Atomic-Force-Microscopic Observations of Dissolution of Mica at Sites Penetrated by keV/nucleon Ions

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With atomic-force microscopy we studied etch pits in muscovite mica that was irradiated with 200-keV Ag ions and with recoiling daughter atoms emitted in alpha decay. Etching occurs by initiation of 1-nm-high steps at the point of intersection of an ion's trajectory with the basal plane and by their subsequent spreading. Along some crystallographic directions in the basal plane, steps are observed to be paired, with a height of 2 nm; in other directions they remain separate. Possible future applications include alpha-recoil geochronology and searches for hypothetical dark-matter particles.

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The near-field microscopies have recently been used to observe lattice disorder due to energetic heavy ions [1-4] in crystals and to study the motion of steps of monatomic height during aqueous growth and dissolution of calcite [5]. We have found that the atomic-force microscope (AFM) provides a powerful technique for studying the etching of tracks of low-energy heavy ions in mica. In addition to its applicability to the mechanism of crystal dissolution, the method may make possible the identification of keV/nucleon heavy ions and the dating of relatively young archaeological objects.

The etching technique for making tracks of energetic nuclei in mica and other nonconducting solids visible by optical microscopy was discovered 30 years ago [6], and the discovery that natural alpha-recoil tracks in mica can be revealed by etching was made 25 years ago [7]. (Alpha particles do not produce a high enough density of radiation damage to affect the local chemical reactivity of mica, but the heavy recoiling daughter nuclei do.) Alpha-recoil tracks in mica have not, until now, proven useful: The etch pits are so shallow that they are essentially invisible in ordinary bright-field optical microscopy, and the range of the alpha recoils is so short (only a few tens of nm) that quantitative measurements of their etch pits could not previously be made, even by electron microscopy. With the advent of the near-field microscopies, this situation has changed. We find that one can use AFM to observe and make quantitative studies of etch pits of natural alpha recoils (Fig. 1) after etching a freshly cleaved surface of muscovite mica in hydrofluoric acid (HF). All of the samples used in this study were etched for 4 h in 49% HF at 20 °C. The surface density of alpha-recoil etch pits in samples of muscovite mica from various locations is typically 10^5 to 10^7 cm^{-2} and is proportional to the age of the mica and its concentration of U and Th atoms (see p. 210 of Ref. [6]). To produce Ag ion tracks (Figs. 2 and 3), we annealed muscovite mica at 450 °C for 1 h to erase the naturally produced alpha-recoil tracks, irradiated it at normal incidence with 200-keV Ag ions at the IICO (Santa Clara, California) ion implantation accelerator, and etched it.

For both types of etch pits, etching proceeds by the nucleation of concentric steps originating at the radiation-damaged site penetrated by an ion, followed by their motion radially outwards on the basal plane. The quasi-geometric shape of the etch pit is related to the crystal symmetry of the mica. The AFM provides a direct measurement of the local height of the surface for each pixel in an image [8]. The step heights and the spacing between steps together determine the mean angle of inclination of the wall of an etch pit with respect to the cleavage

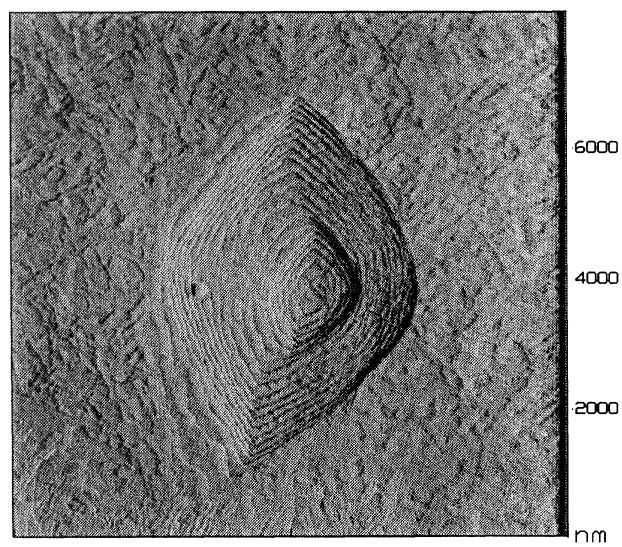

FIG. 1. Alpha-recoil track revealed by etching muscovite mica in 49% HF for 4 h. All such etch pits in the sample have the same symmetry: long axis oriented along the Y axis; shallower wall along the negative X axis with origin at the center of the etch pit; steeper wall along the positive X axis. Along Y the steps are 2 nm in height; along negative X the steps have split into pairs with 1-nm step heights. Along positive X they are too close together to resolve. The images in Figs. 1, 2, and 3 were taken in "constant height mode" with slight feedback gain to highlight the step edges. The step heights were determined by making a second scan, under "constant force mode."

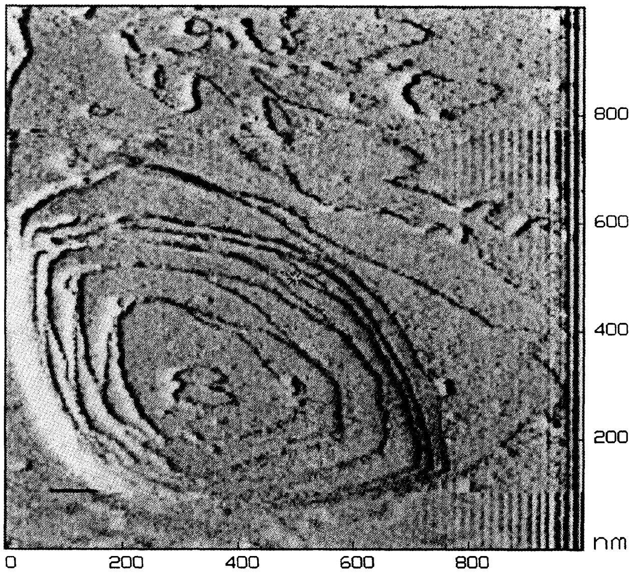

FIG. 2. High-resolution image of an etch pit of a 200-keV Ag ion. In this sample the long axes of etch pits are at an angle to the X and Y axes of the photograph. As in Fig. 1, along the long axis the steps are ~ 2 nm high; in other directions, bifurcations of 2-nm steps into pairs of 1-nm steps are clearly seen. Tortuous 1-nm steps outside the etch pit are the result of general etching at a small but finite rate.

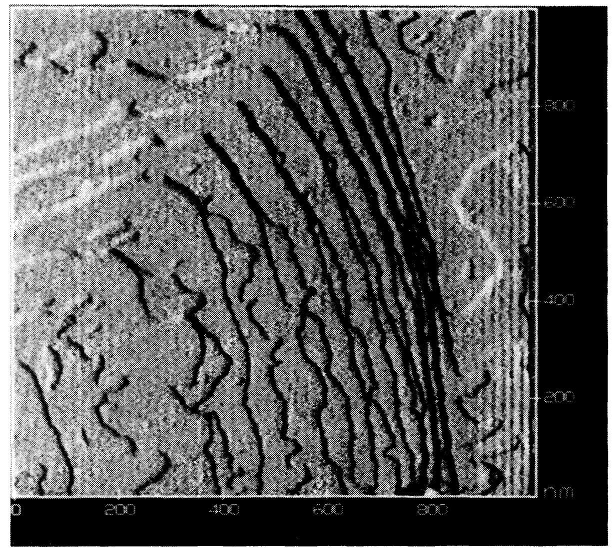

FIG. 3. High-resolution image of steps in a 200-keV Ag ion etch pit joined pairwise near the top of the figure. When split, the steps have a measured height of ~ 1 nm; when joined, the height is ~ 2 nm.

plane. For samples etched 4 h, this angle is 1° to 2° for alpha-recoil etch pits and $\sim 0.5°$ for Ag ion etch pits. Our most striking finding is that all steps have a height of either 1.0 ± 0.1 or 2.0 ± 0.1 nm. The former is the spacing between layers of K atoms, and the latter is the height of a unit cell in muscovite mica, shown schematically in Fig. 4. In Fig. 1, which is a low-resolution image of an alpha-recoil etch pit, a profile taken radially from the center of the etch pit along its long axis shows that the steps have a height of ~ 2 nm. A profile taken toward the left along its short axis shows that each of the 2-nm steps bifurcates into a pair of 1-nm steps. (On the right side of the etch pit the steps are too close together to get a profile.) In Figs. 2 and 3, which are high-resolution images of Ag ion etch pits, the same phenomenon occurs and is much easier to see than in Fig. 1: All steps are ~ 2 nm high in the direction of their long axes and bifurcate into pairs of 1-nm steps in other directions, as follows. In Fig. 2 the bifurcations into 1-nm steps are seen along the short axis, on the shallow side of the etch pit, orthogonal to the long axis. In Fig. 3, which is at higher magnification, the bifurcations are seen on the steep side, almost all the way up to the long axis. Both the etch pit shapes and the locations of the bifurcations are related to the crystallography of muscovite.

For particles with radiation damage rate high enough for preferential etching to take place, the depth of an etch pit is a function of the etch rate along the track, the particle's range, its zenith angle of entry into the mica, the etching time, and the general etch rate $v_\perp$ in an unirradiated region. General etching results from the nucleation of steps, probably at clusters of point defects, and their sideways motion along the basal plane. With increased etch time a background roughness develops that is not detectable in an optical microscope but is resolvable with AFM into regions bounded by steps of 1 nm height, as shown in Fig. 5. This background roughness outside the periphery of an etch pit is visible in Fig. 1 and is resolved as 1-nm curved steps in Figs. 2 and 3. For the 4-h etching treatment the amount of surface etched away, $v_\perp t$, is ~ 120 nm.

For an alpha recoil, the radiation damage rate is a maximum at the moment of alpha decay, falls monotonically to zero as a recoiling daughter slows to rest, then jumps to a high value as a new daughter is emitted. For the series of decays of ^{238}U leading to ^{206}Pb, the full chain consists of eight recoil atoms; for the series of decays of ^{232}Th leading to ^{208}Pb, the full chain consists of six recoils. Depending on the location of the cleavage plane with respect to the start and finish of a decay chain and on whether any of the recoil atoms double back in direction, any number from 0 to 7 changes in step spacing might be seen. The alpha-recoil track in Fig. 1 appears to have one abrupt change in spacing. Its depth measured from the roughened surface is 34 nm, not counting the two 2-nm steps that are faintly visible at the lower left of the photograph; these have almost been eradicated as a result of general etching. It is not clear whether the end of range of this recoil track was reached in the 4-h etch, despite the fact that 120 nm of material has been removed. If all of the recoils in the decay chain of a U or

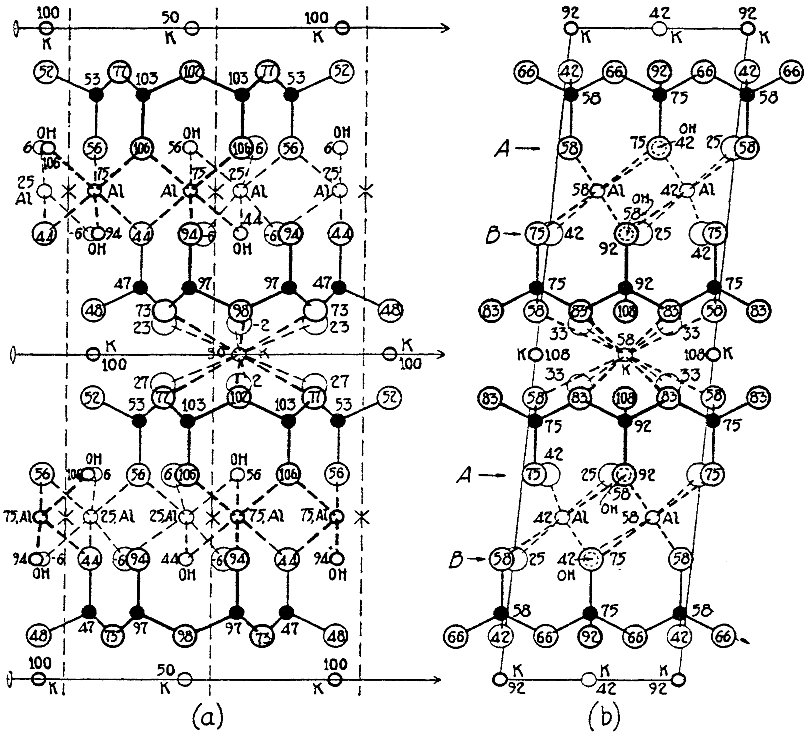

FIG. 4. Structure of muscovite mica projected onto a plane normal to (a) the a axis and (b) the b axis. The double sheets are seen, with K atoms between them surrounded by twelve oxygen atoms. The numbers give the percent of a repeat distance normal to the paper. The height of the unit cell is 2 nm.

Th nucleus happened to be aligned with each other and normal to the cleavage plane, the sum of those ranges would extend slightly beyond 120 nm, but such an alignment would be rare. It is much more likely that the recoil track was originally entirely below the surface and was uncovered by general etching during the etching process.

The thickness of removed surface, $v_{\perp}t \approx 120$ nm, is greater than the 72-nm range of a 200-keV Ag ion. Thus, most or all of the seven 2-nm steps visible in Fig. 2 and the eleven 2-nm steps visible in Fig. 3 must have been created in undamaged material exposed at the base of the etch pits, after the ion tracks had been etched to the end of their range. The smaller inclination of these etch pits ($\sim 0.5°$) to the basal plane than of an alpha-recoil etch pit such as the one in Fig. 1 is a consequence of the fact that the rate of penetration of acid in an undamaged region is slower than along etchable tracks (e.g., alpha-recoil tracks that have been uncovered during etching). The step shaped like a figure "8" at the center of the etch pit in Fig. 2 is probably the result of coalescence of steps nucleated at two nearby clusters of point defects.

The step height of 1 nm reflects the crystal structure and chemistry of muscovite mica [9]. The basic building block in mica is a firmly bound double sheet of silicon-oxygen tetrahedra assembled as shown in Fig. 4. The muscovite structure is a succession of such double sheets with K atoms holding them weakly together. The spacing between K layers is 1 nm, and a unit cell consists of two such double sheets and two K layers, with a spacing of 2 nm measured normal to the basal plane. Cleavage occurs along the K-atom layers. It is not known which atoms

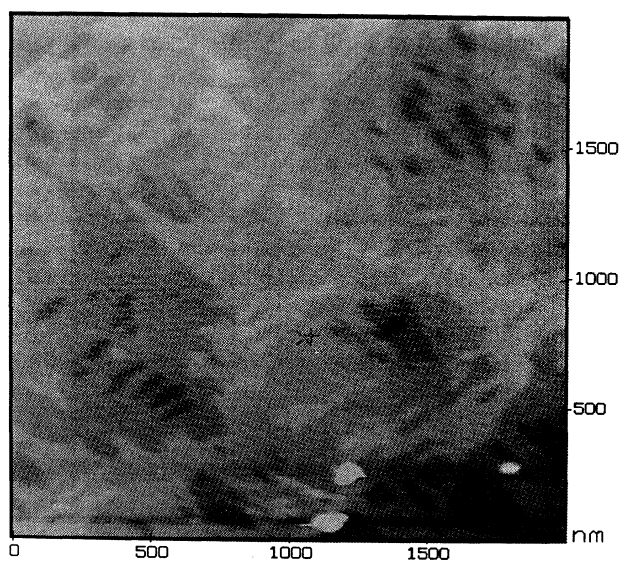

FIG. 5. Etching of unirradiated surface of mica showing regions differing in height by integral multiples of 1 nm. The shading is a measure of height of surface. The image was taken in constant force mode.

are attacked by the HF, but the only layers that repeat every 1 nm are the K layers and the Al layers.

We consider two possible explanations of the pairing of adjacent 1-nm steps into 2-nm steps that form the walls of etch pits. The first is that pairing is the result of a competition for fresh F^- ions, which must migrate along the mica surface to reach a step. Such a process was predicted in 1963 by Mullins and Hirth [10]. Building on an earlier theory of Burton, Cabrera, and Frank [11], they explained the time-dependent motion of steps of infinite length on low-index planes in diffusion-controlled growth and dissolution of crystals. Their analysis showed that finite trains of monomolecular steps can be subject to an instability that causes them to tend to group into pairs.

The second possibility is that the rate of motion of 1-nm steps depends both on the crystallographic direction in the basal plane and on whether an odd or an even layer of chemically reactive atoms is being etched. If odd 1-nm-high layers etch slightly slower than even 1-nm-high layers, the even layers will catch up with the odd layers but cannot overtake them because of the extra surface energy associated with overhanging layers. The perfect reproducibility of the pairing, independent of the distance from the center of the etch pit, favors the second explanation.

Two applications of the AFM technique for observing etch pits of heavy ions appear accessible: The first is its applicability to the question of the origin of the dark matter which comprises more than 90% of the total mass of the Universe [12]. Direct searches for hypothetical nonbaryonic dark-matter particles called WIMPs (weakly interacting massive particles) require the development of detectors sensitive to the keV/nucleon recoils of atoms struck elastically by WIMPs. A search for tracks of WIMP-recoil atoms in mica has been suggested [13]. Three conditions, if satisfied, should make it possible to carry out a stringent search for WIMPs by exploiting the enormous area-time factor attainable with a billion-year-old mica crystal: (i) Etch pits due to WIMP recoils must be distinguishable from etch pits of alpha recoils. The atoms that are the main constituents of mica (H, O, Al, Si, and K) are too light to give rise to recoils that cause etchable damage, but some micas contain several percent of Fe and up to 0.1% of heavier atoms such as Cs, both of which can produce etchable damage. The present study shows that the etchpits of 200-keV Ag ions (which are similar to Cs ions in radiation-damage rate) have much shallower wall slopes than do alpha recoils. Etch pits of Fe ions should have even shallower walls. Thus, it may be possible to use etch pit wall slope to discriminate WIMP recoils from alpha recoils. (ii) Samples with an extremely low concentration of U and Th atoms must be selected, in order to minimize the production rate of alpha recoils. Micas with less than 0.1 ppb of these elements exist and would be suitable. (iii) Samples must have been shielded from both MeV neutrons and high-energy muons, either of which can collide elastically with atoms in mica and simulate WIMP recoils. Neutron-induced recoils are avoided by selecting mica from deposits that are several meters thick and that thus moderate neutrons by virtue of their hydrogen content. Muon-induced recoils are avoided by selecting mica from deep mines; a depth of 100 m is sufficient.

The second potential application would be to use alpha-recoil tracks to extend the fission-track dating technique [6] to very young geological or archaeological materials. If alpha-recoil tracks could be visualized by AFM, the rate of production of events per unit surface area would increase by a factor $\sim 10^4$, making possible the determination of ages as low as $\sim 10^2$ to 10^3 yr in favorable cases. Until now, alpha-recoil tracks have been seen only in mica and in albite [14]. With AFM it might be possible to see them in minerals such as zircons and natural glasses.

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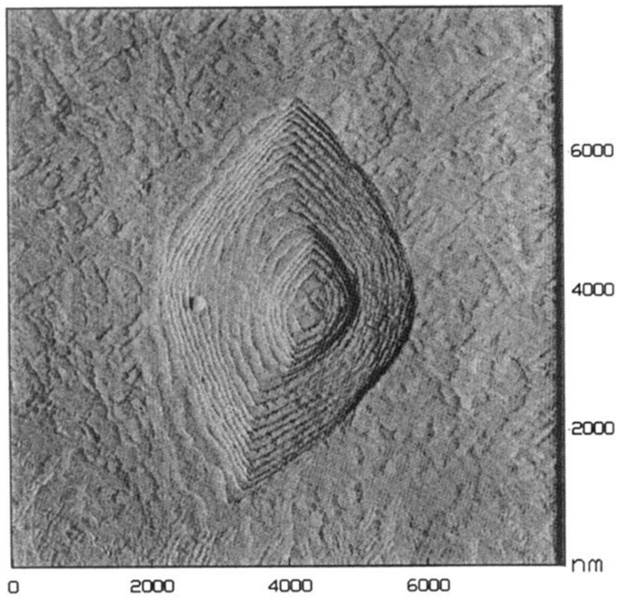

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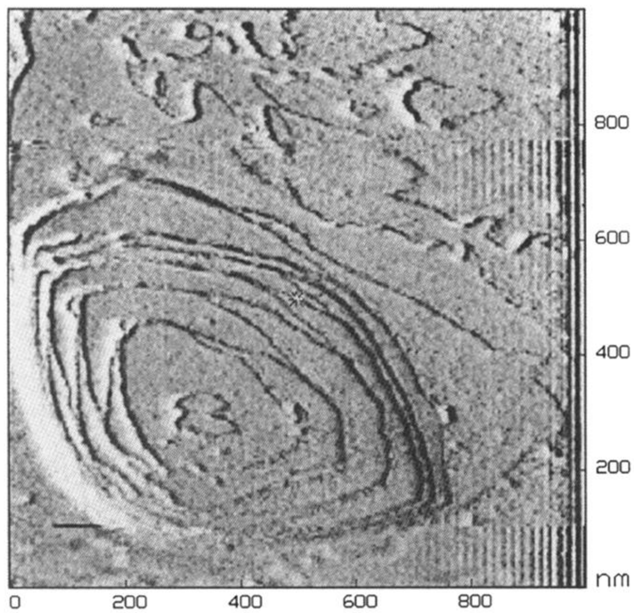
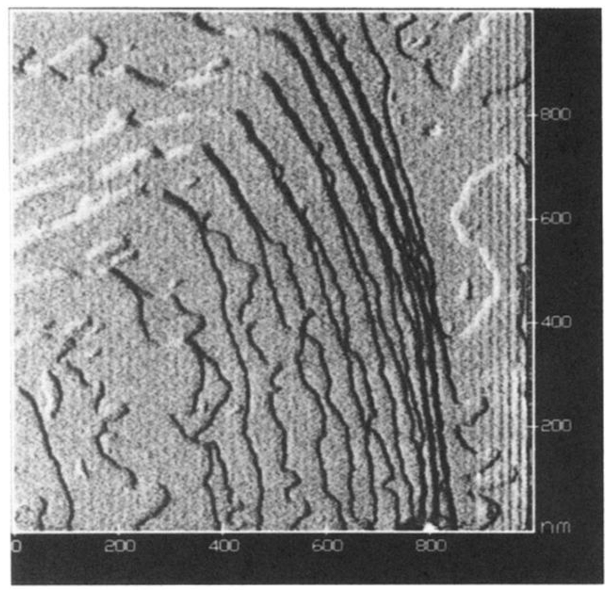


FIG. 2. High-resolution image of an etch pit of a 200-keV Ag ion. In this sample the long axes of etch pits are at an angle to the *X* and *Y* axes of the photograph. As in Fig. 1, along the long axis the steps are ~2 nm high; in other directions, bifurcations of 2-nm steps into pairs of 1-nm steps are clearly seen. Tortuous 1-nm steps outside the etch pit are the result of general etching at a small but finite rate.



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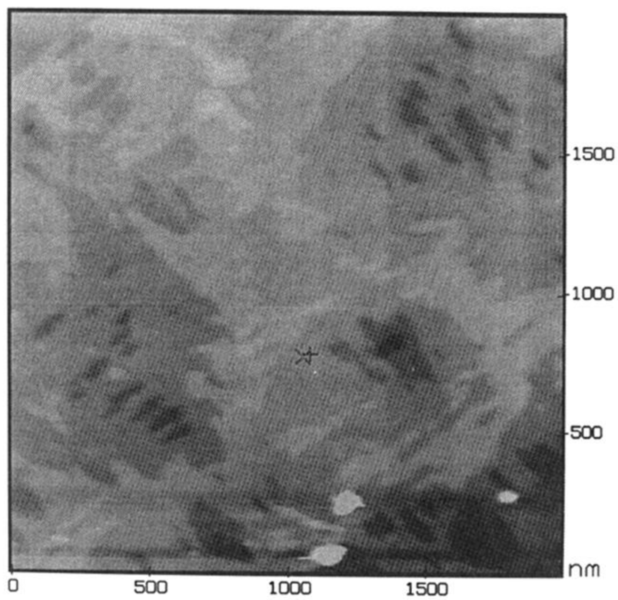

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