Thermal annealing of unetched fission tracks in apatite

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Abstract

Tracks created by fission events in ceramics are randomly-oriented, linear radiation-damage regions about 10 to 25 μm in length but only several nm in diameter. In the absence of a method to observe the entire length of a latent, unetched track, the details of the structure and the process of the thermal-annealing of tracks have remained elusive, despite their importance to fission track thermochronology and radiation damage studies in nuclear materials. Here, we have used a novel sample preparation technique, together with advanced transmission electron microscopy (TEM), to successfully image the entire length and in situ thermal annealing of latent tracks created by 80 MeV Xe ions implanted in apatite. Track annealing significantly increases as the track diameter decreases along the ion trajectory from an initial diameter of 8.9 nm to ~1.5 nm at the end of the track (total track length ~8.1 μm). For the first time, the initial, rapid reduction in etched length during isothermal annealing can be essentially explained by the rapid annealing of the sections of the track with smaller diameters, as observed directly by TEM.

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1. Introduction

The study of heavy-ion tracks has found widespread applications in fission track thermochronology (Crowley et al., 1991; Gleadow et al., 1986), radiation damage in nuclear materials (Ewing, 1999; Ewing et al., 2004; Murakami et al., 1991), particle damage in microelectronics (Dodd and Massengill, 2003), and nanoengineering e.g., creation of nanopore arrays (Mara et al., 2004; Toulmonde et al., 2004; Whitney et al., 1993). However, as an energetic heavy-ion, particularly a fission fragment, slows down along its trajectory, the amount of energy deposited decreases, resulting in a smaller track diameter (Meftah et al., 1993; Szemes, 1995; Villa et al., 1999). Variations in diameter along the track have been proposed to affect the track-shortening rate at elevated temperatures (Li et al., 2011). However, latent tracks can be seen only by TEM or other high-resolution microscopic techniques because of their extremely small track diameter (Fleischer et al., 1975; Tagami and O'Sullivan, 2005). Previous to this work, no one has successfully imaged the entire length of latent tracks, due to the difficulties in the preparation of TEM specimens with a large electron-transparent area. There is no general agreement on the processes that are responsible for track formation (Fleischer, 2004; Szemes, 1995; Tagami and O'Sullivan, 2005) as a result of the very limited understanding of the damage details along the entire track length. The thermal-annealing mechanisms at the atomic-scale are also poorly understood (Gleadow et al., 2002; Jonckheere and Chaderton, 2002; Wagner and Van den haute, 1992).

Although latent tracks are extremely narrow, it is generally straightforward to etch them chemically and increase their diameters to a few microns, so that they are clearly visible under the optical microscope. Such etched tracks, created by spontaneous fission of 238U, in apatite and zircon are extensively used to determine the thermal history of rocks from the upper part of Earth’s crust (Crowley et al., 1991; Gallagher et al., 1998; Gleadow et al., 2002). Fission track thermochronology has therefore found wide application in studies of tectonics, landscape evolution and basin analysis for several decades (Gallagher et al., 1998; Kohn et al., 2005). However, the present understanding of the fission track annealing process, upon which this field is based (Ketcham, 2005), depends almost entirely on empirical mathematical fits to laboratory annealing data for chemically-etched fission tracks, particularly the variation of etched track-lengths as a function of temperature, time and composition (Carlson, 1990; Crowley et al., 1991; Jonckheere and Chaderton, 2002; Laslett and Galbraith, 1996; Laslett et al., 1987). Consequently, there is a significant gap in the understanding of the relation between the annealing behavior of fission tracks as revealed by chemical etching to the underlying diffusion processes responsible for the gradual repair of radiation damage in latent fission tracks. Closing this gap requires a much more detailed understanding of the nature of the
radiation damage at each point along the length of a latent fission track and how each section of the track responds to thermal annealing prior to chemical etching. Here we describe, for the first time, an important advance towards this objective, based on a novel microtome-cutting sample-preparation technique that allows the investigation of the entire length of unetched fission tracks in apatite by TEM. The tracks are also observed in situ during thermal annealing.

2. Materials and methods

For a pair of fission fragments produced by spontaneous fission of $^{238}$U that travel in opposite directions, the total kinetic energy is on average 170 MeV (Fleischer, 2004), corresponding to an ion range of $\sim 20 \mu m$ in apatite. The lighter fragment (e.g., 90–100 MeV Zr) is capable of causing damage over slightly longer distance than the heavier fragment (e.g., 70–80 MeV Xe) (Fleischer, 2004), but details of the damage morphology should be similar for both fragment tracks. Previously, it was assumed that an energetic ion track has a uniform diameter along most of its length (Tagami and O’Sullivan, 2005). In a well-known physical model of fission-track annealing in apatite, Carlson (1990) postulated a simple cylindrical geometry with a constant diameter of 5.0 nm and a length of $\sim 5.7 \mu m$ for one fragment projectile (i.e., about half of a fission track), terminated by one conical tip, $\sim 2.5 \mu m$ in length. His model met with considerable criticism in the absence of actual observations of the atomic-scale structure of a track and its annealing process (Carlson, 1990; Crowley, 1993; Green et al., 1993). Because fission tracks created by spontaneous or neutron-induced fission are randomly-oriented, it has been impossible to observe the entire length of latent fission tracks (Tagami and O’Sullivan, 2005; Yada et al., 1987).

Instead of using randomly-oriented tracks, we have irradiated apatite with ions of typical fission-fragment mass and energy, 80 MeV Xe ions, and prepared cross-sectional TEM specimens containing parallel tracks. This has been achieved by cutting the irradiated sample along the entire ion paths with a diamond knife in a microtome (Fig. 1A). By using the microtome method, we have avoided the possibility of modifying track morphology due to heating or further ion damage, as is highly possible for other common preparation techniques, such as ion milling and focused ion beam cutting. The microtome method has been mainly used for sectioning biological materials because these materials are not brittle (Silva et al., 2008). Previously the relatively harder and more brittle crystalline materials (e.g., apatite) have not been considered as suitable for microtome sectioning, especially when large sample areas are required. However, we have successfully avoided cracking of the brittle specimens by first polishing the irradiated specimens down to a thickness slightly greater than the ion range, and then directly cutting the pre-polished specimens without the usual embedding in resin (Silva et al., 2008).

Parallel tracks were produced in the Durango fluorapatite (e.g., Crowley et al., 1991) from Mexico, by exposing a (0001) surface of $\sim 200 \mu m$ thick single crystal to a perpendicular beam of 80 MeV Xe ions to a fluence of $5 \times 10^{10} \text{ions/cm}^2$ at room temperature (Fig. 1A). All the irradiated specimens were stored at room temperature. Ion irradiations were performed at the Cyclotron DC-60 of Institute of Nuclear Physics, the National Nuclear Centre in Kazakhstan. The irradiated specimen was thinned down to a thickness slightly greater than 10 $\mu m$ by polishing the unirradiated surface. The ion range is $\sim 10 \mu m$, as calculated by the widely-used SRIM (2011) program for the interaction of ions with matter. The total number of runs (or ions) and the density of apatite $[\text{Ca}_{10} \text{(PO}_4\text{)}_6 \text{F}_2]$ were set as, 10,000 and 3.2 g/cm$^3$, respectively. Because the energy of a fission fragment at its very end falls below the energy threshold required to produce an observable track, the track range that can be observed by TEM is $\sim 2 \mu m$ less than the ion range, as shown in Fig. 2. Therefore, the entire track range is captured in the polished sample. A thin layer of gold ($\sim 50 \text{nm}$) was deposited on the irradiated surface as a surface marker. Then the specimen was mounted in an Ultracut E microtome with the polished surface glued onto a flat supporting material, and the irradiated (0001) surface oriented perpendicular to the knife edge (Fig. 1A). Thus, the tracks (parallel to the c-axis) are sectioned along their entire length. The thickness of sections was controlled by the automatic advance of the mounted specimen, $\sim 50 \text{nm}$ for each cut. The sectioned slices were floated onto distilled water before being loaded onto a carbon thin film TEM grid. TEM studies were conducted with a JEM 2010F electron microscope. During the TEM observations, the electron current density was kept as low as possible (0.1 to 1 A/cm$^2$) in order to minimize electron-irradiation-induced microstructural changes. In situ thermal annealing experiments were conducted in the TEM equipped with a Gatan double-tilt hot-stage specimen holder (Li et al., 2012). The temperature is monitored by a Gatan hot-stage controller. The temperature at specimen holder tip is maintained near the temperature of the specimen stage using water cooled specimen rod.

3. Results

3.1. Track profile

A microtomed section, without gap or any obvious cracking along its entire length, may be as long as $\sim 8.7 \mu m$, $\sim 170$ times greater than...
its thickness of ~50 nm, as shown in the low magnification image of 2500 times (Fig. 1B). The track profile along the entire path of 80 MeV Xe ion irradiated apatite was obtained by taking a series of TEM images at a higher magnification of 30,000 times along the whole length of the section (Fig. 2). Thus, the error in the measurement of target depth, or the distance from the irradiation surface is as small as 0.1 to 0.2 μm as the positions in the higher-magnification images can be precisely located at lower-magnifications.

As measured by TEM, the change of track diameter along the entire ion range of 80 MeV Xe ions in apatite can be divided into four zones (Fig. 2A). Approximately ten tracks were measured at each target depth. Thus, the measured track diameters are not from a single track but from numerous tracks in the sample. At smaller target depths (0 ≤ x ≤ 3.5 μm) (Zone I in Fig. 2A), the mean track diameter decreases from 8.9 ± 0.2 to 7.3 ± 0.5 nm (refer to Fig. 2D). The tracks begin with a very uniform diameter at the beginning and become more and more irregular along the ion trajectory, which is consistent with the trend for the gradual increase in the standard deviation. As the decrease in track diameter per unit depth, −dR/dx, is relatively low in Zone I, this zone is marked as “low − dR/dx”. Zone II at greater depths (3.5 ≤ x ≤ 7.0 μm) is marked as “high − dR/dx” (refer to Fig. 2E), because the −dR/dx here is obviously higher than that at the lesser depths. When the mean diameter drops to ~2.5 nm at a depth of 7.0 μm, the tracks are for the most part still continuous, but some portions begin to segment into disconnected “droplets” (refer to Fig. 2F), which causes a rapid increase in the standard deviation of the measured track diameter. The −dR/dx near the end of the ion trajectory (7.0 ≤ x ≤ 8.1 μm, or Zone III) is close to that of Zone II. However, the track becomes a line of totally disconnected droplets (e.g., mean diameter of 1.6 ± 1.5 nm at a depth of 7.6 μm, as shown in Fig. 2G). The entire etchable length of a fission-fragment pair is ~16 μm (Crowley et al., 1991; Laslett and Galbraith, 1996). As a typical fission-fragment pair, the ion ranges that can be calculated by SRIM (2011) are ~10 μm for the heavier 80 MeV Xe ion and ~12.5 μm for the lighter 90 MeV Zr ion, respectively. Therefore, the etchable length contribution of the heavier 80 MeV Xe ion alone can be roughly estimated to be ~7 μm. This estimate is the same as the depth at which the track begins to segment (Zone III in Fig. 2A, and F). Therefore, the corresponding diameter threshold for chemical etching is tentatively taken to be ~2.5 nm, below which tracks can no longer be etched, as Zone III is marked as an “unetchable track”. As no track remnants were observed by TEM at depths larger than 8.1 μm, Zone IV is marked as “no observable track”.

The ballistic interactions between the incoming projectile and the target atoms may deflect the ion path from its original trajectory. However, the nuclear part of the energy loss per unit path length, −dE/dx, for an energetic ion is usually negligible as compared with the electronic part, especially at the beginning of the ion trajectory (Fig. 2C). Therefore, the tracks are initially continuous and highly parallel to one another (i.e., the angles between the tracks and their original trajectories, parallel to the c-axis, are nearly zero) (Fig. 2D). At greater depths, besides the decrease in track diameter, the tracks gradually deviate from their original trajectories (no longer parallel to the c-axis) (Fig. 2B, and D to G), as the ratio of nuclear to electronic stopping power increases, and the nuclear-collision induced track deflection gradually accumulates along the ion paths. For the first time, we have experimentally obtained the angles of tracks deviating from the original trajectories, as shown in Fig. 2B, D and E, along the entire track length. Approximately ten tracks (or ten deviation angles) were measured at a specific depth. In general, the deflection angles as measured by TEM are in good agreement with those simulated by SRIM (2011) in the two dimensional collision plots (Fig. 2C).
however, the measured deflection angles are slightly greater than the simulated angles near the end of the ion paths. This suggests a possible underestimation of this track-orientation distribution in the simulation for this region. Furthermore, as compared with the very regular morphology and homogeneous contrast variations at the beginning of the ion paths (Fig. 2D), the tracks become irregular with segments of smaller and larger diameter but without much periodicity in the intervals with increasing target depth (Fig. 2E to F).

As previously demonstrated (Li et al., 2011), the relatively regular track morphology before annealing gradually becomes irregular during in situ thermal annealing and finally segments into separate droplets. This segmentation process accounts for the decrease in etching rate (Li et al., 2011). Similarly for unannealed tracks, the irregular damage morphology close to the end of track range, together with the reduced diameter, also hampers the track etchability (Meflah et al., 1993), leading to the reduced length of etched tracks, as compared with the length of the observed latent damage trail.

3.2. Thermal annealing

The actual process of track-shortening is complicated, as it is affected by many factors: temperature, time, chemical composition (Crowley et al., 1991), crystallographic orientation (Green et al., 1986), and α-decay dose (Murakami et al., 1991). In contrast to the extensively-used chemical etching method, the ability to observe changes in track structure in situ along the entire ion path using a TEM provides a unique tool for studying these factors. Here we demonstrate in situ thermal annealing of latent tracks induced by 80 MeV Xe ions in apatite by a TEM specimen-heating holder in order to observe the thermally-induced micro-structural evolution of tracks along the ion trajectories (Fig. 3).

Between obtaining each TEM image, the electron beam was moved away to avoid electron-beam-induced changes. Three target depths, $x_0 = 0$, $x_0 = 4.5$ and $x_0 = 7.2 \mu m$, represent the three different track zones identified above: I, low $-dR/dx$; II, high $-dR/dx$, and III, unetchable tracks, respectively. We found that the annealing rate of a track significantly depends on the track diameter, as summarized in Table 1. After heating at 330 °C for 1 h and additional heating at 380 °C for 1 h, the change in the tracks near the irradiated surface is insignificant, with only a slight decrease in diameter from $8.9 \pm 0.2$ to $8.6 \pm 0.4$ nm (Fig. 3A1 and A2). The change of relative position of parallel tracks is due to the slight bending of the supporting carbon thin film during heating. In clear contrast, the track sections with a reduced diameter at a depth of $4.5 \mu m$ show a significant shrinkage in track diameter from $5.5 \pm 0.6$ to $3.9 \pm 1.5$ nm after the same heat treatment (Fig. 3B1 and B2). The shrinkage of essentially porous tracks in apatite (Li et al., 2010, 2011) results from the thermal emission of vacancies from the track to the surrounding solids and is different from the gradual recrystallization of amorphous tracks in zircon (Li et al., 2011). However, the shrinkage rate for a void or a porous track depends on its initial diameter and the applied temperature (Li et al., 2011; Olander, 1976). The significant increase of the track-diameter distribution (or the increase of standard deviation, as shown in Fig. 3B1 and B2) after annealing mainly results from track segmentation into smaller droplets and their subsequent random motion (Glaeser, 2001; Li et al., 2011; Olander, 1976). The annealing rate has an inverse-exponential relation to the diameter of a void cylinder (Glaeser, 2001), which explains the more rapid damage recovery of

![Fig. 3](image-url)
the section of the highly porous track with smaller diameters. Within deeper sample layers of 7.2 μm, the greatly reduced size of tracks (2.8 ± 0.7 nm) leads to almost complete annealing at only 330 °C for 16 min (Fig. 3C1 and C2), which is in clear contrast to track regions I and II.

4. Discussion

Crowley et al. (1991) estimated the activation energies for track shortening, using Arrhenius plots for three apatite samples fitted by the fanning model [refer to Crowley et al., 1991 for details], in an effort to assess its implications for the underlying atomic-scale annealing process. The decrease in track length can be expressed as \( l/l_0 \), normalized to \( l_0 \), the etchable length for an unannealed track. The derived activation energies for track shortening have similar values to the activation energies for diffusion (Crowley et al., 1991) and increase with progressive fading (Crowley et al., 1991; Naeser and Faul, 1969). This increase in activation energy actually suggests that the rate of track shortening decreases with progressive annealing (Crowley et al., 1991). A similar observation is made here in terms of the change in track diameter for unetched ion tracks. Fig. 4 shows a comparison of track diameter and activation energy as function of target depth (or its corresponding \( l/l_0 \)). Here \( l_0 \) is ~7 μm for the Xe ion-induced tracks. As the value of \( l/l_0 \) decreases from 1 to 0.5, both track diameter and activation energy increase rapidly. After passing a similar \( l/l_0 \)~0.5 (or target depth ~3.5 μm), the rates of increase for both track diameter and activation energy become slower with decreasing \( l/l_0 \). The similarity between the trends for these two different sets of observations further confirms the qualitative interpretation from the in situ TEM observation: changes in track morphology along their length are responsible for the observed annealing behavior of chemically etchable tracks.

The dependence of the track annealing rate on track diameter along its length provides a simple, but clear picture, of the track-shortening process. For an unetched fission track, the track diameter is largest near the midpoint of the track, where fission occurs, decreasing towards each end. During annealing, the etchable track length is gradually reduced from each end towards the midpoint because the ends of the track have much smaller diameters and anneal much more rapidly than at sections with larger track diameters. One expects a rapid annealing at the earlier times followed by slower annealing at later times during isothermal annealing (Green et al., 1988), considering the inverse-exponential relation between annealing rate and track diameter (Glaeser, 2001; Li et al., 2011). After passing about half of the distance from each etchable end towards the midpoint (Fig. 4B), however, the diameter-increase rate for a track becomes slower, causing a significant reduction in track-shortening rate at the correspondingly late stages of track fading.

The standard deviation of the mean lengths increases very gradually from ~0.9 μm for unannealed tracks with a mean length of ~16 μm, to ~1.0 μm for annealed tracks with a mean length of ~10.5 μm (Green et al., 1986). This is in clear contrast to the very sharp increase in the standard deviation (e.g., around 2.1 μm for a mean length of ~8 μm) for the mean lengths below ~10.5 μm (Green et al., 1986). Despite the gradual reduction of the mean lengths from ~16 to 10.5 μm, the almost unchanged standard deviation (~0.9 vs. 1.0 μm) of the mean lengths clearly shows that the tracks have almost the same paces (or rates) of length reduction for small degrees of annealing. In general, the track length shortens from each end towards the middle, where the track is larger and difficult to anneal as directly observed by TEM. There are few segmentation (or breakup) events far from a track end as they would cause the abrupt reduction of the track. These observations suggest that the annealed tracks with very uniform lengths are actually the remainder of the middle portion of the latent tracks. The middle portion is left because the occurrence of the segmentation (or breakup) dominates near the ends of each track. After obtaining the mean length (\( l \)), the “very regular” segmentation and length reduction from each end of a track provides an extremely important opportunity to estimate the position of each end, which is actually the target depth (\( x \)) for a fission-fragment. The corresponding track diameter can be obtained if the track profile (diameter vs. target depth) of a fission-fragment pair is known. Alternately, the ratio of ion ranges, as calculated by

![Table 1](image)

**Table 1**

<table>
<thead>
<tr>
<th>Target depths (μm)</th>
<th>Diameter before annealing (nm)</th>
<th>Diameter after annealing (nm)</th>
<th>Annealing temperature and time</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2</td>
<td>2.8 ± 0.7</td>
<td>Almost disappear</td>
<td>330 °C for 16 min (additional 380 °C for 1 h)</td>
</tr>
<tr>
<td>4.5</td>
<td>5.5 ± 0.6</td>
<td>3.9 ± 1.5</td>
<td>330 °C for 1 h and additional 380 °C for 1 h</td>
</tr>
<tr>
<td>0</td>
<td>8.9 ± 0.2</td>
<td>8.6 ± 0.4</td>
<td>330 °C for 1 h and additional 380 °C for 1 h</td>
</tr>
</tbody>
</table>

![Fig. 4](image)

**Fig. 4.** The length of a fission track is reduced from the etchable end where the track is small and more easily annealed, to the beginning where the track is large and difficult to anneal. In the case of unannealed latent tracks induced by 80 MeV Xe ions in apatite, the etchable length, \( l_0 \), is ~7 μm.

(A) As \( l/l_0 \) decreases from 1 to 0.5, activation energies for track shortening (estimated by Crowley et al., 1991 for three different apatites) increase rapidly during the initial stages of annealing, followed by a much slower increase at later stages with \( l/l_0 \) decreasing from 0.5 to 0. (B) This trend agrees well with our observations of variations in diameter along a track. Track diameter shows an initial rapid increase as target depth decreases from 7 to 3.5 μm (equivalent to \( l/l_0 \) from 1 to 0.5), followed by the slow increase with target depth decreasing from 3.5 to 0 μm.
SRIM (2011), of a fission-fragment pair, can be used for the estimation if this track fragment is unavailable. For the mean lengths below ~10.5 μm, the sharp increase in the standard deviation suggests that the segmentation of a track can occur at any location for a heavily annealed sample, although annealing is most pronounced at the end of the track. Once any breakup event occurs far from the end, the length of a track can be abruptly reduced, which results in the sharp increase in standard deviation of the mean lengths. Due to the abrupt length reduction, the heavily annealed track becomes hard to detect. Actually, the mean lengths below ~8 μm (other than zero), equivalent to $l_0<~0.5$, are very rarely encountered (Crowley et al., 1991; Green et al., 1986). As the sections of a track in Zone I have large diameters (7.3 < D < 8.9 nm), the track segmentation rarely occurs in Zone I ($l_0<~0.5$). If this does happen during annealing, the very short tracks, due to the random segmentation, are difficult to detect. Therefore, the track sections in Zone I make only a limited contribution to the mean track lengths. In contrast, the sections of a track in Zone II ($l_0>~0.5$) make a major contribution for the length measurements and mathematical fitting because of the “very regular” segmentation and length reduction from each end of a track.

5. Remarks

In order to describe track formation in different solids with a physical model, the correlation of diameter and $d\mathrm{E}/d\mathrm{x}$ has to be accurately determined. Thus, many experimental studies have focused on the measurement of track diameter in different solids as a function of $d\mathrm{E}/d\mathrm{x}$ (Lang et al., 2006; Meftah et al., 1993; Szenes, 1995; Villa et al., 1999). In the absence of a high-resolution technique suitable to determine the track diameter along the entire track, however, different irradiation experiments have been performed by adjusting $d\mathrm{E}/d\mathrm{x}$ with different ion masses and energies (Meftah et al., 1993; Szenes, 1995; Villa et al., 1999). By the new experimental approach of this study, we are able to measure precisely the track diameter of the same projectiles along their entire length, which eliminates uncertainties due to different projectiles (e.g., ion charge state (Lang et al., 2006) and velocity (Meftah et al., 1993)) and experimental conditions (e.g., sample preparation). Further, the evolution of the damage morphology of tracks in deeper samples layers can be studied, such as the deviation angle from the original ion trajectory.

Currently, fission track thermochronology is based on purely empirical track-annealing models that are quite independent of any fundamental understanding of track structure and annealing behavior at the atomic-scale. This contrasts with the much more theoretical basis for the $^{40}$Ar/$^{39}$Ar (McDougall and Harrison, 1999) and (U-Th)/He (Wolf et al., 1996) methods of thermochronology that depend on the diffusion of noble gases in minerals. Given that the repair of radiation damage in fission tracks during annealing is also controlled ultimately by diffusion (Crowley et al., 1991), it should be possible to model fission track annealing behavior directly from measured diffusion parameters, provided the physical form of the latent tracks is known. The detailed structure of latent tracks in apatite along their entire length reported here, and the way in which the tracks change during annealing, provide an important step toward realizing this goal, with important implications for unifying all the methods of thermochronology.

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