IMAGING THE INTERNAL ATOMIC STRUCTURE OF LAYER SILICATES USING THE ATOMIC FORCE MICROSCOPE

FRED J. WICKS

Department of Mineralogy, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6

KEVIN KJOLLER

Digital Instruments, Inc., 6780 Cortona Drive, Santa Barbara, California 93117, U.S.A.

RAY K. EBY*

Department of Mineralogy, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6

FRANK C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

GRANT S. HENDERSON AND GORDON A. VRDOLJAK

Department of Geology, University of Toronto, 22 Russell Street, Toronto, Ontario M5S 3B1

ABSTRACT

Use of the atomic force microscope (AFM) need not be restricted to the uppermost surface. A high tracking force on the cantilever tip can be used to remove atoms that comprise the upper surface layer and thus reveal a material's near-surface internal structure. This technique was used to study the 1:1 layer silicate lizardite, $Mg_3Si_2O_5(OH)_4$. Forces of up to 325 nN on the cantilever tip rapidly remove both the oxygen and silicon atoms of the sheet of tetrahedra to reveal the hydroxyl groups and oxygen atoms that form a central plane common to both the sheets of tetrahedra and octahedra of the 1:1 layer structure. Similar results were obtained with two other layered silicates, muscovite and clinochlore. The large hexagonal rings of the sheets of tetrahedra appear to be a key factor in the layer-by-layer removal by providing an opening for the initiation of the process. The large rings also allow access of ambient H_2O molecules, which could dissociate to H^+ and OH^- and satisfy the bonds broken by the removal of the surface atoms.

Keywords: lizardite, clinochlore, muscovite, atomic force microscope, atomic resolution, hydroxyl groups, sheet of octahedra, sheet of tetrahedra, surface structure, internal structure.

*Present address: TopoMetrix, 1 Robertson Drive, Bedminster, New Jersey 07921-1716, U.S.A.

SOMMAIRE

Le microscope à force atomique ne sert pas uniquement à étudier la surface externe d'un matériau. Avec une force de gravure plus forte sur l'aiguille en cantilever, il est possible de déplacer les atomes qui constituent la couche supérieure pour ainsi révéler la structure interne d'un matériau. Nous avons utilisé cette technique pour étudier la lizardite, phyllosilicate 1:1 ayant la composition idéale $Mg_3Si_2O_5(OH)_4$. Une force atteignant 325 nN sur l'aiguille peut éroder à la fois les atomes d'oxygène et de silicium du feuillet de tétraèdres, pour révéler les groupes hydroxyles et les atomes d'oxygène qui forment le plan central en commun avec les feuillets de tétraèdres et d'octaèdres de la structure 1:1. Nous avons obtenu des résultats semblables pour deux autres silicates en feuillets, muscovite et clinochlore. Les anneaux hexagonaux des feuillets de tétraèdres semblent être le facteur clé dans l'ability de déplacer les atomes couche par couche, en offrant une ouverture pour l'initiation du processus. Ces anneaux permettent aussi l'accès aux molécules d'eau ambiantes, qui peuvent se dissocier en H^+ et OH^- et ainsi satisfaire les liaisons rompues lors de l'élimination des atomes de surface.

(Traduit par la Rédaction)

Mots-clés: lizardite, clinochlore, muscovite, microscope à force atomique, résolution atomique, groupes d'hydroxyle, couche d'octaèdres, couche de tétraèdres, structure de la surface, structure interne.

INTRODUCTION

The development of the atomic force microscope (Binnig *et al.* 1986) has opened exciting new areas in the mineral sciences. Although few minerals have been examined with the AFM, a variety of applications have been developed. Most studies have been carried out in air on cleavage surfaces in order to image growth features and cleavage topography on a nanometer scale (Drake *et al.* 1989, Hochella *et al.* 1990, Johnsson *et al.* 1991), groups of atoms at molecular resolution (Drake *et al.* 1989, Weisenhorn *et al.* 1990, Hartman *et al.* 1990, Johnsson *et al.* 1991, Drake & Hellmann 1991, Wicks *et al.* 1992, Rachlin *et al.* 1992), individual atoms at atomic resolution (Lindgreen *et al.* 1991, Wicks *et al.* 1992, Vrdoljak *et al.* 1993), and radiation damage in mineral structures (Thibaudau *et al.* 1991, Eby *et al.* 1993). The use of fluid cells has allowed observation of crystallization and dissolution of mineral surfaces (Hillner *et al.* 1992a, b). Other AFM uses developed by physicists and chemists have been reviewed by Leung & Goh (1992) and include images of surface topography at high resolution, and studies of atomic scale friction, elasticity, and surface forces. Leung and Goh used the AFM cantilever tip to create nanometer-scale features in a polymer laid down on a mica substrate. Similarly, Delawski & Parkinson (1992) have used the AFM cantilever tip to produce layer-by-layer nanometer-scale "etching" of a variety of two-dimensional metal dichalcogenides. We present results here that demonstrate the potential for removing layers of atoms from a mineral surface and for recording, at atomic resolution, images of atoms within a mineral. Thus, the AFM is not restricted to the study of the original, uppermost surface, but also is a valuable instrument for studying the internal atomic structure of minerals *via* layer-by-layer removal, particularly in layer silicates.

EXPERIMENTAL

We chose the serpentine mineral lizardite, ideally $Mg_3Si_2O_5(OH)_4$, for our study because it has a 1:1 layer structure in which one sheet of octahedrally coordinated magnesium atoms is linked to one sheet of tetrahedrally coordinated silicon atoms (Fig. 1). In our AFM study in air (Wicks *et al.* 1992), we obtained images of the hydroxyl groups and magnesium atoms of octahedra along the {001} surface at atomic resolution (Fig. 2), and images of the hexagonal rings of basal oxygen atoms of tetrahedra along the same surface at molecular resolution (Fig. 3). This lack of resolution of individual basal oxygen atoms making up the tetrahedra is a feature noted in our examination of other layer silicates such as muscovite (Eby *et al.* 1993) and clinochlore (Vrdoljak *et al.* 1993), and by other researchers in studies of muscovite (Drake *et al.* 1989), and illite and montmorillonite (Hartman *et al.* 1990). An explanation of this lack of resolution can be found in the work of Gould *et al.* (1989), who calculated images of the hexagonal structure of graphite using a single-atom and various double-atom models of the cantilever tip. The calculated single-atom image reproduced the hexagonal graphite image well. The various double-atom images reproduced the anomalous effects seen in published images of graphite. These anomalous effects include the lack of resolution of individual atoms, departures from the expected hexagonal symmetry, and apparent differences in height between adjacent coplanar atoms. Although graphite and layer silicates are obviously chemically and structurally different, some of the calculated anomalous images for graphite that assume a double-atom tip match the anomalous images obtained from layer silicates. This match suggests that resolution is strongly affected by the configuration of the atoms forming the tip of the cantilever and the way in which these interact with the oxygen atoms forming the
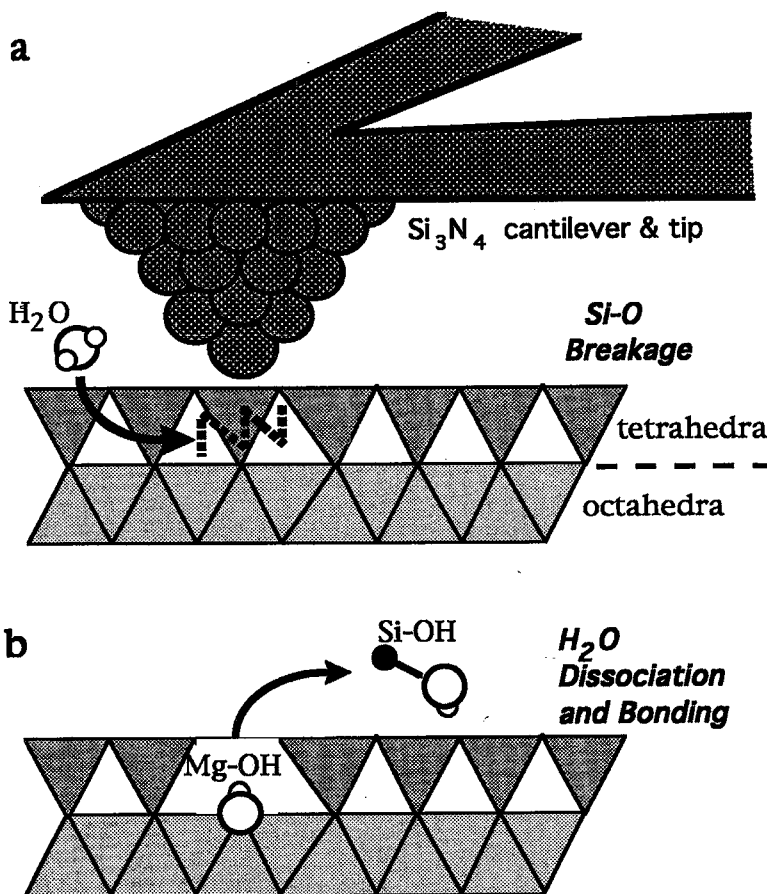
a

Si$_3$N$_4$ cantilever & tip

H$_2$O

Si–O Breakage

tetrahedra

octahedra

b

Si-OH

H$_2$O Dissociation and Bonding

Mg-OH

FIG. 1. A schematic diagram of the 1:1 layer structure of lizardite showing the sheet of silicon–oxygen tetrahedra and the sheet of magnesium–O,OH octahedra. The central O,OH plane of the structure, marked by the dashed line, is composed of oxygen from the sheet of tetrahedra and hydroxyl groups from the sheet of octahedra. a) The juxtaposition of the tip, H$_2$O, and the tetrahedra at the surface during breakage of bonds (not to scale). b) Dissociation of H$_2$O and bonding.

surface of layer silicates.

The AFM images of lizardite were acquired using a Nanoscope II Atomic Force Microscope produced by Digital Instruments, Inc. The images of clinochlore and muscovite were acquired using a Nanoscope III Atomic Force Microscope. All observations were made in air. A description of the instruments and the operating conditions used were given in Wicks *et al.* (1992) for Nanoscope II and Rachlin *et al.* (1992) for Nanoscope III.

RESULTS

In an effort to improve the resolution of the images of the basal plane of oxygen atoms in lizardite, a range of forces was used on the cantilever of the AFM. At a

high tracking force, an interesting phenomenon was observed. During repeated scanning, reasonably clear images of the hexagonal rings of basal oxygen atoms (Fig. 3) gradually deteriorated into featureless images. However, after continued scanning, an image of a triangular array of atoms with ~3 Å separation, similar to those recorded on the outer OH surface in our previous study (Fig. 2), appeared and remained the stable image during continued scanning. Figure 4 is a lower-magnification scan over an area on the cleavage plane of lizardite where this phenomenon was recorded. A shallow, roughly square pit is present, 150 Å wide, the same size as the area scanned, and approximately 2.5 Å deep. A force of 325 nN produced such a pit in 30 seconds, a force of 130 nN produced a pit in 3 minutes. Once a pit has formed, it will continue to grow
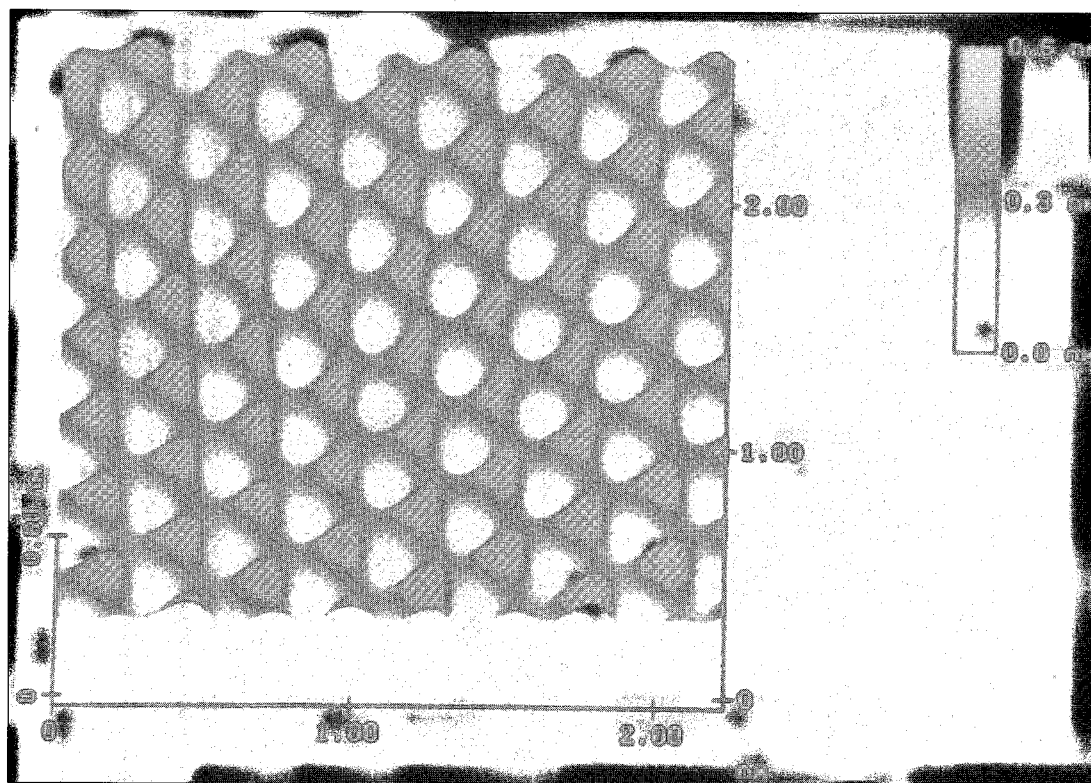
FIG. 2. An oblique view of a filtered AFM image of the hydroxyl groups and magnesium atoms of the sheet of octahedra forming the surface of a lizardite crystal. The hydroxyl groups (pale grey) are triangularly arranged and bonded to magnesium atoms (medium grey). The black areas are empty sites. All divisions are in nanometers.

laterally, even at low tracking forces during regular scanning. This, combined with the high level of noise in the image, explains the irregular outline of the etch pit in Figure 4. Similar cantilever forces and scantimes were used to scrape through surface layers of clinochlore (Vrdoljak *et al.* 1993) and muscovite (Eby *et al.* 1993).

Figure 5a is an image recorded during this process. It is a particularly important image because the upper part shows hexagonal rings of tetrahedra at a separation of 5 Å and the lower part shows a triangular arrangement of atoms at a separation of 3 Å. The initial image (Fig. 5a) is quite noisy because the surface was being continuously scraped away during scanning. Under these nonideal conditions, it is remarkable that an image could be captured. The removal of the higher-frequency noise improves the image somewhat (Fig. 5b). Separation of the two patterns of atomic arrangements, *i.e.,* the top and bottom halves of the image, filtering each pattern using two-dimensional fast-Fourier transforms, and reassembling the two halves, produce Figure 5c, in which the two patterns can be distinctly seen.

The pattern of rings at a spacing of 5 Å, although far from ideal, is clearly that of the hexagonal rings of the sheet of tetrahedra (compare top of Fig. 5 with Fig. 3). The triangularly arranged atoms with a spacing of 3 Å are the same as the hydroxyl groups of the sheet of octahedra (compare bottom of Fig. 5 with Fig. 2). Continued scanning removed the atoms of the sheet of tetrahedra and left the full view of the scan with an interatom separation of 3 Å. Evidently, the basal oxygen and silicon atoms of the sheet of tetrahedra were being removed by the silicon nitride tip. The remaining atoms with a 3 Å spacing must be the oxygen atoms and hydroxyl groups common to both the sheets of tetrahedra and octahedra. Thus, in the course of the present study and the previous study (Wicks *et al.* 1992), images of both the OH plane and (O, OH) plane of the sheet of octahedra have been recorded. The images of the (O,OH) plane remained stable as the atoms could not be removed during scanning, even at high tracking force for more than 10 minutes. However, the quality of these images was not as good as those recorded on the original cleavage plane. Scans at high tracking forces of up to 325 nN for peri-
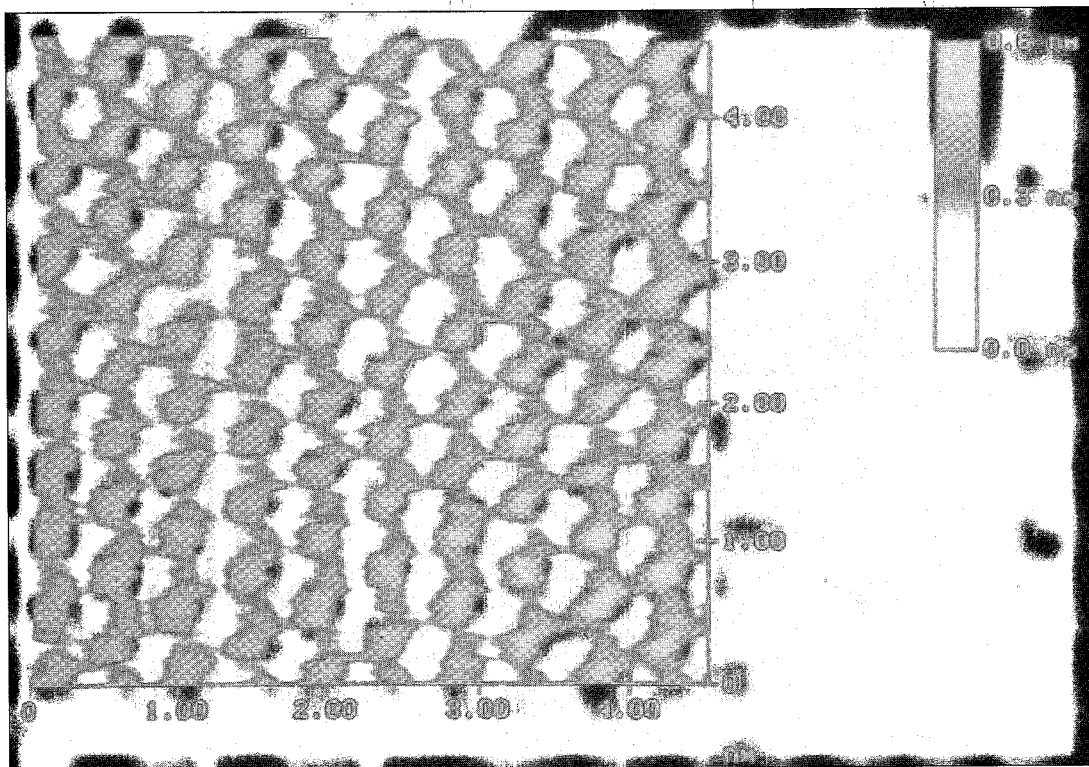
FIG. 3. An unfiltered AFM image of the hexagonally arranged array of basal oxygen atoms of a sheet of tetrahedra. The individual oxygen atoms are not resolved. All divisions are in nanometers.

ods of 10 minutes on the outer OH plane of the sheet of octahedra of the lizardite structure did not produce deterioration of the images.

Repeating the layer-removal procedure on the sheets of tetrahedra in clinochlore and muscovite also removed the oxygen and silicon atoms, to allow imaging of the (O,OH) plane within each structure. Figure 6 is an image of muscovite, taken after scraping at high force (>175 nN); it appears to correspond to the (O, OH) plane of the sheet of octahedra. Instrumental drift is responsible for the image distortion in Figure 6; therefore, trigonal symmetry is not observed in the sheet of octahedra. Layer-by-layer scraping is a necessity in order to image the sheet of octahedra in micas. The arrangement of atoms shown in Figure 6 lasted less than 10 seconds. The structure was quickly scraped away down to the next sheet of tetrahedra. Work is underway to further characterize the dioctahedral layer silicates.

DISCUSSION

The stability of the sheet of octahedra relative to the instability of the sheet of tetrahedra during AFM scanning is puzzling. The oxygen atoms of the sheet of

tetrahedra are more tightly bound than the hydroxyl groups of the sheet of octahedra, suggesting that the latter should be more susceptible to removal by abrasion than the former, as were the more weakly bonded atoms in the AFM study of Delawski & Parkinson (1992). However, this argument ignores the mechanistic aspects of the process. Delawski and Parkinson found that layer-by-layer etching of two-dimensional metal dichalcogenide is initiated at sites of surface defects caused by missing chalcogenide atoms. Etching and layer removal could not be initiated on high-quality stoichiometric crystals without defects. The large opening in the hexagonal rings in the sheet of tetrahedra of layer silicates most likely plays an analogous role to the defect sites in the dichalcogenide structures by providing an open site for the initiation of the removal process (Fig. 1a).

As the oxygen and silicon atoms are removed, it seems reasonable to assume that the coordination numbers of cations are preserved to maintain charge balance, and this requires the introduction of additional anions to the system. In this step, the structure of the surface also is an important factor. The lizardite surface in air would be covered by at least a mono-
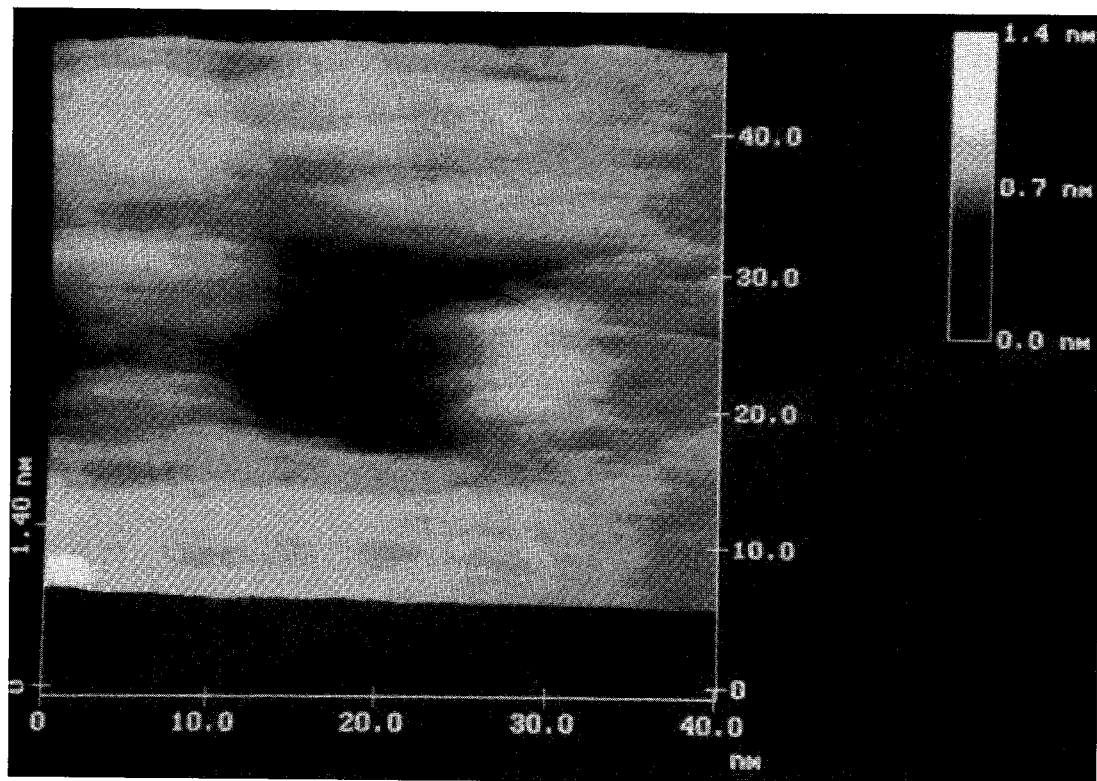
FIG. 4. A low-magnification scan showing the shallow (2.5 Å), roughly square pit (150 × 150 Å) produced by the high-force scans. All divisions are in nanometers.

layer of adsorbed molecules of H_2O (Newman 1987). It is usually assumed that these molecules are routinely swept away by the tip on the cantilever of the AFM during scanning, but no measurement of the force required has been made. Certainly, in our case, where much more strongly bonded oxygen and silicon atoms are removed, the adsorbed molecules of H_2O must be removed early in the process. These H_2O molecules (and both oxygen atoms and H_2O molecules in the ambient air) would be available as the additional anions. When the tip is scanning the sheet of octahedra, the continuous, closely packed nature of the sheet does not allow access of ambient "atmospheric" molecules to the underlying plane of anions common to the sheets of octahedra and tetrahedra, except perhaps at defects. Consequently, breakage of bonds would not be promoted by adjacent, potentially anionic, species that could immediately bond to one of the cations and produce a low-energy configuration. On the other hand, when the tip is scanning the sheet of tetrahedra, the situation is very different. These sheets consist of hexagonal rings of tetrahedra with large hexagonal holes distributed throughout the sheet (Fig. 3). These 4-Å-diameter holes are large enough

for species such as H_2O to have access to the surface common to the sheets of tetrahedra and octahedra. Thus, breakage of bonds at this surface can be promoted by local molecules of H_2O that dissociate and immediately form a bond with the cation involved in the bond-breaking reaction (Fig. 1b). This can be represented by an equation such as

$$Si-O-Mg_3 + H_2O \rightarrow Si-OH + Mg_3-OH.$$
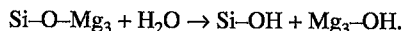
Silicon atoms are detached from the surface, and the nonbridging oxygen becomes an OH^- anion. The resulting arrangement involves an OH^- bonded to three Mg cations, with a structure identical to the outer OH plane of the sheet of octahedra. Thus, the AFM image resulting from such a process (bottom of Fig. 5) should be identical to the AFM image from the other side of the sheet of octahedra (Fig. 2).

In terms of the proposed mechanism of detachment, there are two possible alternatives: (i) the H_2O group becomes a ligand to Si, with breakage of the $Si-O-Mg_3$ bond and detachment of a H^+ ion from the H_2O group; (ii) the H_2O group becomes a ligand to Mg_3, with breakage of the $Si-O-Mg_3$ bond and detachment of an H^+ ion from the H_2O group. The
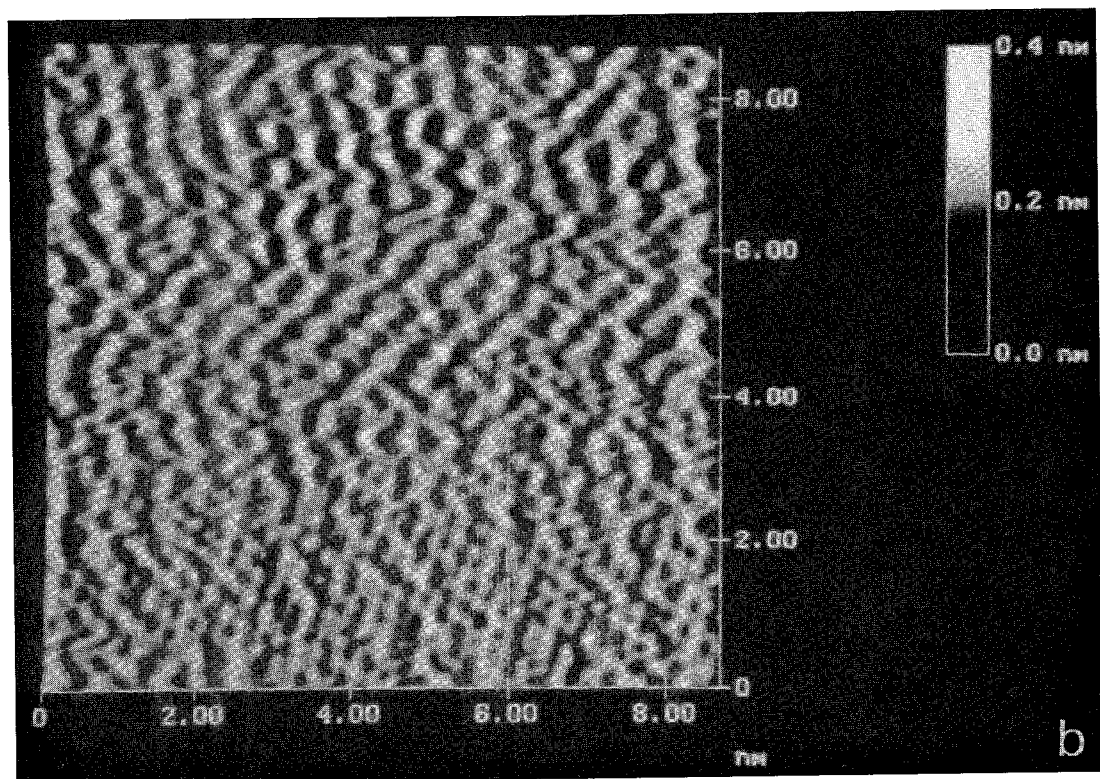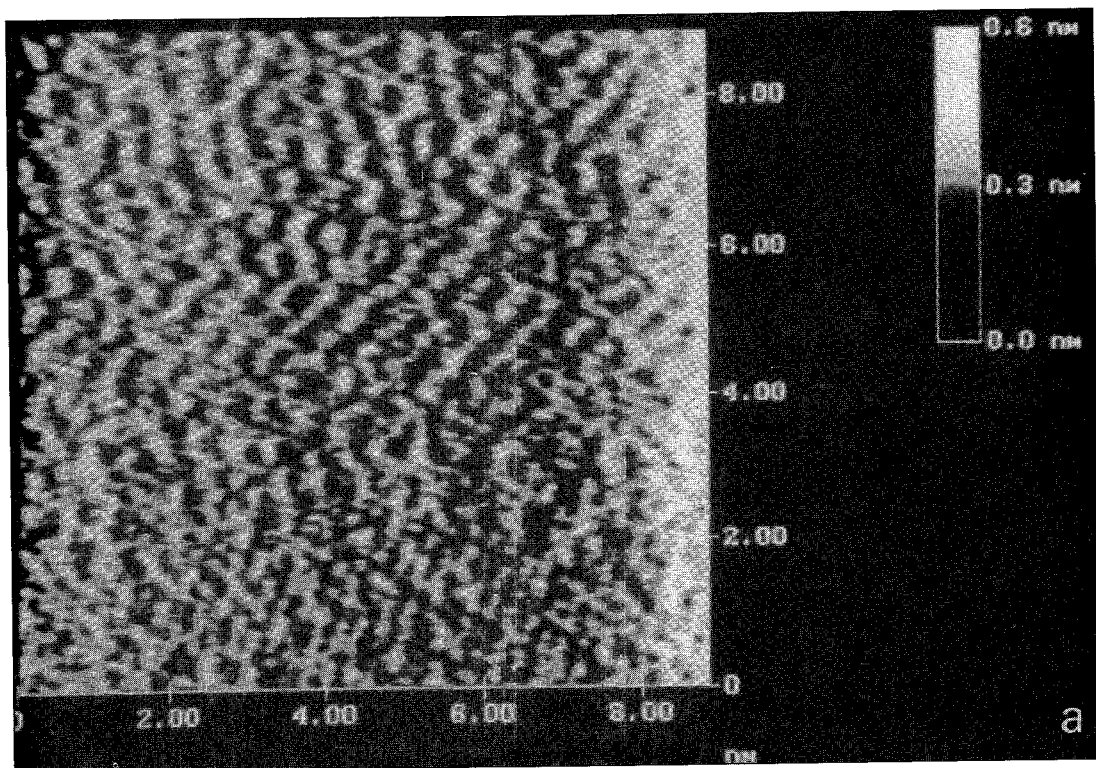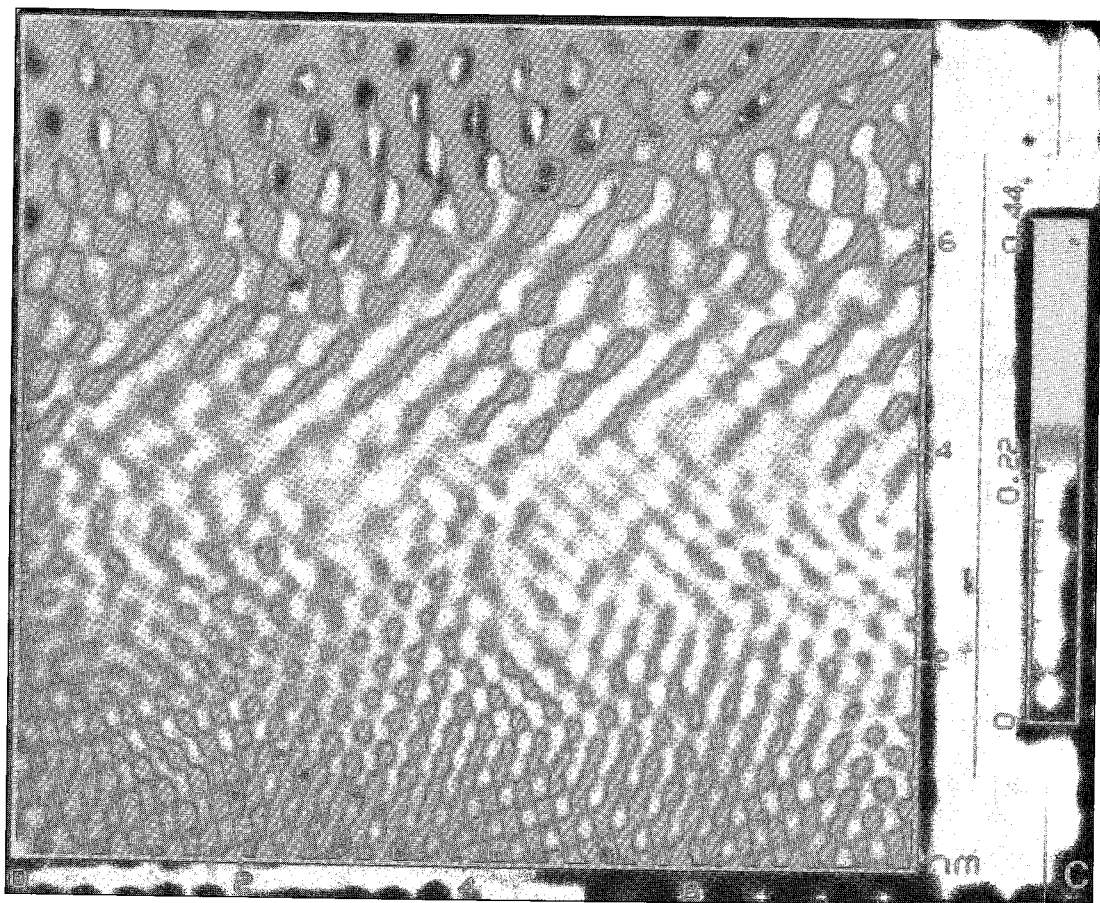
FIG. 5. An AFM image captured during the removal of the basal oxygen and silicon atoms of the tetrahedra. There is considerable noise in this image because the surface was being severely disrupted at the time the image was being captured. a) The unfiltered AFM image. b) The same image with only the high-frequency noise filtered out. c) The same image after the upper and lower pattern were separated, filtered with two-dimensional fast-Fourier transforms, and then reassembled. Each image shows the plane of hexagonal rings of oxygen atoms at ~5 Å spacing in the upper half of the image, which has been scraped away to expose, in the lower half of the image, the triangular arrangement of hydroxyl groups at ~3 Å spacing. This central plane of atoms is common to both the sheets of tetrahedra and octahedra. All divisions are in nanometers.

Si–O and O–Mg$_3$ bonds are of approximately equal aggregate strength; thus neither mechanism seems favored. However, the spatial relationships within the sheet suggest that mechanism (i) will be preferred. Bonds between silicon and some oxygen atoms also will be broken. The entire process can be represented by

$$Mg_3Si_2O_5(OH)_4 + 2H_2O \rightarrow 3Mg(OH)_2 + SiO(OH)_2 + SiO_2.$$
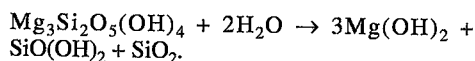
It must be emphasized that this equation is given to represent what we think occurs and to aid in the discussion of this process. It may or may not be what actually takes place.

Our proposal for the role of H_2O in the process of removal of oxygen and silicon atoms from layered silicates is supported by the results of Delawski & Parkinson (1992). They found that etching is promoted by high humidity, which further highlights the importance of H_2O in this process.

The dynamics of the interaction between the tip and the sample are not, as yet, well understood. However, there are clues upon which further speculation can be based. Atomic resolution of individual OH groups making up the surface of the sheet of octahedra in lizardite and in the interlayer sheet of clinochlore is fairly easily attained. In contrast, atomic resolution of individual basal oxygen atoms in the sheet of tetrahe-
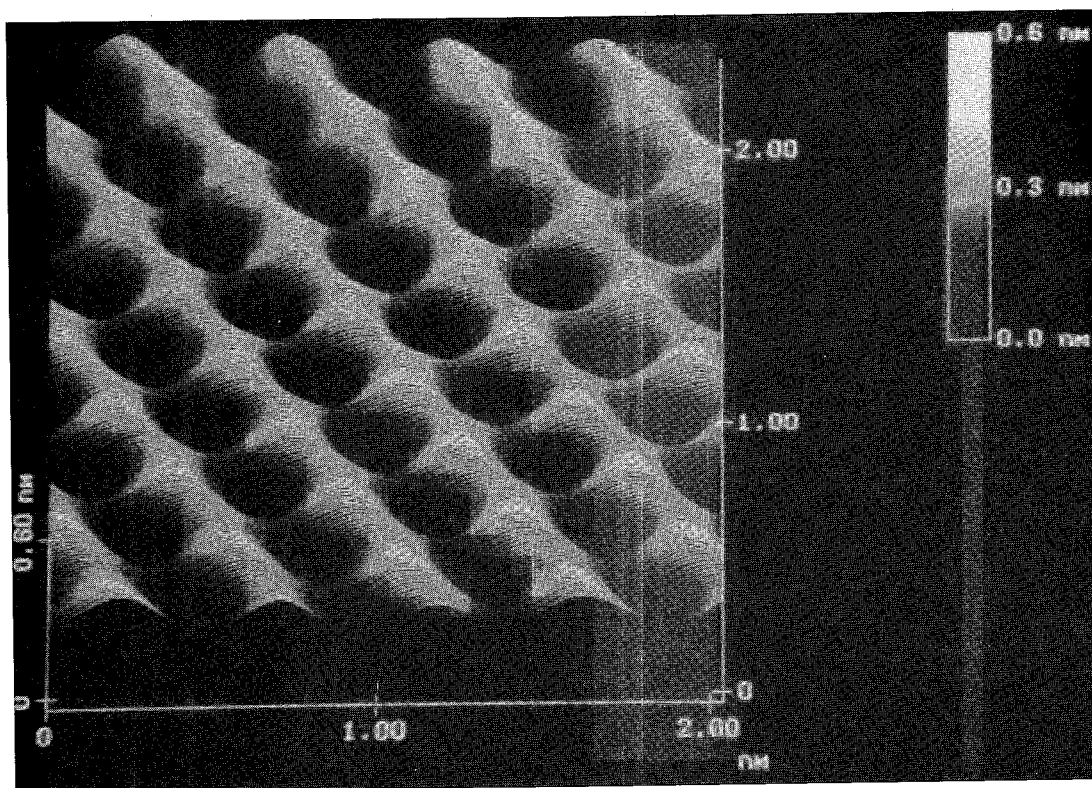
FIG. 6. An oblique view of a filtered AFM image of the internal oxygen–hydroxyl plane common to both the sheets of tetra-hedra and octahedra in muscovite. All divisions in nanometers.

dra of layer silicates is difficult to achieve. It appears that the dipolar OH groups promote atomic resolution. Perhaps the dipolar nature of the OH groups allows them to interact with the atoms of the silicon nitride tip to establish a single atom tip. Further work is necessary to establish this as a viable hypothesis.

CONCLUSIONS

The AFM has been developed and used to study the atomic topography of surfaces. The results of our study demonstrate that the AFM has potential in examination of the near-surface structure as well. There are difficulties to be addressed, such as how the newly revealed surface is changed by the removal of the overlying atoms. However, the possibility of using the AFM to remove surface layers should be examined to establish its usefulness. As the instrument is further refined and our understanding of scanning-probe techniques grows, this type of study could become one of importance in the study of the internal structures in solids.

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