lead to a confusing array of apparent atomic-scale surface structures. The effects of multiple tips on atomic-scale imaging have been the subjects of numerous investigations. Such investigations should continue in light of Ohnesorge and Binnig's (1993) reevaluation of atomic-scale imaging. At microtopographic scales, tips with irregular structures can lead to equally erroneous and potentially misleading results. This tends to be an especially major problem when imaging soft and deformable surfaces from which material can be scraped up and deposited on the tip. Figure 6 shows a surface that was imaged with a "dirty" tip. Small bird-foot-shaped features appear scattered across the surface, with the same orientation. These features are not part of the surface, but rather the result of convolution between an imperfection or "dirt" on the tip and surface features. Figure 7 shows apparent doubling of particles that results from a double tip.



Figure 7 TMAFM image in air of hydroxypyromorphite (HPY) needles deposited on pc membrane filter paper. The apparent doubling of features is the result of a double tip shape. Scan area is $1.10 \mu m$ on a side.

III. EXAMPLES OF APPLICATIONS

A. ATOMIC-SCALE AFM

Mineral surface structure is seldom or perhaps never an exact extension of the bulk; rather, we can expect some relaxation and/or reconstruction to occur at most surfaces. Until recently, mineral surface structure had to be inferred, for the most part, due to a lack of surface structural techniques. Although TEM on microtomed sections may provide surface and near-surface structural data, some sample disturbance may occur, and the sample must be analyzed in vacuum. LEED can give symmetry and spacing information, although the diffraction pattern is a statistical representation that does not work optimally for small particles, such as clays, or for heterogeneous surfaces.

The advent of AFM during the mid- to late 1980s raised considerable excitement within the community of scientists studying mineral surfaces and surfacerelated phenomena, because AFM appeared to be a simple and straightforward technique for determining atomic-scale surface structure under environmentally appropriate conditions, e.g., on particles in air or immersed in aqueous solutions. During the late 1980s and early 1990s, a number of articles were published showing the apparent molecular- to atomic-scale structures of several important soil minerals. However, it was quickly noted that these images for the most part showed perfectly ordered periodic arrays, with none of the small-scale defects, such as monoatomic steps and kink sites, commonly present in STM images (e.g., Eggleston and Hochella, 1992). This eventually led many researchers to suspect that, like all techniques, atomic-scale AFM imaging could be subject to a variety of potential pitfalls.

In 1993, Ohnesorge and Binnig published a landmark paper that is helping to redefine atomic-scale AFM imaging. These authors argued that most pre-1993 supposed atomic-scale imaging had been conducted with too high a force between the tip and the sample. Given that the typical force constant for a chemical bond is on the order of 100 Nm^{-1} , tip-sample interaction forces greater than 100 nN, as commonly encountered in repulsive-mode (contact-mode) imaging in air, would displace the atoms in a bond by nm distances (Eggleston, 1994). Such strong forces would likely break bonds and damage the sample surface. Additionally, strong forces may result in the tip being driven into the sample such that the contact point between the tip and sample consists of several atoms. Images with periodicity related to crystallographic structure can occur at high contact forces, but the images do not show individual atoms, and high forces can distort relative atomic positions.

Ohnesorge and Binnig (1993) argued that these problems could be overcome by imaging in solution and in the attractive mode. In a study of calcite structure, they demonstrated that true atomic-scale resolution, including imaging of monoatomic steps, could be achieved only when the estimated net repulsive loading force between the tip and the sample was less than or equal to 10^{-10} N. According to Ohnesorge and Binnig (1993), the four keys to true atomic-scale resolution are using sharp tips, imaging in solution, systematically regulating forces, and, when possible, imaging in the attractive-force regime. Their true atomic resolution images on calcite were obtained with tip-attractive forces of $\sim 10^{-11}$ N. Images collected in air or with relatively high forces may still be valuable in that the observed structures should be related to crystallographic parameters, even though individual atoms are not accessible. However, previous work on molecular- to atomic-scale imaging of mineral surfaces should be reevaluated and perhaps improved upon with the help of these guidelines.

Clear, regular, repeatable atomic-scale images are needed to evaluate atomicscale surface structure. Unfortunately, atomic-scale AFM imaging is at present extremely difficult. Thus, many noisy, irregular images have been published. One common problem is that images often are published containing just one isolated regular unit cell, or several unit cells, surrounded by irregular features that may be either noise or noncrystalline material. However, reproducibility both within a single image and from one image area to another is essential.

AFM studies of atomic-scale surface structure should include 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. Feedback oscillations with a periodicity that could be confused with atomic-scale structure can occur if the gains are set too high. It is therefore important to confirm that apparent atomic-scale structure is "real" by systematically altering scan rate, scan size, scan angle, scan direction, and gains. Although atomic-scale imaging is time-consuming, such painstaking work is required. Publication of unfiltered images and transform plots is important for proper image interpretation. Two-dimensional fast Fourier-transform filtering can remove noise without introducing extra spots, but unfiltered images are needed to evaluate the reliability of the data. Transform plots succinctly summarize data and are useful for determining artifacts such as drift and double-tip effects. Combination of AFM with other techniques such as STM, LEED, XPS, XRD (X-ray diffraction), and TEM is crucial, especially considering that mineral surfaces tend to be heterogeneous and that structural data may be ambiguous. There is a critical need within the AFM community to address sampling statistics and to set standards for image quality and reproducibility.

B. AFM as a Probe of Double-Layer Forces

The use of AFM as a probe of double-layer forces is one of the most exciting developments from the standpoint of mineral-water interface geochemistry. Prior to AFM development, the most widely regarded technique for measurement of surface forces was the Israelachvili-Adams force apparatus, which works by measuring the force between two cylindrical macroscopic surfaces. Israelachvili and Adams (1978) measured the forces between two muscovite sheets at close approach, in solutions of different pH and ionic strength. A limitation of their experiments was the use of multiple beam interference to measure surface roughness. Visible light interference probably is not sensitive enough to detect small-scale features of limited lateral extent, e.g., ultrafine particles and small pits. Johnsson et al. (1992) showed that muscovite may develop small etch pits and other surface features rapidly upon exposure to aqueous solution. Additionally, muscovite is brittle and may form fine fractures upon bending (into cylindrical form). AFM circumvents these problems because surface microtopography may be measured at the nanometer scale, although sample drift makes it difficult to define the exact area of measurements.

Butt *et al.* (1995) recently reviewed AFM force measurements in liquid environments. Tip-sample interaction forces can be measured by recording force curves, wherein the deflection of the cantilever is monitored as the tip approaches

the sample, the tip and sample come into contact with one another, and the tip is subsequently retracted. Ducker et al. (1991, 1992) succeeded in probing the forces between a tip consisting of a silica sphere and a planar silica surface oxidized to a depth of ~ 30 nm, immersed in solutions of different ionic strength. The authors collected force-vs-tip-sample displacement data in solutions of ionic strength 10⁻⁴ to 10^{-1} M. To convert these measurements to force-vs-distance data, zeros of force and distance had to be defined. The zero of deflection was chosen where the deflection was constant, i.e., with the spherical tip and sample far apart. The zero of distance was defined based on the point at which the photodiode output became a linear function of displacement of the sample, i.e., where the spherical particle was in contact with the surface. The resulting force-vs-distance curves generally were in agreement with double-layer theory. However, deviations were observed at very short distances. The authors noted that these deviations could be due to hydration forces, i.e., relatively ordered water bound to the mineral surface, but that the potential effects of surface roughness could complicate the interpretation. Experiments by Ducker et al. (1991, 1992) pioneered the measurement of colloidal forces between colloidal-sized probes (tips) of different compositions and various sample surfaces. Butt (1994) extended this technique to measure the forces on a colloidal-sized glass particle as it entered an air bubble or a water droplet.

Weisenhorn *et al.* (1992) recorded force-vs-distance curves for interactions between a Si₃N₄ tip and mica in KCl solutions at pH ~6.6 and ionic strengths of 0.1-30 mM. They found that the force curves showed repulsive behavior in the noncontact regime, presumably due to double-layer forces. The repulsion decayed exponentially with increasing distance, as expected from double-layer theory. Plots of the Debye length (1/ κ) versus inverse square root of the concentration from 0.1 to 30 mM KCl showed that 1/ κ decayed with increased ionic strength, as expected from double-layer theory; the measured slope of 0.308 compared favorably with the predicted value (0.305).

Butt *et al.* (1991a,b) showed that electrostatic tip-sample forces depend strongly on both pH and salt concentration. They showed that the pH and/or salt concentration may be adjusted so that attractive VdW forces are in effect cancelled out by repulsive electrostatic forces. Thus, careful choice of solution may allow one to minimize potentially damaging adhesive tip-sample interaction forces.

Radmacher *et al.* (1994) used laterally resolved force curves to study the adsorption of organic (lysozyme) molecules on mica. They showed that the adhesion forces between the Si_3N_4 tip and the mica surface were different from the forces between the tip and the adsorbed molecules. These results demonstrate the potential for development of a form of atomic force spectroscopy based on force-curve characteristics (see Section IV). Manne *et al.* (1994) utilized noncontact-mode AFM, based on double-layer repulsion between tip and sample, to image surfactant hemimicelles on highly oriented pyrolitic graphite (HOPG). Hence, the double layer can be utilized to image delicate structures.

C. IN SITU AFM STUDIES OF MINERAL GROWTH AND DISSOLUTION

1. Fundamentals of in Situ AFM

Until recently, most studies of mineral-water interface reactions have relied primarily on macroscopic observations, e.g., monitoring the concentrations of reactants or reaction products in solution. For example, dissolution experiments traditionally are conducted over a range of saturation states, the concentrations of constituents released to solution are measured at various intervals, and a curve is fit to the data. The "order" of this curve often is taken to give an indirect indication of the reaction mechanism. In reality, simple curve fitting does not provide direct evidence of the type of reaction mechanism and may result in misleading interpretations (e.g., Inskeep and Bloom, 1985; Rimstidt and Dove, 1986; Shiraki and Brantley, 1995). Hence, kinetic studies need to incorporate some means of directly documenting a process as it occurs at the mineral surface.

In situ AFM is being used to fill this void in mineral-water interface chemistry by permitting researchers to directly monitor changes in mineral surface microtopography over the course of reaction in aqueous solution, at micron to subnanometer scales. Indeed, the potential exists for watching changes in atomic-scale features, such as movements of monoatomic steps, over the course of reaction although this potential is not yet fully realized. By monitoring changes in microtopography in response to varying reaction parameters, such as time, saturation, and pH, researchers can directly support or refute hypotheses developed based on macroscopic observations or modeling. Whereas macroscopic observations give information about overall reactions, AFM provides insight into surface heterogeneity and variations in reaction rates and "mechanisms."

AFM has advantages over other "*in situ*" microscopic techniques. Scanning tunneling microscopy (STM) also may be used in solution, but its use is generally limited to conductors or semiconductors, and the tunneling current may promote electrochemical reactions. Environmental SEM (ESEM) may be used on hydrated surfaces but not on surfaces fully immersed in solution; hence, reaction progress cannot be monitored.

Dove and Chermak (1994) provide a comprehensive review of the application of *in situ* AFM to studies of mineral-water interface geochemistry. Herein, we provide a more concise review, focusing on experimental considerations and potential artifacts.

AFM offers distinct advantages by providing extremely high-resolution imaging in solution, while generally having little or no effect on reaction progress (Dove and Hochella, 1993). However, the technique is subject to a variety of limitations and pitfalls. First, by its very nature, AFM is a *microscopic* technique. Bosbach *et al.* (1996) studied the influence of different electrolyte solutions on the growth kinetics of gypsum, and they were able to decipher different growth "mechanisms." They demonstrated that growth rates and "mechanisms" varied on a microtopographic scale, suggesting that bulk growth rates of certain minerals cannot be easily predicted based on microscopic observations. *In situ* experiments are difficult and time-consuming; hence, it is difficult to obtain a statistically meaningful sampling of surface reactivity. To put microscopic AFM results in context, they always need to be coupled with macroscopic experiments. Indeed, we recommend coupling *in situ* (in solution) imaging on mm-scale crystals with *ex situ* imaging of particulates prior to and following reaction, to try to get a handle on the effects of surface heterogeneity (e.g., Maurice *et al.*, 1995).

Second, because AFM images are collected as lines of information that eventually form an image, very fast or very slow reactions may be difficult to study in real time. Dove and Platt (1996) estimate that AFM can be used to observe the "real-time" growth and dissolution of monolayer surfaces occurring at rates of between 10^{-10} and 10^{-6} mol m⁻²s⁻¹. Mineral surfaces with reaction rates outside of this range can be adjusted to fit the AFM-compatible range by carefully controlling pH, saturation, and so on. For example, Bosbach and Rammensee (1994) were able to observe the dissolution of gypsum surfaces by using partially saturated solutons that lowered the reaction affinity, thereby decreasing reaction rates. Reaction rates that are slower than the AFM-compatible range may be increased by adjusting pH or saturation state, although oftentimes these changes are insufficient. At times, it may be easier to rely on ex situ observations of the mineral surface before and after reaction, using a statistical sampling regime. One problem with this technique is that surface microtopography of some minerals may change considerably on drying. In some cases, in situ AFM may be used over a period of hours or days to observe the general progress of a surface reaction, although it is not always possible to image one area for prolonged periods of time.

Third, as commonly used, AFM provides structural, micromorphologic, and microtopographic information. Other techniques, such as AES and XPS, must be used to determine surface composition.

Fourth, *in situ* AFM is only useful for imaging processes that occur at the surface of the subject mineral. Processes that occur strictly in solution, such as homogeneous nucleation in solution, cannot be directly accessed by AFM. However, AFM can be used to obtain indirect evidence of homogeneous nucleation (e.g., Lower *et al.*, manuscript in preparation).

Fifth, although AFM is for the most part a nondestructive imaging technique, some surface damage can occur. As described in Section II.B.1, forces are minimized when working in solution. Nevertheless, damage of the sample surface can occur during contact-mode imaging, especially during small-region scans (<1 μ m) and when soft features are present; for example, over the course of dissolution or during growth of an amorphous precipitate. Maurice *et al.* (1995) presented an example of scan-induced sample erosion during a dissolution experiment. In

this experiment, an etch pit was observed to nucleate and grow on the basal-plane surface of hematite immersed in citric acid. The original pit shape was hexagonal. However, near the end of the experiment, the scan area was decreased (from ~ 10 μ m on a side to <1 μ m) to the region immediately surrounding the pit. During this procedure, the pit edges began to align with the scan direction and the image frame, suggesting that scan-induced erosion occurred during the small-region scans. Scan-induced erosion also was observed during small scan imaging of the growth of "active" Cr-hydroxide precipitate on the surface of hematite (Eggleston et al., manuscript in preparation; Maurice-Johnsson, 1994). Marchant et al. (1991) showed that $1-2 \mu m$ scans disturbed the structure of von Willebrand Factor (a blood plasma glycoprotein) sorbed to mica, whereas $\sim 8 \mu m$ scans did not produce a noticeable disturbance. The reason for the enhanced small-region scan erosion is currently under debate. It has been suggested that enhanced erosion during small-region scans is a result of the rapid scan rate needed to compensate for drift at high resolution (Barrett, 1991). However, slowing scan rate does not always resolve the problem.

In situ growth experiments often show isolated holes or pits that appear on the sample surface and remain stable over long periods of time, even when several steps migrate over the holes (Hillner *et al.*, 1992a,b; Bosbach and Rammensee, 1994). These features have been observed during both small- (less than 1 μ m) and large- (greater than 5 μ m) region scans. Whether or not they are scan-induced, perhaps by frictional mechanisms (Delawski and Parkinson, 1992), remains to be determined.

Scan-induced 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., less than 1 μ m) to a large-scan area (e.g., 16 μ m). To evaluate scan-induced artifacts, *in situ* reaction studies should include careful calibration and monitoring of forces, systematic alteration of scan angle, periodic disenablement of the y-scan direction, periodic change in scan size, and occasional tip withdrawal and reengagement (Maurice *et al.*, 1995). Additionally, scan-induced erosion should be suspected whenever there is evidence of the tip sticking to the sample surface, e.g., when the zero of height is reset, requiring application of a flatten filtering procedure. Finally, it should be understood that surface erosion may not be limited to small-region scans, particularly when the sample surface is soft and easily deformable or when imaging forces have not been minimized. Thus, although AFM is a powerful technique for studying growth or dissolution *in situ*, the experiments must be performed with caution.

TMAFM should be less likely to erode sample surfaces. However, TMAFM does not appear to give as high a resolution as contact-mode AFM; indeed, it can be difficult to obtain resolution below several tens of nanometers during *in situ* TMAFM experiments. Additionally, if force modulation tips are used, *in situ* TMAFM can be quite expensive. Despite these current drawbacks, with time,

TMAFM probably will become the method of choice for most *in situ* experiments of changes in surface microtopography.

2. The in Situ Experiment

Researchers have used a variety of different approaches to *in situ* experiments, and the best approach depends upon the particular problem at hand. The fluid cell provided by Digital Instruments (Fig. 8) consists of a square of glass with inlet and outlet openings, a clip for the integrated probe cantilever-tip, and a circular groove made to fit an O-ring that is used to seal the glass cell to the underlying sample or sample stub. A small amount of an appropriate grease can be used to help prevent leakage from around the O-ring. The system may be used in either static, pulsed-flow, or continuous-flow conditions. One common experimental setup is shown in Fig. 9. In this experimental setup, which was used by Maurice *et al.* (1995), a freshly fractured mm-scale piece of specular hematite was placed in the AFM fluid cell. The sample was monitored first in deionized water. Then, an oxalic acid solution was added and allowed to drip through the fluid cell using gravity feed from a syringe, at a very slow flow rate of only $\sim 1 \text{ mL hr}^{-1}$. The slow flow rate helped to provide stable images; faster flow rates may result in fluid convection or turbu-



Figure 8 Cross-sectional view of the Digital Instruments AFM fluid cell. Using this cell, the tip and sample are completely immersed in solution.



Figure 9 A gravity-flow-through fluid-cell experiment with the Digital Instruments AFM. Flow rate can be modified using a small clamp on the inlet or outlet tube. These tubes can be clamped off entirely to run in static conditions. Adapted from Maurice *et al.*, 1995.

lence, which enhances drift and degrades cantilever stability. Fast flow rates also may result in bubbles being introduced into the fluid cell. The effluent from the cell can be collected and analyzed, although sample volumes tend to be low. Dove and Hochella (1993) used a similar setup to image calcite dissolution and growth features. They began their experiments in a flow-through reactor and transferred the calcite crystals to the AFM fluid cell, along with solution at the appropriate saturation state. The experiment was then run as a closed (static) system, thus mimicking a batch reactor. One problem was that the surfaces tended to dry during transport between the reactor and the AFM fluid cell, resulting in changes in microtopography. In the case of reactive surfaces, it may be important to try to prevent the surfaces from drying completely during transport. Alternatively, allowing a surface to dry can sometimes provide nuclei for growth experiments.

Temperature control is another important consideration. Dove and Chermak (1994) reported that energy transfer from the AFM laser resulted in temperature increases of as much as 8°C in the fluid cell over six hours of continuous imaging at room temperature (22°C). Jordan and Rammensee (1996) modified the fluid cell to permit temperature control and precise temperature monitoring. Thus, it may be

possible to prevent unwanted temperature increases. In the absence of such modifications, we recommend that the experiment may be stopped periodically, and the laser light turned off, to help prevent excessive warming of the fluid cell. The difficulty of this approach is that it is not always possible to return to the same spot upon re-engagement. Jordan and Rammensee's (1996) experimental apparatus also opens the door for a range of kinetics experiments, although it should be noted that increased temperature can be expected to lead to enhanced thermal drift that may limit the range of viable experimental temperatures.

When single mm-scale crystals are imaged in the fluid cell, it is important to provide an appropriate substrate if the typical steel sample stub might be reactive in the solution of choice. We have used either a piece of glass coverslip, a piece of mylar, or a piece of parafilm glued to the steel stub. We have also succeeded in imaging powders on the order of 200 μ m or more in diameter in the TMAFM fluid cell, by dispersing the powders on the surface of double-sided cellophane tape attached to the sample stub (Lower *et al.*, manuscript in preparation). At this point, we are assuming that the tape does not add reactive products to the experiment. Dove and Chermak (1994) discuss imaging clay-sized particles in solution and note that Nagy (Dove and Chermak, 1994, personal communication) recommends using a small puff of air from a compressed air source to disperse clay particles over epoxy. They note that although this method does have limitations, it appears to work.

In general, we have found that fluid cell experiments tend to show a large amount of drift during initial imaging (see Fig. 10), but this drift generally settles down after ~ 15 minutes. Thus, it is often best to begin experiments with "nonreactive" solution and then introduce the reactive solution of interest after the drift has died down and good images can be produced. Many experiments also benefit from first monitoring surface microtopography in a "nonreactive" solution and then watching the changes that occur upon introduction of the solution of interest. Unfortunately, changing solutions generally requires withdrawing-disengaging the tip from the sample surface for a brief interval. Upon reengagement, the image area often changes. We have found that if we work with a scan head allowing images 16 μ m on a side, we can generally return to an area that at least overlaps the original image area.

Several other considerations are important for *in situ* imaging. First, it is important to avoid introducing air bubbles into the fluid cell since they not only can negate the experiment (if the air bubble overlies the scan area) but also can complicate the laser signal if they occur within the path of the laser light. Second, because solutions and the glass of the fluid cell have different refractive indices than air, the laser, the mirror, and the photodetector generally require substantial realignment. Third, it is imperative to prevent leakage of the fluid cell onto the AFM since electrical shortages could ensue. We generally keep a substantial supply of rolled up Kimwipes ready to blot up even the smallest leak. If a leak develops, it



Figure 10 An example of drift. The top of the image is drifted, resulting in elongation of features and some curvature. Drift may occur at any time but often is more pronounced within the first few minutes of imaging, when the scan direction turns around from upscan to downscan (or vice versa) or when the tip is having difficulty tracking the sample surface and is close to disengagement. Scan area is $3.11 \, \mu$ m on a side.

is important to turn the AFM off immediately and allow it to dry completely before proceeding. Other researchers have developed plastic aprons that fit over the AFM base to protect from leaks. As the sample reacts in the fluid cell, reaction products or bits of torn-up surface may accumulate on the tip and result in a multitude of interesting tip-sample "convolution" artifacts. Multiple images are commonplace (e.g., Maurice, 1996). Reaction products also may accumulate on the cantilever; for example, we have found that supersaturated solutions may result in accumulation of nucleated materials on the cantilever, leading to destabilization of the imaging process (Lower *et al.*, manuscript in preparation). In general, the fluid cell tends to be relatively difficult to use, and fluid-cell experiments can be tedious and time-consuming. However, the benefits of working in solution greatly outweigh the drawbacks.

3. Examples of in Situ Studies

AFM has been used to study mineral surface growth (e.g., Dove and Hochella, 1993; Bosbach et al., 1996), dissolution (e.g., Gratz et al., 1991; Hillner et al.,

1992a,b; Bosbach and Rammensee, 1993; Gratz *et al.*, 1993; Maurice *et al.*, 1995; Putnis *et al.*, 1995), and heterogeneous nucleation processes (e.g., Junta and Hochella, 1994; Eggleston *et al.*, manuscript in preparation) *in situ* since the early 1990s. A few examples will be discussed herein.

One of the most enlightening fluid-cell experiments to date was conducted by Dove and Hochella (1993). These authors used fluid-cell AFM to study near-equilibrium calcite growth and dissolution. Calcite fragments were reacted for 1 to 2 days in a flow-through reaction chamber and then transferred to the AFM fluid cell, along with aliquots of the same solutions. Dove and Hochella (1993) observed that when solution saturation states relative to calcite were greater than 1 or 2, precipitation began with the formation of surface nuclei that spread, coalesced, and continued to grow. A transition to a spiral-growth-type mechanism did not occur until after nearly 2 hours. Dove and Hochella (1993) also found that upon introduction of a phosphate-containing solution into calcite growth media, smooth straight-edged steps transitioned into widely spaced, jagged-edged steps. This observation was consistent with predictions by Stumm and Leckie (1970) and Berner and Morse (1974) that phosphate may bind to step edges and poison further growth. Hence, the *in situ* microscopic studies by Dove and Hochella were able to directly verify predictions based on macroscopic and theoretical considerations.

Jordan and Rammensee (1996) used in situ AFM to study the kinetics of brucite (Mg(OH)₂) dissolution on the (001) surface. They used a gravimetric liquid-feed system that consisted of silicone tubes and allowed in situ exchange of solution while scanning the sample surface. A flow rate of 2.5 mL min⁻¹ was used. Experiments were conducted at elevated temperature (to 35°C) by immersing the liquid-supplying tube in water in a thermostated vessel next to the microscope. A micro-NTC-resistor was placed in the outflow section of the fluid cell. Using this experimental setup, Jordan and Rammensee (1996) were able to monitor the retreat of steps across the brucite (001) surface and the growth of etch pits. From these data, they calculated dissolution rates as a function of temperature. The resulting Arrhenius plot was used to calculate an activation energy of $60.2 \pm 12 \text{ kJ}$ mol^{-1} for dissolution on the (001) surface. This activation energy is within the realm of surface-controlled dissolution. However, the authors observed some interstep interaction, which suggests that surface diffusion might contribute to the rate-controlling process, as well. Jordan and Rammensee's (1996) pathbreaking work opens the door for a wide range of studies on the kinetics of mineral growth and dissolution.

Eggleston *et al.* (manuscript in preparation) used *in situ* contact-mode AFM and XPS to study the formation of "active" Cr(III) hydroxide (ACH) precipitate (e.g., Giovanoli *et al.*, 1973) on a hematite surface by surface-catalyzed reduction of aqueous Cr(VI). The subsequent mobility of Cr bound in ACH depends on gradual aging of the reactive precipitate toward less reactive forms with less solid-solution interfacial area. The results of Eggleston *et al.* (manuscript in preparation)

showed that ACH aging proceeds by layer-by-layer growth from an initial thin precipitate layer. The rate of growth (or dissolution) of a given layer depends on its position in a stack of layers and on the distance between the steps bounding each layer. However, clear evidence was seen for influences on AFM scan processes on the dissolution and growth of ACH. The tip appeared to scrape material off the surface, leading to alignment of some features with the scan direction. Use of XPS was important for determining reaction mechanism. XPS showed Cr(III) on the reacted surface; however, these results were not unambiguous since XPS may itself cause photoreduction of Cr(VI) to Cr(III). Nevertheless, Eggleston *et al.* believed that at least some, or perhaps all, of the Cr(III) was present before XPS analysis. These experiments demonstrated the importance of combining different surficial techniques and of carefully analyzing *in situ* images for potential tip-related effects on apparent growth and dissolution.

D. Ex Situ Studies: Particulate Imaging

1. Fundamentals of ex Situ Particulate AFM

Although *in situ* imaging of mm- to cm-scale crystals can provide direct mechanistic and kinetic data, soil chemistry ultimately revolves around the properties of soil *particles*. Imaging of particles can provide nanometer-scale data on particle surface microtopography under environmentally appropriate conditions, i.e., air or, in some cases, aqueous solution. Because AFM provides three-dimensional data, the technique also can be used to determine particle micromorphology, leading to calculations of aspect ratios and ultimately to estimations of external geometric surface areas. Particles can be imaged *ex situ* prior to and following reaction and changes in surface features; e.g., formation of etch pits can be directly linked to macroscopic data.

AFM offers distinct advantages over most other imaging techniques in that it provides nanometer- to potentially atomic-scale three-dimensional surface images under environmental conditions, without the need for surface coatings, and in a nondestructive manner. Despite these capabilities and advantages, particle imaging by AFM is neither simple nor straightforward, and it entails a number of difficulties and disadvantages. First, AFM is by its very nature a surface technique. As such, it cannot probe the internal surfaces of intact particles, including internal pore spaces. Second, due to the finite shape of the tip, tip-sample "convolution" artifacts abound and may be more or less severe depending upon the particle micromorphology as well as sample preparation. Third, particle imaging requires some method of stabilizing the particles onto an imageable surface. Friedbacher *et al.* (1991) showed that particulate material could be imaged by pressing powdered samples into pellets. However, this technique has two disadvantages: (1) particles often overlap, obscuring some features; and (2) the rough surfaces of pressed powders may be subject to significant tip-convolution artifacts. Hence, correct imaging of isolated, single particles requires use of a sample substrate.

2. Preparation of Samples

Choice of substrate material is of paramount concern and may vary with the specific application. Maurice (1996) listed the following criteria for a good substrate material: (1) the substrate needs to be flat and regular on a scale greater than the scale of the particles of interest; (2) if the particles to be imaged are to be deposited from solution, the substrate must be unreactive; (3) the substrate must be readily imaged, and have consistent nanometer- to micron-scale topography; (4) the atomic-scale structure and nanometer-scale microtopography of the substrate should be distinguishable from that of the material of interest; (5) the substrate should not be easily deformed by the scanning process; and (6) particles should adhere well.

Maurice et al. (1995) and Maurice (1996) showed that Nucleopore polycarbonate (pc) membrane filters originally developed for SEM work can serve as excellent substrate materials for imaging particle microtopography and micromorphology. These filter membranes provide several distinct advantages: (1) the substrate can be easily distinguished from mineralogic particles due to the filter pores and the fibrous nature of the filter materials; (2) the filters can be used both to separate solid from solution and to image the solid fraction; and (3) most mineralogic particles adhere well to the filter surfaces (Maurice, 1996). However, pc membranes have several disadvantages. First, the pc membrane surface is not as flat on an atomic to molecular scale; and, hence, the membranes are not suitable for particle thickness measurements and detailed measurements. As described later, muscovite mica is recommended for quantitative analysis of particle thicknesses. Also, the frictional properties of the filter membrane may be different from the frictional properties of mineralogic specimens, leading to frictional artifacts, such as inverted topography. Frictional artifacts generally occur only during conventional contact-mode AFM imaging and not during TMAFM imaging. Generally, we have found that pc membranes retain materials far smaller than their reported pore sizes.

Muscovite mica is perhaps the most commonly used substrate for AFM imaging in air, and it has the advantage of containing large molecularly flat areas and frictional properties similar to clay materials. However, it exhibits two major drawbacks. First, muscovite is reactive in water (Lin and Clemency, 1981) such that muscovite surfaces exposed to water for even short periods of time may contain etch pits and secondary precipitates (Johnsson *et al.*, 1992; Blum, 1994). Second, muscovite surface structure resembles the surface structures of clay minerals. Ultrafine particles of muscovite caused by imperfect cleavage may be confused with the particles of interest, and molecular-scale imaging cannot be used to differentiate the substrate and sample materials. Nevertheless, muscovite often is the substrate of choice for measurements of environmental particles. It should be noted that in this section, we are specifically speaking about mounting particles for imaging in air; particles cannot be expected to remain attached to substrates, such as pc membranes and muscovite mica, when immersed in solution.

Blum (1994) used contact-mode AFM to analyze the morphology of smectiteillite particles deposited on muscovite. After deposition, the solution was allowed to evaporate, leaving the particles attached to the surface. Blum (1994) found that ultrasonic dispersion of the suspension was necessary to isolate individual particles, although ultrasonic dispersion may lead to cleavage parallel to the basal plane. With careful attention to sample preparation and imaging, he concluded that AFM can be used to determine the heights of clay particles with an accuracy of ± 1.5 Å for particles on the order of several nm in thickness and xy dimensions greater than 100 nm. Height accuracy for thicker and/or less laterally extensive particles was reported to be ± 3.0 nm. Particle thickness measurements were found to agree well with measurements on the same samples by TEM and XRD.

Maurice et al. (1995) and Lower et al. (manuscript in preparation) have imaged particles on pc membrane filters. Sample preparation is simple, but results are optimized by following a few careful procedures. Successful imaging requires deposition of an extremely low particle density on the filter membrane. High particle densities result in particle overlap, which obscures some features, and in diverse orientations may lead to increased tip-sample convolution. Hence, we try to start with a suspension containing less than 0.5 g of solids per liter of solution. We generally use 13-25 mm diameter, 0.1 µm filter membranes and syringe filters, and filter no more than $\sim 0.5-2$ mL of suspension through the filter membranes. Depending upon the exact nature of the experiments, e.g., how reactive the particles are, we sometimes put through a small amount of either deionized water or another appropriate solution to rinse and then force a small amount of air from a clean syringe through the filter membrane to remove potential reaction products that otherwise might precipitate upon drying. A gentle vacuum also may be used. After the filter membrane is removed from the filter housing, the membranes should be allowed to continue drying under a protective dust cover. Subsequent to filtration and drying, an optical microscope should be used to ensure that individual particles or small aggregates are dispersed across the membrane. We have found that most samples should be imaged within a few hours to a few days after filtration, because particles may detach from the membrane surfaces.

After the sample membrane has dried, the membrane can be cut into pieces a few mms on a side, and mounted to a stainless steel sample stub with double-sided cellophane tape. We generally dab the sample surface with a clean piece of Parafilm to ensure that air bubbles are removed from beneath the tape and sample. This must be performed gently to prevent potential damage of the sample surfaces.

Subsequent to AFM imaging, these same samples can be coated with Au or C and analyzed by SEM and/or EDS.

3. Imaging Procedures

Once the sample has been prepared, there are several factors to consider before intiating the imaging procedure. TMAFM reduces the frictional drag between tip and sample surfaces and is hence a better choice than contact-mode AFM for imaging of particles. A binocular optical microscope attachment is a vital asset to the successful imaging of particles, because a specific location can be chosen. For imaging of isolated particles with a size too small to be detected with an optical microscope, we generally choose an area of the sample–substrate surface that looks under the optical microscope to be essentially free of particles and then move from place to place to try to find isolated particles. This is a laborious process. For imaging of aggregates, we have found that the edges of the aggregates are easiest to image because features tend to lie relatively flat, and particle density is reduced. It should, of course, be recognized that the edges of the aggregates may have different structure than the bulk of the aggregates. As described later, combination of AFM with SEM and TEM can sometimes provide greater insight into particle and aggregate structures.

Traditionally, AFM data are collected in the so-called height mode. This mode of operation provides the most accurate height measurements. However, we found that the amplitude mode (for TMAFM) complements the height mode, and it can be particularly useful for rough, aggregate surfaces. The amplitude mode, which may be collected simultaneously with the height mode data, is essentially a record of the error in the height image. It should be noted that amplitude mode for TMAFM is analogous to "deflection" images collected in contact-mode AFM (see Blum, 1994).

The height image is a record of lateral changes in the *z*-axis piezoelectric cylinder and directly represents the microtopography of a sample surface. All quantitative height information should be gathered from this image. The amplitude image is a record of lateral changes in the photodiode voltage and reflects the magnitude of lag between the tip's deflection by a topographic feature and the movement of the *z*-axis piezoelectrode to maintain a constant force between the tip and the sample. The amplitude image displays the rate of change in surface microtopography. The magnitude of the tip deflection is a function of the steepness of the microtopography and is greatest in regions where the sample is roughest. For aggregates of particulate materials, which tend to be rough, the amplitude image is perhaps the most important part of the "real-time" imaging procedure because it provides the investigator with an easily interpretable representation of the surface. Figure 11 provides a comparison of height- and amplitude-mode data.

Even using low particle densities and pc membrane filters, imaging of particles





Figure 11 Comparison of TMAFM "height-mode" (a) and "amplitude-mode" (b) images of particulates deposited on pc membrane filter (see pores in upper-right corner). The images were collected simultaneously using TMAFM in air on samples of hydroxylapatite (HAP) reacted with 100 mg L⁻¹ Pb at pH 6, 22°C. The needles in these images are of the mineral hydroxypyromorphite (HPY), which formed upon reaction. While the height-mode image gives vertical data, the amplitude-mode image is clearer, while maintaining horizontal scale. For explanation of sample chemistry and structure, see section III.D.4. Scan area of each image is 2.30 μ m on a side.

(a)

often proves difficult. The tip-convolution problems described earlier need to be considered. Additionally, particles can be dislodged from the surface, resulting in noisy images and potential damage to the tip. When imaging particles, it is generally best to start with a scan region less than 1 μ m on a side, and to slowly increase the scan size. Imaging with a very slow scan speed (less than 1 Hz) also can prove helpful. Scanning at 90° may result in less drag between the tip and the sample. In general, TMAFM is much more reliable than contact-mode AFM for particle imaging. Finally, imaging particles within a few days of sample preparation generally works best because particles tend to detach from substrate materials with time.

4. Pb "Sorption" to Hydroxylapatite

AFM can be used as an *ex situ* technique for imaging particulates subjected to batch growth or dissolution experiments. In so doing, micromorphological and microtopographical AFM data may be used to help identify solid phases and to elicit such information as the types of reaction mechanisms (e.g., surface vs diffusion controlled). However, imaging of particulates presents a challenge because AFM traditionally does not provide chemical data. Therefore, solid phases must be identified primarily based on morphology.

To successfully use AFM to identify solid phases, one should take a systematic approach. First, reactant and product materials should be characterized as fully as possible by XRD or EDS and other chemical techniques, such as infrared (IR) or Raman Spectroscopies. Second, it is essential to compile a large catalog of AFM images of the solid reactant. These images of reaction "blanks" may be compared with images of the reaction product to identify newly formed solid phases or changes in the original reactant. Unless there are distinct morphological forms for various solid phases, it will be difficult to use AFM to identify individual phases in heterogeneous samples. Finally, AFM should be compared with established forms of microscopy, such as SEM and TEM. As with any new emerging technique, there is a critical period of "validation." AFM can produce numerous artifacts. Comparing AFM images to SEM or TEM images of the same material will provide the necessary documentation to ensure that AFM images are real. Additionally, different microscopic techniques offer complementary information.

As part of a systematic approach to developing AFM application to studies of reaction products, TMAFM was applied to studies of Pb sorption to the mineral hydroxylapatite ($Ca_5(PO_4)_3OH$) (HAP) (Lower *et al.*, manuscript in preparation). Aqueous solutions of Pb, ranging in concentration from 0–500 mg L⁻¹, were reacted with 0.5 g L⁻¹ of HAP in batch experiments that proceeded for 2 hours. XRD analysis of the reaction product revealed that a new phase, hydroxy-pyromorphite (Pb₅(PO₄)₃OH) (HPY) was produced. TMAFM analyses of the reaction product



Figure 12 Surface of an HAP particle reacted at pH 6, 22°C, in the absence of Pb, and imaged with TMAFM in air. Scan area is $2.00 \ \mu m$ on a side.

filtered onto a 0.1 μ m pc membrane showed two distinct particle morphologies: elongate needles and clusters of material (Fig. 11). The chemical data provided by XRD, as well as a comparison of AFM images of the reaction product to a catalog of images of HAP reaction blanks (Fig. 12), allowed us to conclude that the needles were HPY and the clusters of material were HAP. Next, we conducted SEM/EDS analyses of the same samples subjected to AFM (Fig. 13). In general, we found that AFM shows good agreement with results using SEM. On the one hand, AFM provides higher resolution and more detail; on the other hand, SEM gives more information about larger-scale features and association of phases. EDS provides chemical information not available by AFM. SEM results showed that the tips of HPY needles generally were pointed; yet, they appeared to be rounded in AFM images. This suggests that even the sharp TMAFM tips can "convolve" with tip edges, distorting details of micromorphology.

The ability to identify solid phases based on their morphology, as well as the increased resolution afforded by AFM, allowed us to make several hypotheses concerning the types of reaction mechanisms controlling Pb sorption to HAP (Lower *et al.*, manuscript in preparation). At initial Pb concentrations of 10–500 mg L⁻¹, needles of HPY form concurrently with HAP dissolution. At lower concentrations



Figure 13 SEM image of HAP (platey structures) and HPY (needle-like structures) following reaction of HAP with 100 mg L⁻¹ Pb at pH 6, 22°C. This image agrees well with Fig. 11, which was from the same sample. SEM permits imaging at a larger scale, which helps to put features in context. Also, tip-convolution features are not a problem with SEM. However, TMAFM provides higher resolution and greater detail of the surface structures. Scale bar is 5 μ m.

of initial Pb, fewer needles of HPY were dispersed across the pc membrane (Fig. 14). At higher concentrations of Pb, numerous intergrown needles of HPY were detected with AFM (Fig. 15 on p. 36). These needles were smaller than the needles produced at lower initial Pb concentrations. The small size and intergrown nature of HPY needles at high concentrations (Fig. 15) suggests rapid homogeneous nucleation. At initial Pb concentrations less than 10 mg L^{-1} (Lower *et al.*, manuscript in preparation), we saw evidence of heterogeneous nucleation in the form of needles appearing to grow "epitaxially" on the HAP. This suggests that both mechanisms may be responsible for Pb sorption, although the importance of these different mechanisms may vary with solution conditions (Lower *et al.*, manuscript in preparation). In situ studies are underway to help further our understanding of growth mechanisms.

These experiments demonstrate the potential usefulness of AFM in studies of complex reaction "mechanisms." By using AFM simultaneously with other techniques and designing scientifically relevant, carefully controlled laboratory studies, scientists are able to better understand multidimensional soil processes. In so doing, one is able to make powerful statements concerning natural systems.



Figure 14 TMAFM image in air of HAP and HPY reaction products following reaction of HAP with 10 mg L^{-1} Pb at pH 6, 22°C. Based on XRD, microtopographic, and micromorphologic analysis, we believe that there are only a few scattered needles of HPY (see twin in upper-left portion of image) and that the bulk of the material imaged is HAP. Some filter-membrane substrate appears in this image (see pores). Tip-sample convolution artifacts appear near the upper-central portion of this image. Scan area is 3.64 μ m on a side.

5. Measurements of Kaolinite Particles: Comparison of A_s Measurements

Kaolinite is one of the most abundant minerals in earth-surface environments (Moore and Reynolds, 1989). Because kaolinite occurs primarily as clay-sized particles with large surface-area-to-volume ratios, it may strongly influence the distribution of species in solid-solution systems at the earth's surface. Additionally, kaolinite is widely used in ceramic, paper, and coating-pigment industries. The performance of kaolinite in such industrial applications depends largely on the mineral's surface properties. Surficial properties affect interaction with chemical compounds and media, as well as particle-to-particle interactions. Thus, study of kaolinite's surface characteristics has important implications for both fundamental and applied research.

Zhou et al. (manuscript in preparation) used AFM to compare the particle mor-



Figure 15 TMAFM image in air of reaction products following reaction of HAP with 500 mg L⁻¹ Pb at pH, 22°C. The intergrown nature of the HPY needles suggests rapid homogeneous nucleation. Similar aggregates were observed with SEM, although details of the structure were difficult to discern with that method. We cannot determine from this image whether rounded structures are HAP or the ends of needles. XRD, however, did not detect any HAP remaining in this sample after reaction. Scan area is 2.00 μ m on a side.

phology, surface microtopography, and estimated geometric surface areas of two American Clay Minerals Society standard kaolinites, Kga-1b (well crystallized) and Kga-2 (poorly crystallized). Qualitatively, the two kaolinite standards were found to have notably different surface microtopographies and micromorphologies. Particles of Kga-1b generally had crisp hexagonal outlines and basal-plane surfaces showing clear crystallographic control. In contrast, particles of Kga-2 tended to have more rounded hexagonal outlines, with curved edge steps and irregular basal-plane surfaces. AFM also was used quantitatively to measure grain size, thickness, and size distribution of the two samples. The average diameter and thickness were found to be 785 and 58 nm, respectively, for Kga-1b; and 447 and 45 nm, respectively, for Kga-2.

Three dimensional data were used to estimate geometric specific surface areas (A_s) , as shown in Table I. The average values of A_s of the two kaolinites, calculated from AFM measurements, were intermediate between relatively lower values determined by BET surface-area analysis, thermogravimetric analysis (TGA), and relatively higher values measured by XRD. Mode values determined by AFM

Sample ^a Kga-1b	Specific surface area $(A_s) (m^2/g)$								Ratio edge/basal	
	AFM mean 21	AFM mode 13	BET 12.5	XRD		TGA	BET [₺]	Mean Mode		
				52.1	64.4	12.6	8.5-10.05	0.17	0.10	
Kga-1bc	27	16	12.6	48.5	62.6			0.17	0.10	
Kga-2	30	22	22.4	56.7	71.6	21.7	20.6-24.0	0.18	0.12	
Kga-2c	37	24	22.2	57.5	72.5			0.19	0.14	

Table 1	ľ
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^aSample cleaned in 1 *M* NaCl adjusted to pH 3 wth HCl, followed by deionized water washings. ^bData from van Olphen and Fripiat (1979).

were close to BET and TGA values, suggesting that the AFM samples might have been subject to systematic sampling error. Values determined by XRD were double to triple the values determined by AFM, BET, and TGA, suggesting that XRD may measure small domains rather than entire crystals. Overall, the A_s values determined by the different methods could lead to substantial differences in estimated surface reactivities. AFM surpassed the other methods by providing additional detail in the form of grain size and A_s distributions (see Zhou *et al.*, manuscript in preparation), as well as estimations of edge vs basal-plane surface areas (see Table I and Zhou, 1996). However, one major problem of AFM was that numerous artifacts precluded application of a strict point-counting regime. Hence, some sampling bias was inevitable.

IV. SOME NEW FRONTIERS IN AFM RESEARCH

One of the most promising new frontiers in AFM research appears to be *chemical sensing*. Chemical sensing relies on the fact that AFM force measurements are extremely sensitive to the properties of the tip and the sample. A variety of techniques may be used to distinguish chemically distinct surfaces. For example, Burnham *et al.* (1990) used force-curve measurements to differentiate between two similar samples covered with organic monolayers. One surface had $-CH_3$ group terminations, and the other had $-CF_3$ group terminations; these different terminations resulted in different tip-sample interaction forces. Chemical modification of AFM tip surfaces is opening a whole new realm of chemical sensing. For example, Frisbie *et al.* (1994) deposited various functionalized thiol monolayers on gold-coated tips and samples. By systematically varying the functional group terminations on the tips and the samples, the authors were able to map out different

adhesion and friction properties between various combinations of carboxyl (-COOH) vs methyl ($-CH_3$) functional groups. Hence, although AFM cannot give direct chemical determinations, it can be used to distinguish materials with different physicochemical properties, such as different hydrophobic-hydrophilic characteristics, surface charges, and charge densities.

Another new technique is known as *phase imaging*. Phase imaging (see DI Web page, http://www.di.com) is an extension of TMAFM that maps the phase of the cantilever oscillation during the scan. The phase of cantilever oscillation may vary with composition, adhesion, friction, viscoelasticity, and potentially other properties of sample materials. Hence, phase imaging can help to differentiate different materials on a sample surface. Generally, phase data are displayed next to TMAFM height information, so that the two types of data can be compared.

Force modulation imaging is another method that may be useful for distinguishing materials with different stiffnesses. According to the DI Web page, in force modulation imaging, the sample is scanned with a small vertical (z) oscillation (modulation) that is significantly faster than the scan rate. The force on the sample is modulated about the setpoint scanning force in such a way that the average force on the sample is equivalent to that in contact-mode AFM. When the probe is brought into contact with a sample, the surface resists the oscillation and the cantilever bends. Under the same applied force, a stiff area on the sample surface will deform less than a soft area. Stiffer surfaces cause greater resistance to the vertical oscillation, and thus results in greater bending of the cantilever. Thus, the variation in the amplitude of cantilever deflection gives a measure of the relative stiffness of the surface. Microtopographical information ("height" data) is collected simultaneously with the force modulation data so that the two may be compared.

Within the realm of soil surface chemistry, two of the most important new frontiers of research involve imaging humic substances and soil bacteria. Both of these research areas require use of specialized techniques, because humic substances and bacteria are soft materials. Namjesnik-Dejanovic and Maurice (1997) imaged soil and stream humic and fulvic acids deposited on muscovite surfaces. The humic substances were deposited on muscovite from solution, allowed to dry, and the samples were imaged in air by TMAFM. Spheroids, branched-chain structures, fibrous networks, and perforated sheets were observed at successively higher concentrations of humic substances. Results agreed well with results of previous studies utilizing TEM and SEM on similarly prepared samples (e.g., Stevenson and Schnitzer, 1982). Maurice *et al.* (1996b) imaged soil bacteria on Fe(III) oxide surfaces, using *ex situ* TMAFM and *in situ* contact-mode AFM. Grantham and Dove (1996) used *in situ* TMAFM to investigate the adhesive properties of soil bacteria.

One major problem with the humic-substances research (Namjesnik-Dejanovic and Maurice, 1997) is that humic substances can be expected to have different con-

figurations when adsorbed in solution than when dried and imaged in air. Recent developments in AFM techniques should make in situ imaging of sorbed humic substances possible. In situ TMAFM is one technique that may allow such imaging by permitting low-force imaging in solution. Contact-mode imaging in solution may also be possible, with the help of force-minimization techniques. Use of soft cantilevers may prove beneficial. Some of the long Si cantilevers provided by DI (450 µm length) may have spring constants less than 0.06 N/m; sharpened Si_3N_4 probes with spring constants ~0.04 N/m also may be used. Specialized tips may also be important. For example, recent images with Buckey-balls attached to cantilevers have provided high resolution on polymer surfaces. Use of chemically modified tips (chemical imaging) may help to map out hydrophobic-hydrophilic materials, or areas with different adhesion and laterial forces, and should be useful for imaging humic materials. Because the elastic moduli of soft materials, such as bacteria and humic substances, should be quite different from substrates such as muscovite, force-modulation imaging should also prove useful. Phase imaging can be used to map surface hardness or elastic modulus. Phase-imaging techniques have been used to image soft mesophase (liquid crystal) structures, and should therefore be applicable to bacteria and humic substances, as well.

These are just a few of the recent frontiers in AFM. Techniques and applications continue to advance at a rapid rate, and keeping track of recent advances is one of the greatest challenges for the AFM practitioner. One of the best ways for keeping up-to-date is the World Wide Web. DI, for example, maintains an award-winning Web page, including recent application notes, up-to-date press releases, and search engines for a variety of AFM-related topics. AFM discussion groups on the Internet are also useful, especially for the neophyte user.

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