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IMAGING THE HYDROXYL SURFACE OF LIZARDITE AT ATOMIC RESOLUTION WITH THE ATOMIC FORCE MICROSCOPE

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ABSTRACT

The {001} surface of lizardite has been examined in air with the atomic force microscope (AFM). Images of the hydroxyl groups on the outer OH surface of the sheet of octahedra and the tops of the magnesium atoms just below the hydroxyl groups were recorded at atomic resolution. Images of the hexagonal rings of basal oxygen atoms of the sheet of tetrahedra were recorded at molecular resolution. The images were obtained both from fresh cleavage surfaces prepared immediately prior to examination and from unprepared surfaces of crystals. There was no difference in the results from the two surfaces. The OH surface of lizardite is similar to the outer OH surface of chrysotile asbestos. Recent work on modifying chrysotile asbestos to reduce its chemical reactivity in the environment has centered on chemical alteration of the surface of the fibers using $POCl_3$ and organosilicon compounds. The success of the AFM study of lizardite suggests that the AFM can be applied to studies of surface reactions of chrysotile asbestos, as well as to studies of other layer silicates and modulated layer silicates.

Keywords: lizardite, chrysotile asbestos, antigorite, atomic force microscope, atomic resolution, hydroxyl groups, magnesium atoms, octahedral sheet, tetrahedral sheet.

SOMMAIRE

La surface {001} de la lizardite a fait l'objet d'un examen dans l'air avec un microscope à force atomique. Les images des groupes d'hydroxyle sur la surface externe des feuillets d'octaèdres et des atomes de magnésium au dessous de ceux-ci ont été enregistrées avec résolution atomique. Les images des anneaux hexagonaux des atomes d'oxygène formant la base des feuillets de tétraèdres ont été obtenues avec résolution moléculaire. Les images ont été obtenues à partir de surfaces de clivage fraîches, créées immédiatement avant l'examen, aussi bien que de surfaces de cristaux non préparées. Il n'y a aucune différence dans ces deux surfaces. Le niveau des groupes OH de la lizardite est semblable à la surface externe du chrysotile asbestiforme. Des travaux récents visant à modifier la surface externe du chrysotile afin d'en réduire la réactivité chimique dans l'environnement ont concentré sur l'altération chimique de cette surface des fibres au moyen de $POCl_3$ et de composés organosiliceux. Le succès de notre étude de la lizardite par microscopie à force atomique inspire confiance pour une telle étude des réactions de surface dans le cas du chrysotile et d'autres phyllosilicates, avec modulations ou non.

(Traduit par la Rédaction)

Mots-clés: lizardite, chrysotile asbestiforme, antigorite, microscope à force atomique, résolution atomique, groupes d'hydroxyle, atomes de magnésium, feuillet d'octaèdres, feuillet de tétraèdres.

INTRODUCTION

The recently developed atomic force microscope (AFM) has the potential to image the surface details of solids at atomic resolution. We have used the AFM to study the {001} cleavage plane of lizardite in air at atomic and molecular resolution, as part of ongoing studies of the serpentine minerals. The well-characterized lizardite crystals are also a good material with which to assess the capabilities of the AFM.

The atomic force microscope was developed in 1985 (Binnig *et al.* 1986) as an outgrowth of work on the scanning tunnelling microscope (STM). The atomic force microscope makes use of the interatomic forces between atoms forming the surface of the sample under study and the atoms forming the end of a sharp tip mounted on a cantilever. The application of a small tracking force keeps the tip in contact with the surface. The deflection of the tip as it is traversed over the surface atoms of the sample reflects the atomic topography of the surface and can be used to produce an image of this topography. The AFM can be used to study nonconducting, semiconducting and conducting materials. In contrast, the STM utilizes a tunnelling current between the surface atoms and the atoms forming the end of the tip and thus can only be used for conducting and some semiconducting materials.

The AFM has been used to obtain molecular-scale images of the {001} surface of 2:1 layer structures (Fig. 1a) such as muscovite (Drake *et al.* 1989), illite and montmorillonite (Hartman *et al.* 1990). In these studies, the hexagonal rings of basal oxygen atoms in the sheet of tetrahedra are recognizable, but the individual oxygen atoms were not resolved. More recently, atomic-scale resolution of basal oxygen atoms of a mixed-layed illite/smectite has been obtained by Lindgreen *et al.* (1991). Molecular-scale resolution also has been obtained on the zeolite *clinoptilolite* (Weisenhorn *et al.* 1990) and on hematite (Johnsson *et al.* 1991). Atomic resolution has been obtained on graphite (Binnig *et al.* 1986), boron nitride (Albrecht *et al.* 1987), germanium (Gould *et al.* 1990) and sodium chloride (Meyer & Amer 1990).

Lizardite, ideally $Mg_3Si_2O_5(OH)_4$, has a 1:1 layer structure composed of one sheet of octahedra linked to one sheet of tetrahedra (Fig. 1b). Any given cleavage fragment or single crystal has one outer surface composed of the OH plane of the sheet of octahedra (Fig. 1c) and the other outer surface composed of the basal O plane of the sheet of tetrahedra (Fig. 1d). Thus in AFM studies of lizardite, and of other 1:1 layer structures, it is possible to examine two different surface structures simply by turning over the cleavage fragment.

EXPERIMENTAL

The lizardite crystals used in this study (ROM #M45037) come from a serpentine vein in a serpentinite at Smrček in western Moravia, Czechoslovakia, sampled by P. Černý in 1965. A detailed description of this material will be presented elsewhere. The lizardite occurs in subhedral crystals 1 to 2 mm across, rarely up to 10 mm. They cleave easily and produce a pearly lustrous cleavage plane that generally is gently curved, which suggests that the crystals have been

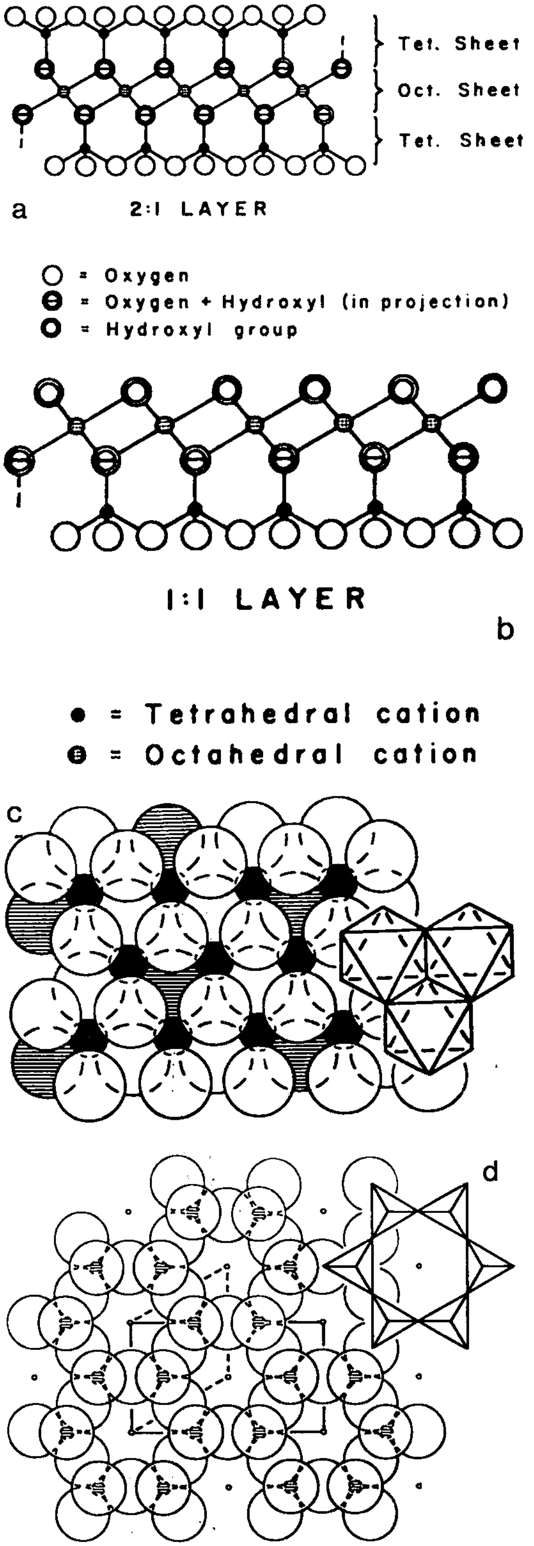

FIG. 1. Idealized structures from Bailey (1988): a) [010] projection of a 2:1 layer structure, b) [010] projection of a 1:1 layer structure, c) [001] view of a sheet of octahedra, and d) [001] view of a sheet of tetrahedra.

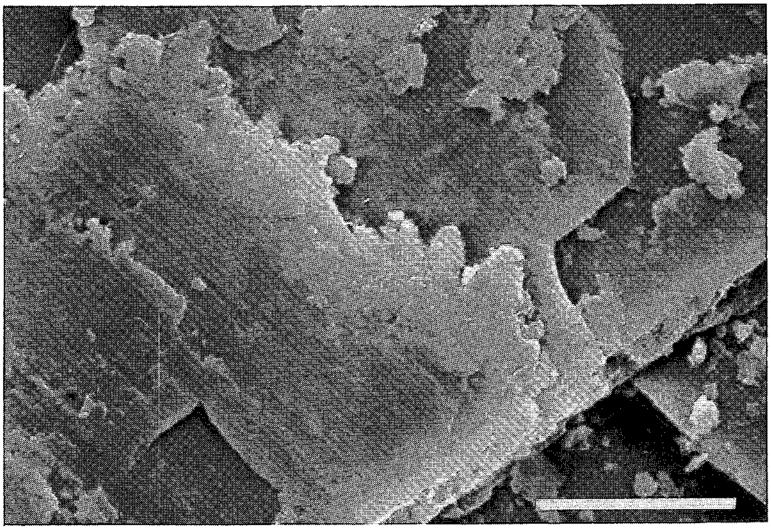

FIG. 2. A scanning electron microscope view of the {001} cleavage face of lizardite. Scale bar represents 10 μm.

slightly deformed (Fig. 2). A scanning electron microscope (SEM) examination of the surface shows that there is significant dissolution of the crystal in some areas. Although the cleavage faces appear quite smooth to the eye and by SEM at moderate magnifications (Fig. 2), they are quite irregular at high magnifications (Fig. 3). Finding a flat regular surface for AFM scans was difficult. Thus what appeared at low magnification to be ideal material proved at high magnification to be less than ideal. Nevertheless, with persistence, excellent results were obtained. All AFM scans were done in air, both on fresh cleavage planes that were produced immediately prior to scanning and on unprepared surfaces of crystals taken from the glass vials after 25 years of storage. There was no difference in the results from the two types of surfaces.

Both the surface of basal oxygen atoms of the sheet of tetrahedra and the outer OH surface of the sheet of octahedra were examined by AFM during two sessions, one on April 27, 1990, and one on November 6 and 7, 1990. The OH surface was examined in the April session, and both surfaces were examined in the November session.

The AFM images were acquired using a Nanoscope II Atomic Force Microscope produced by Digital Instruments, Inc. The specimen to be imaged is rastered by means of a piezoelectric translator (Fig. 4), under a silicon nitride cantilever and integral tip. If the force, between 10^{-7} and 10^{-10} N, exerted by the cantilever on the surface of the specimen is lower than the force between adjacent atoms in the tip and the specimen, the tip will move up and down in response to the repulsion of the atoms over which the tip moves. The movement of the tip is detected by a laser beam reflected off the back of the cantilever to a photodiode. This produces a profile of the atomic topography; a series of successive profiles (rasters) builds up a three-dimensional image of the surface. An 0.7-μm scanning head was used with a 100-μm tip calibrated using a force constant of 0.58 N/M. A contact force in the order of 100 nN was used during scanning to obtain the images of lizardite. The scanning head was calibrated at the factory using a muscovite standard to define x and y, and mechanical calibration of the piezoelectric crystal to define z. Specific areas of interest were isolated from the initial unfiltered images, and filtered using a two-dimensional fast Fourier transform to remove the higher-frequency terms. Further details of the operation of this instrument are given in Hochella *et al.* (1990).

RESULTS AND DISCUSSION

Images of the hexagonal rings of oxygen atoms in the basal O-plane of the sheet of tetrahedra were recorded (Fig. 5). A comparison of the rings shown in Figure 5 with those in Figure 1d confirms this interpretation, but it also is clear that the individual oxygen atoms within the rings were not resolved. Repeated effort could not extend the resolution past the molecular resolution of the hexagonal rings of oxygen. Because the hexagonal ring is clearly

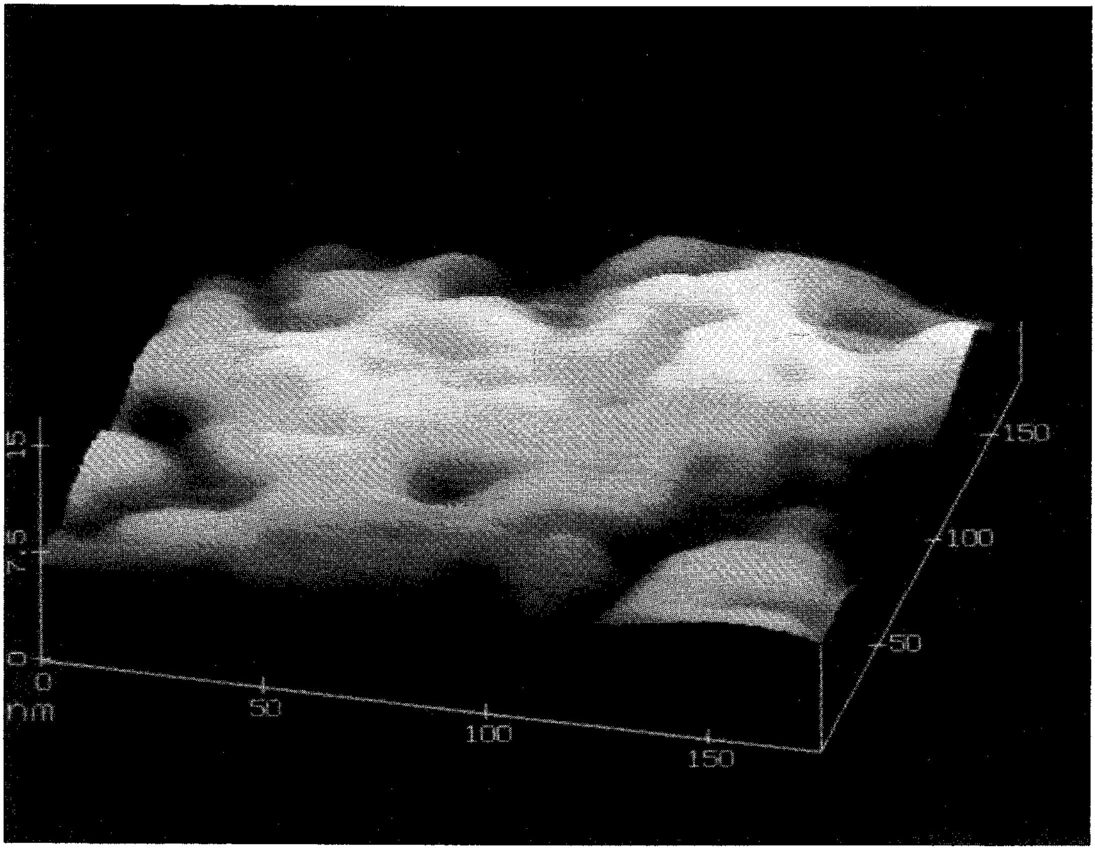

FIG. 3. An oblique AFM view of the {001} cleavage face of lizardite. The field of view is 175 × 175 nm. All divisions are in nm.

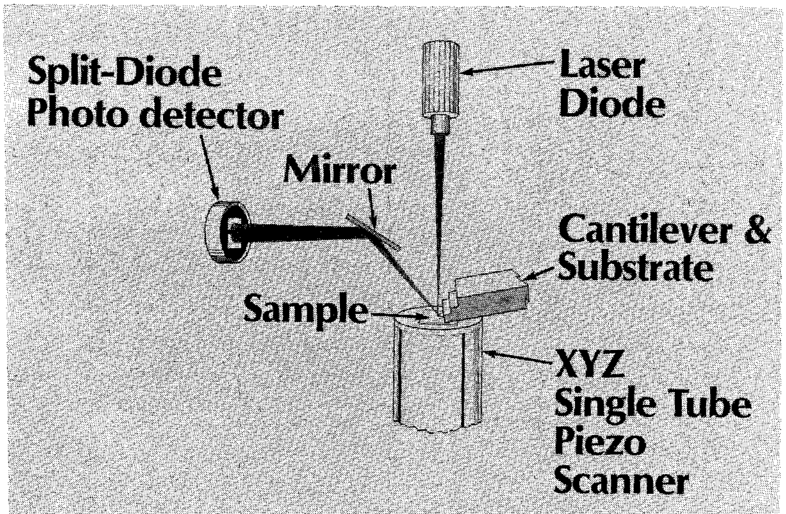

FIG. 4. Schematic drawing of the atomic force microscope.

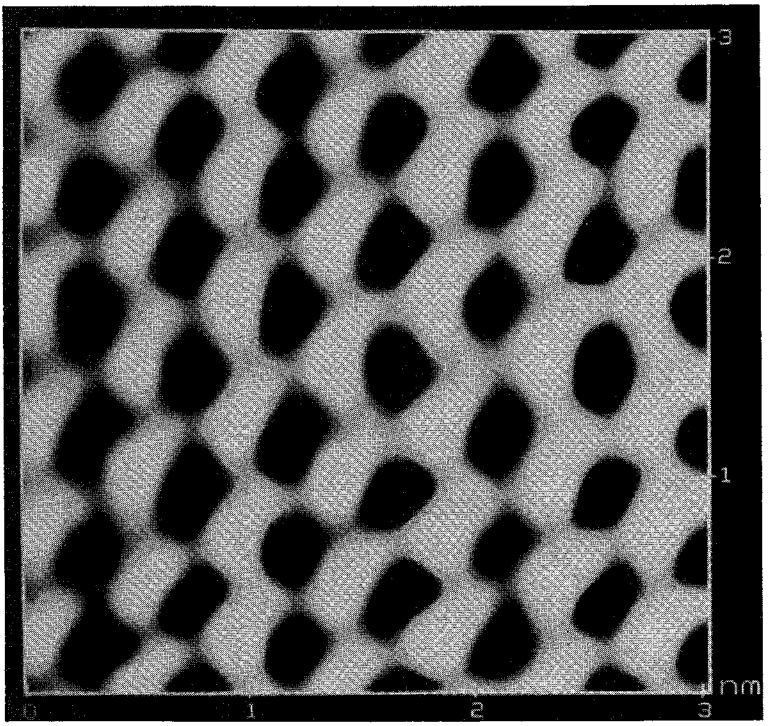

FIG. 5. A filtered AFM image of the hexagonal arrangement of basal O of the sheet of tetrahedra at molecular resolution. Compare with Figure 1d. The field of view is 3 × 3 nm. All divisions are in nm.

resolved, these results (Fig. 5) are a slight improvement on the resolution of the earlier AFM studies of 2:1 layer silicate structures (Drake *et al.* 1989, Hartman *et al.* 1990) but not as high as the resolution obtained by Lindgreen *et al.* (1991). Our results on lizardite are similar to unpublished results on kaolinite obtained earlier by one of us (KK).

In contrast, atomic resolution of hydroxyl groups was obtained on AFM scans of the OH surface of the sheet of octahedra. Unfiltered images, such as shown in Figure 6, show ragged light and dark patches in a triangular arrangement. Filtering out the noise in the initial images using a two-dimensional fast Fourier transform produces a triangular array of hemispheres shown in Figure 7. The distance between centers of adjacent hemispheres is 3.06 Å (average of 5 measurements). The OH-OH distance in the lizardite 1T structure refinement by Mellini (1982) is 3.08 Å. In a comparison of the outer OH plane of Figure 1c with the image in Figure 7, it is clear that the hemispheres occupy the OH positions and image individual hydroxyl groups.

The scale on Figure 7 represents the differences in recorded vertical relief of the surface. Black areas represent the lowest point, and white, the highest. Inspection of Figure 1c shows that the center of any three adjacent hydroxyl groups in a triangular configuration encloses either a point immediately above the magnesium atom at the middle of the sheet of octahedra, or a point immediately above an oxygen or a hydroxyl group in the O, OH plane on the far side of the sheet of octahedra. Applying these relationships to Figure 7, the grey areas at the midpoint between adjacent hydroxyl groups represent the positions of magnesium atoms at a depth of greater than 1 Å below the upper OH plane. This compares well with a distance of 1.3 Å, taken from Mellini's (1982) structure refinement of lizardite. In the same way, the black areas are the holes over the oxygen or hydroxyl positions in the O, OH plane on the far side of the sheet of octahedra. Thus the recorded AFM images match the results of the crystal-structure refinement of lizardite in all essential details.

An oblique view of the AFM images (Fig. 8) gives a more obvious three-dimensional sense to the geometrical relationships amongst the hydroxyl groups of the OH plane, the magnesium atoms, and the holes over the O, OH positions on the far

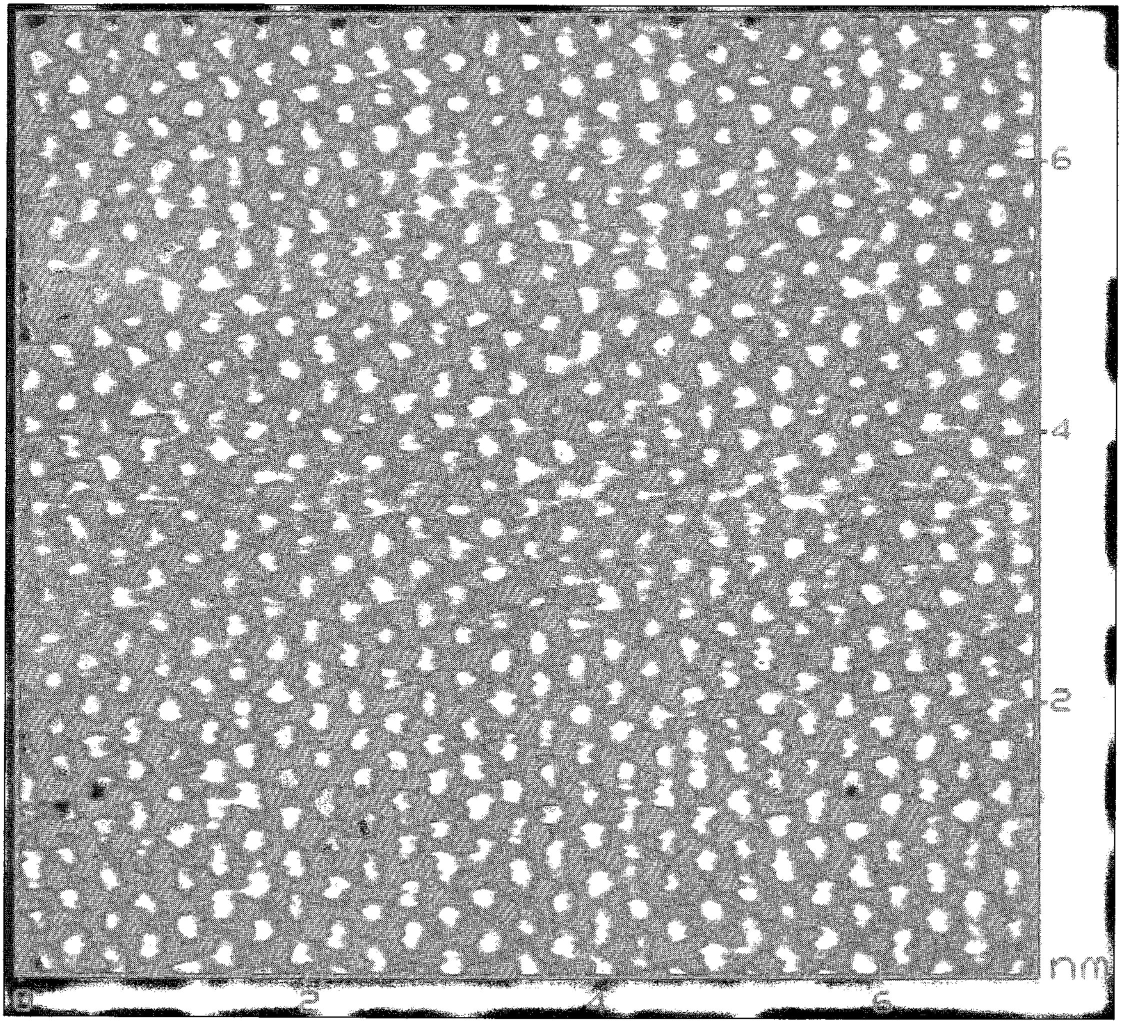

FIG. 6. An unfiltered AFM image of the OH plane of the sheet of octahedra. The field of view is 7 × 7 nm. All divisions are in nm.

side of the sheet of octahedra. Thus the images obtained by AFM on lizardite surfaces allow us to see images of atoms that are coincident with the calculated atomic positions obtained in a single-crystal refinement of the structure of lizardite.

It is encouraging that such good resolution could be obtained from surfaces that are far from ideal (Fig. 3). However, the results were found to be reproducible in two experimental sessions seven months apart. It did not seem to matter if a freshly cleaved surface or an "old" surface, either an original crystal surface or cleavage surface produced during separation 25 years ago, was used. These results suggest that AFM is a technique with great potential, which will only improve as we gain understanding of the dynamics of the interaction between the tip and the surface, and become familiar with the critical factors controlling the resolution that can be obtained.

The success of this AFM study of lizardite suggests that AFM can be applied to other problems. For example, the crystal structures of lizardite and chrysotile are closely related (Wicks & O'Hanley 1988). Lizardite has a planar structure (Fig. 1b), and chrysotile has a concentrically or spirally rolled structure, but the basic chemistry and the relationship among the atoms within the layers of the two structures are similar. Chrysotile is the most common form of asbestos.

Studies in recent years have been directed at the

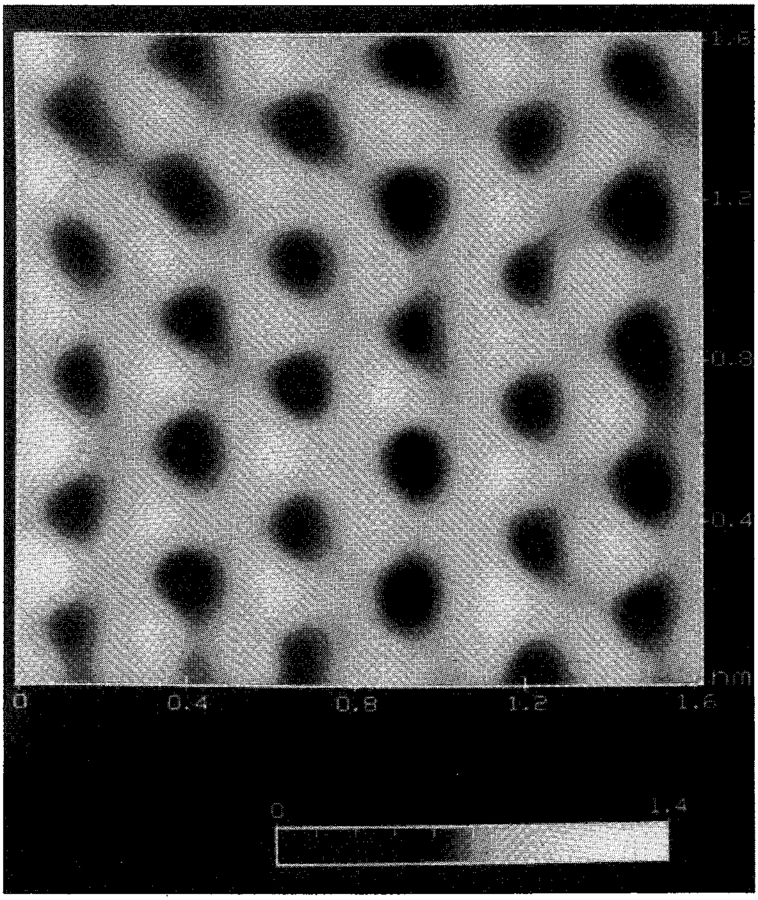

FIG. 7. A filtered AFM image of the OH plane of the sheet of octahedra. The OH and Mg positions and the holes over the underlying O and OH are visible. The field of view is 1.6 × 1.6 nm. All divisions are in nm. Scale at the bottom represents vertical relief in nm.

modification of the surface of chrysotile asbestos to reduce its chemical reactivity in the environment (Poisson 1988, Berghmans *et al.* 1990). The objective of these studies is to reduce the potential of chrysotile asbestos as an environmental hazard without reducing its strength and flexibility, the features that make it an important and useful industrial mineral. Most studies have centered on the reactivity of $POCl_3$ and organosilicon compounds with the outer surface.

In chrysotile, the sheet of tetrahedra faces in, and the sheet of octahedra faces out, so that the outer surface is composed of the OH plane of the sheet of octahedra, the same surface for which we have obtained images using lizardite. Thus, the images we have recorded likely are similar to the appearance of reaction sites involved in the surface reaction of chrysotile asbestos with $POCl_3$ and organosilicon. We thus anticipate that AFM studies of natural and treated chrysotile will increase our understanding of these surface modifications of chrysotile asbestos, and have begun a study of these materials.

We are now beginning AFM studies of other layer silicates, particularly chlorite, which contains the same structural elements as lizardite, and modulated layer silicates (Guggenheim & Eggleton 1988), particulary antigorite and carlosturanite. The modulated layer silicates contain structural perturbations that are not well understood at the atomic level and thus are ideal subjects for AFM studies.

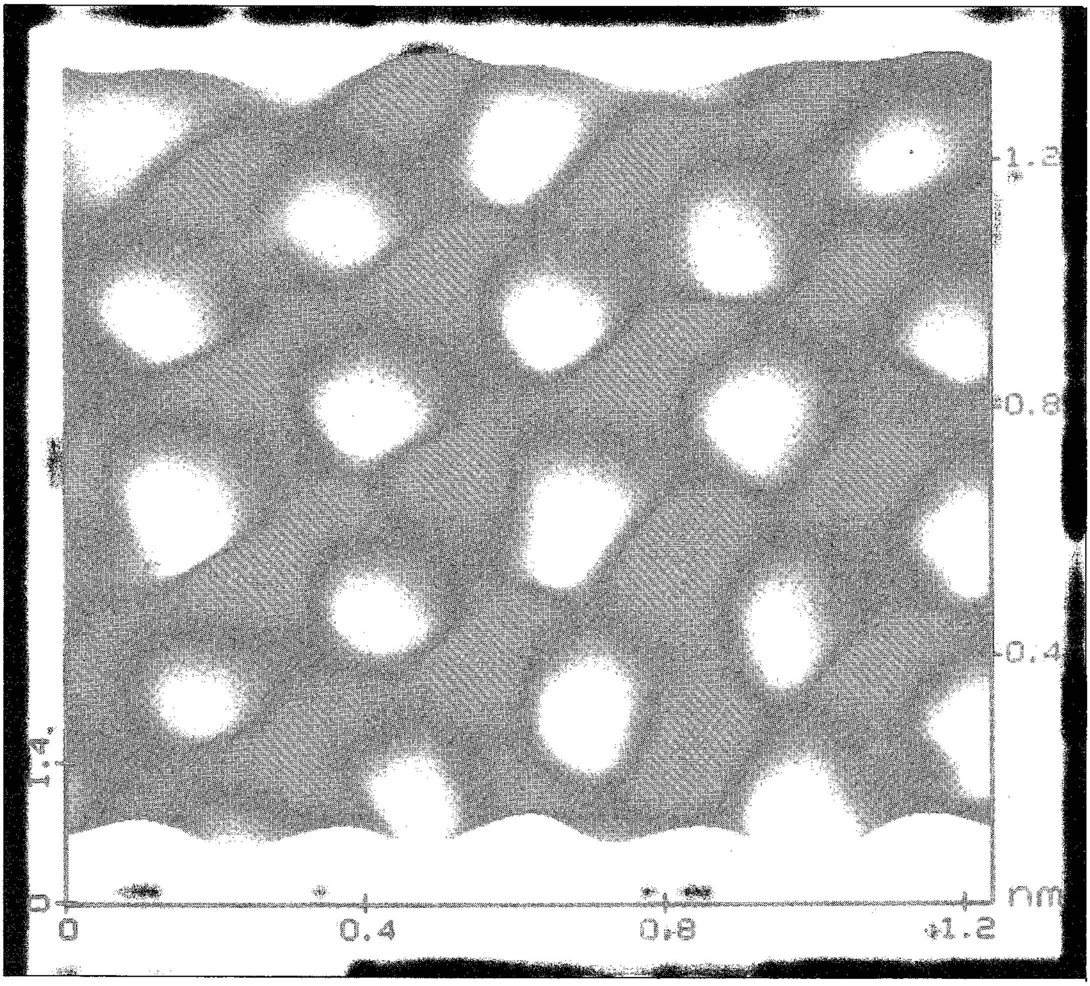

FIG. 8. An oblique view of a filtered AFM image showing, in three dimensions, the details in Fig. 7. The field of view is 1.2 × 1.2 nm. All divisions are in nm.

CONCLUSIONS

AFM images of the OH surface of the sheet of octahedra in lizardite at atomic resolution and images of the basal O surface of the sheet of tetrahedra at molecular resolution have been recorded. Images of both the hydroxyl groups and the magnesium atoms of the sheet of octahedra were recorded. These results suggest that the AFM can successfully be applied to studies of other layer silicates, and modulated layer silicates.

Serpentinite is an abundant rock-type, and lizardite serpentinite occurs more widely than antigorite or chrysotile serpentinites. Thus lizardite is commonly the principal serpentine mineral involved in weathering processes, in which surface reactions on the OH and basal O surfaces are important. The AFM will be an important technique for future studies of the weathering of serpentinites.

Attempts to modify the reactivity of chrysotile asbestos in the environment have been directed at chemical modification of the chrysotile fiber surface. This outer surface of chrysotile is an OH surface similar to the OH surface of lizardite. AFM examination of unaltered and chemically altered surfaces of chrysotile asbestos should illustrate details of the process of surface alteration.

The results in this paper demonstrate that the AFM can be used successfully to study the surface of silicates; this approach has applications in the study of both geological and industrial materials.

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