Effect of orientation on ion track formation in apatite and zircon

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Abstract

Fission track (FT) thermochronology is essentially based on empirical fits to annealing data of FTs revealed by chemical etching, because, until now, unetched, latent FTs could not be examined analytically at the atomic-scale. The major challenge to such an analysis has been the random orientation of FTs and their extremely small diameters. Here we use high-energy ions (2.2 GeV Au or 80 MeV Xe) to simulate FT formation along specific crystallographic orientations. By combining results from transmission electron microscopy (TEM) of single tracks and small angle X-ray scattering (SAXS) for millions of tracks, a precise picture of track morphology as a function of orientation is obtained. High-resolution analysis reveals that orientation affects the shape of tracks in apatite and zircon through the preferential creation of damage along directions with highest atomic density. However, track radius does not depend on orientation, contradicting previous reports. Independent of track orientation, track radii, as measured at each point along the entire length of 80 MeV Xe ion tracks in apatite, can be understood using the thermal spike model of Szenes. Thus, the well-known track annealing anisotropy of apatite is not due to track...
radius anisotropy. The combination of ion-irradiations with TEM and SAXS analysis provides a unique opportunity to understand and model track formation and annealing under a variety of geologic conditions.

Keywords: ion tracks, fission tracks, apatite, zircon, orientation effects, thermal spike, TEM, SAXS

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Introduction

Swift heavy ions (SHIs) create a narrow track of damage in an irradiated solid along the trajectory of the ion. Such SHI irradiations have widespread applications in nanoengineering (Akcoltekin et al. 2007; Mara et al. 2004), and particle damage in electronics (Dodd and Massengill 2003). More interestingly, SHI irradiations can be used to simulate the formation of fission tracks (FTs), damage trails that were caused by spontaneous fission events of uranium impurities in minerals that have been widely used for age dating and thermochronology (Donelick et al. 1999; Gleadow et al. 2002; Jonckheere and Chadderton 2002; Yamada et al. 1995). Generally, tracks in transverse cross section are circular, but in a few cases (Bursill and Braunshausen 1990; Hebert et al. 1998; Paul and Fitzgerald 1992; Vetter et al. 1994), they have a tendency to facet along specific crystallographic directions, with an important indication that orientation may play a role in track formation. However, details of how orientation affects track formation remain elusive, because there are very few systematic studies of the shape and radius of latent, unetched tracks as a function of orientation at the atomic-scale. According to a highly cited transmission electron microscopy (TEM) study (Paul and Fitzgerald 1992), the mean radius (~4.5 ± 3.7 nm) of latent FTs || c (or the c axis) of the hexagonal apatite [Ca_{10}(PO_4)_6F_2] is significantly larger than that (~2.5 ± 2.8 nm) of FTs ⊥ c. The anisotropy of track radii in apatite has gained general acceptance (Carlson 1993; Jaskierowicz et al. 2004; Rabone et al. 2008; Schouwink et al. 2010), and has been used to explain (Carlson 1993; Paul and Fitzgerald 1992) the well-known track annealing anisotropy (Donelick et al. 1999; Gleadow et al. 2002; Green and Durrani 1977), i.e., tracks || c anneal more slowly than
tracks $\perp c$, however, a molecular dynamics simulation concluded that track size was insensitive to orientation (Rabone et al. 2008). Because of the random orientation of FTs, TEM imaging of the track radius requires considerable effort to accurately determine the orientation of any individual track that is measured, essentially requiring the alignment of the electron beam parallel to major zone axes of the grain. In this study, we overcome this problem by investigating parallel tracks produced by the irradiations of SHIs (2.2 GeV Au or 80 MeV Xe) along known zone axes of apatite ($P6_3/m$) and zircon ($\text{ZrSiO}_4$: $I4_1/amd$), two minerals that have anisotropic structures and figure prominently in FT thermochronology. By combining the results from TEM analysis of single tracks and small angle X-ray scattering (SAXS) for millions of tracks (Afra et al. 2011), a precise picture of track morphology as a function of orientation is obtained. High-resolution TEM analysis reveals how orientation affects track shape and size at the atomic-scale. Using the microtome cutting method and the thermal spike model, we compare variations in radius at each point along the entire length of 80 MeV Xe ions in apatite $\parallel c$ and $\perp c$.

**Experimental methods**

Two types of SHIs were used in this study. For the 2.2 GeV Au ion irradiation experiments, the ion range is $\sim$70 and 85 $\mu$m, as calculated by the SRIM code (SRIM 2012), for zircon and apatite, respectively (Fig. 1). The electronic energy loss per unit length, or stopping power, $(-dE/dx)e = S_e$, as a function of target depth was calculated by SRIM simulation with the function of Calculate Quick Range Table. The densities of apatite and zircon were set as 3.2 and 4.52 g/cm$^3$, respectively. The total number of runs (or ions) was set 10,000 to calculate ion distribution and damage along the ion trajectories. The SRIM simulation shows that the
angle of each track deviated from the original trajectory for the 2.2 GeV Au ion is negligibly small, especially at the lower target depths (< 40 µm). The samples were pre-polished to a thickness ~40 µm to ensure that the GeV projectiles completely penetrate the sample thickness, inducing an approximately uniform energy deposition, -dE/dx, and producing a nearly constant track radius throughout the entire sample thickness (Li et al. 2013). In contrast, as the 80 MeV Xe ions, which have a typical mass and energy of fission fragments, slow down, -dE/dx decreases (Fig. 1), resulting in a significantly smaller track radius in apatite toward the end of the track (Li et al. 2012). Variations in radius along the entire length (up to 8.1 µm) of ion tracks along the c-axis of apatite were first obtained by the microtome method (Li et al. 2012). For a fission fragment (e.g. 80 MeV Xe ion), the track range that can be observed by TEM is ~2 µm (Li et al. 2012) less than the ion range because the energy at its very end falls below the energy threshold required to produce an observable track. Although the energy of 2.2 GeV Au is significantly larger than that of a typical fission fragment, the difference in -dE/dx is small at the point of impact (for apatite: ~27 keV/nm for 2.2 GeV Au vs. ~16 keV/nm for 80 MeV Xe) (Fig. 1). More importantly, this difference in -dE/dx does not result in significant differences in the track morphology (Li et al. 2010).

Tracks (|| c or ⊥ c) were produced in bulk samples ~40 µm thick by exposing (0001) and (0 4 1 5) surfaces of Durango fluorapatite, and (001) and (100) surfaces of synthesized single crystal zircon, respectively, to 2.2 GeV Au ions in 5×10¹⁰ ions/cm² at normal incidence at the UNILAC accelerator, GSI, Damstadt, Germany. Without further preparation, bulk samples were investigated after irradiation using transmission SAXS at the Australian...
Synchrotron in Melbourne, Australia. See Kluth et al. (2008) and Li et al. (2013) for details of the SAXS measurements. TEM studies were completed with a JEOL 3011 electron microscope. The irradiated bulk samples were crushed and suspended on a carbon film supported by Cu grid for the TEM studies. To simulate FTs, tracks $\parallel c$ or $\perp c$ of apatite were produced by irradiating a single crystal $\sim 200 \mu m$ thick with 80 MeV Xe ions to a fluence of $5 \times 10^{10}$ ions/cm$^2$ at the Cyclotron DC-60 at the National Nuclear Centre in Kazakhstan.

Cross-sectional TEM specimens containing parallel tracks were prepared by cutting the irradiated sample along their ion trajectories ($\parallel c$ or $\perp c$) with a diamond knife in a microtome to show variations in track radius along the entire track. See Li et al. (2012) for details of the microtome method.

**Results and discussion**

**2.2 GeV Au Ions**

High resolution TEM (HRTEM) analysis of 2.2 GeV Au tracks was obtained in transverse cross section, i.e., tracks are parallel to electron beam, by carefully tilting a crushed specimen to align its zone axis ($\parallel c$ or $\perp c$), which is parallel to the tracks in this case, to the incident electron beam. In apatite, the central core region of the tracks has the same bright contrast as the free space (Figs. 2a, 2b, and 3a), indicating the highly porous nature of tracks, as has been discussed in detail in (Li et al. 2010). This is significantly different from the amorphous core region of tracks in zircon (Figs. 2c, 2d, and 3b). For each track $\parallel c$ of apatite, there is clear hexagonal faceting (Fig. 2a) (Paul and Fitzgerald 1992), as compared with the circular tracks $\perp c$ (here along $[\overline{5} \overline{4} 0]$) (Figs. 2b and 3a). In a fast Fourier transformation (FFT) image, a vector pointing from (0000) to a diffraction spot represents...
the corresponding crystal direction in the imaging plane. Thus, the preferential faceting

directions in Fig. 2a can be determined as the six equivalent, close packed

<1120> directions, which are parallel to the six diagonals of a hexagonal projection onto

(0001) for etched tracks || c (Jonckheere and VandenHaute 1996; Paul and Fitzgerald

1992). In zircon, tracks along [001] appear to be approximately square in shape (Fig. 2c)

with the diagonals parallel to the four equivalent <100> directions, as this tendency can be

further confirmed in a low magnification image (Fig. 3b), which shows multiple square

tracks with the diagonals pointing in the same directions. Within the (001) plane, the

atomic density is highest along the <100> directions, similar to the case in the close packed

directions. Tracks along [100] of zircon appear to be elliptical with the long axis in the

<001> direction, which have the highest atomic density within the (100) plane (Fig. 2d). The ratio (1.106) of the long axes to the short axes (7.8 nm vs. 7.1 nm) in Fig. 2d

corresponds to the reciprocal ratio of the unit cell constants (a/c =1.105), as well as the

corresponding d spacings (d_{200}/d_{002}=1.105). This is similar to the case for GeS, where the

long axis of the elliptical tracks are parallel to the close packed <001> direction (Vetter et

al. 1994). Thus, the atomic-scale resolution reveals that the shape of tracks in apatite and

zircon depends on track orientation in the crystal as a result of preferential creation of

radiation damage along the directions with highest atomic density.

As the scale bar can be precisely calibrated by the known d spacings (Fig. 2), the mean

track radius can be measured reliably: 4.0 ± 0.2 nm for tracks || c vs. 3.9 ± 0.4 nm for tracks

⊥ c in apatite; 3.8 ± 0.4 nm for tracks || c vs. 3.7 ± 0.4 nm for tracks ⊥ c in zircon, which is

consistent with a previous HRTEM measured radius (~4 nm) for 2.9 GeV Pb ion induced
tracks \perp c of zircon (Bursill and Braunshausen 1990). The mean radius was determined by averaging the radii of approximately 5 tracks for each orientation (\parallel c or \perp c) in apatite and zircon. Within the errors, the HRTEM measured track radii are actually indistinguishable for the different orientations. However, the track shape changes significantly for the different orientations.

In addition to the images of tracks in transverse cross section, the structure and morphology of tracks can be viewed in longitudinal cross section, i.e., tracks are perpendicular to the electron beam by the under focus low magnification images (Fig. 4). For apatite, the average radius of tracks \parallel c and \perp c is 4.6 ± 0.4 nm and 4.6 ± 0.5 nm, respectively. For zircon, the average radius is 4.3 ± 0.4 nm \parallel c, close to 4.1 ± 0.5 nm for \perp c.

Ten tracks were measured for each orientation. Thus, the mean values of the track radii are insensitive to orientation, which is consistent with the HRTEM measurements.

As compared with the limited number of tracks in a localized area as observed by TEM, the strong scattering oscillations, as detected by SAXS from a very large number of well aligned, identical tracks in a bulk sample, provide an extremely reliable means for determining the mean track radius. The scattering intensities of tracks and corresponding analytical fits to the hard cylinder model (Afra et al. 2011; Li et al. 2013) are shown in Fig. 5. The GeV Au ions induce tracks \parallel c of apatite with a mean radius of 4.81 ± 0.03 nm, which is slightly larger than that (4.72 ± 0.03 nm) of tracks \perp c. In zircon, the mean track radius \parallel c is 4.43 ± 0.03 nm, slightly larger than that (4.32 ± 0.03 nm) of tracks \perp c. The SAXS
measurements are consistent with the TEM measurements in that the mean radii of tracks $|| c$ are very close to those of tracks $\perp c$.

80 MeV Xe Ions

In addition to the GeV ions, the influence of track orientation on track radius was investigated by TEM comparing the damage at each point along latent tracks created by 80 MeV Xe ions $|| c$ or $\perp c$ of apatite (Fig. 6). Using the microtome method (Li et al. 2012), the track profile was obtained by taking a series of images along the ion paths (Figs. 6a-6d). Three examples of under focus TEM images of tracks $\perp c$ measured at different depths ($x = 0$, $3$, and $6.7 \, \mu m$) from the ion-irradiated surface are shown in Figs. 6a-6c. Approximately 10 tracks were measured at each target depth. The changes of track radii along the ion paths $|| c$ and $\perp c$ in apatite are plotted in Fig. 6e. Within experimental error, the mean radii for tracks $\perp c$ are very close to the radii of tracks $|| c$ at almost all the depths. This provides direct evidence that latent ion tracks in apatite do not have different sized radii as a function of orientation, in constrast to the previous observation of significantly larger FTs $|| c$ than those $\perp c$ in apatite (Paul and Fitzgerald 1992). This discrepancy is due to the difficulty of determining the precise orientation of any individual track [of the total 293 randomly orientated FTs that were measured (Paul and Fitzgerald 1992)]. For complex materials (e.g., apatite) where different zones may have similar diffraction patterns, the incorrect indexing of the zone axis of a grain is possible. Furthermore, because it is impossible to determine the target depth of a randomly orientated FT by TEM, the decrease in radius along a FT, as clearly shown in Fig. 6, could not be considered, resulting in significantly larger errors.
For both track directions, the decrease in track radius per unit depth, \(-dR/dx\), is relatively low at shallower depths \((0 \leq x \leq 3.5 \, \mu m)\). The track radii at shallower depths (Figs. 6a and 6b) can be described by a relation of \(R \sim S_e^{1/2}\) (Fig. 6e), as this relation was applied to tracks in \(Y_3Fe_5O_{12}\). However, at greater depths \((x \geq 3.5 \, \mu m)\) (Fig. 6c), \(R\) falls below the curve of \(R \sim S_e^{1/2}\), as the \(-dR/dx\) is obviously higher than that at the shallower depths (Fig. 6e). The \(-dE/dx\) as a function of target depth \(x\) was simulated by the SRIM code (2012), and \(R\) was measured at different depths by TEM (Fig. 6e). Therefore, \(R\) as a function of \(-dE/dx\) for both directions can be obtained, and these values are plotted in Fig. 6f. These data were compared with the theoretical prediction from the thermal spike model of Szenes (1995).

Depending on the value of \(S_e\), the track radius \(R\) (the maximum radius of the melt during the heating-cooling process) can be determined by two different expressions (Szenes 1995). For \(S_e \geq 2.7S_{et}\), the melted zone expands and reaches its maximum,

\[
R^2 = [(a(0)^2/2.7)][S_e/S_{et}], \quad (1)
\]

where \(S_{et}\) is the threshold energy for the production of continuous tracks. \(a(0)\) relates to thermal diffusivities, but it can be determined by fitting. This expression is consistent with our analysis shown in Fig. 6e that \(R \sim S_e^{1/2}\) for tracks at shallower depths. For \(2.7 \geq S_e/S_{et} \geq 1\), the melted zone shrinks with time, and it has the maximum radius at \(t = 0\) when the cooling spike begins,

\[
R^2 = a(0)^2 \ln(S_e/S_{et}). \quad (2)
\]

This regime \((2.7 \geq S_e/S_{et} \geq 1)\) corresponds to tracks at greater depths where the values of \(S_e\) are smaller (Fig. 6c). There is a smooth transition from the logarithmic to linear regimes, as both Eqs. 1 and 2 provide the same \(R^2\) at \(S_e=2.7S_{et}\). In this study, the transition point is at \(x \sim 3.5 \, \mu m\) in Fig. 6e. Thus, the corresponding two parameters for the fits \((R = a(0) = 3.6 \, nm)\)
\( S_e = 2.7 S_{et} = 1065 \text{ eV/Å} \) can be directly determined from the transition point in Fig. 6e. As shown in Fig. 6f, all experimental data for 80 MeV Xe ions follow a single curve as a good approximation in both the logarithmic and linear regimes. The data for the 2.2 GeV Au induced tracks (measured from Figs. 4a-4b) are below the curve (Fig. 6f). This is due to the velocity effect (Meftah et al. 1993), which describes the decrease of track radius with the ion speed at certain high energy regimes.

**Remarks**

The hexagonal apatite has an open anion channel || \( c \) (Calderin et al. 2003). The exact details of how structural anisotropy affects anisotropic annealing behavior remain unclear, although there is certainly a connection between the two types of anisotropy (Gleadow et al. 2002; Green and Durrani 1977). As mentioned above, the slower annealing rate of tracks || \( c \) was attributed to the larger tracks || \( c \) (Paul and Fitzgerald 1992). Besides the weaker intermolecular bonds along the \( c \)-axis (Paul and Fitzgerald 1992), smaller dielectric constants || \( c \) were used to explain the larger tracks along this direction (Rabone et al. 2008). In this study, except for the orientation-related difference in track shape as discussed above, the detailed TEM and SAXS experimental evidence on parallel tracks with well-defined orientations in the structure clearly demonstrates that the track radii have no apparent dependence on track direction in apatite, which is in agreement with a previous molecular dynamics simulation (Rabone et al. 2008). Based on the direct observation of *in situ* thermal annealing of unetched FTs in apatite (Li et al. 2011), the annealing anisotropy as observed in chemically-etched tracks can be attributed to the preferential motion of FT
segments || c during annealing. Similarly, no obvious track radius anisotropy was detected in zircon by the TEM and SAXS measurements, although zircon is structurally anisotropic with a chain of alternating edge-sharing SiO\textsubscript{4} tetrahedra and ZrO\textsubscript{8} triangular dodecahedra extending || c (Robinson et al. 1971).

Currently, FT thermochronology is based almost entirely on empirical fits to annealing data of FTs revealed by chemical etching. One of the main obstacles to quantitative modeling of FT behavior has been the need to investigate the morphology of latent tracks as a function of temperature and time. For a single track created by a fission fragment pair, the radius is largest near the midpoint of track where the fission event occurs, and decreases toward each end as the $S_e$ decreases, as shown in Fig. 1. At elevated temperatures, the etchable track length is gradually reduced from each end of a FT towards the midpoint because the track ends have much smaller radii, and anneal much more rapidly, which was observed by in situ TEM (Li et al. 2012). As a result, only the sections with smaller $S_e$ (as well as R) near each end of the FT make a major contribution for the length measurements of etched tracks and mathematical fitting [see Ref. (Li et al. 2012) for details]. Therefore, the description of the two different regimes with a single curve, especially the description of the regime with smaller $S_e$ by a simple logarithmic equation (i.e., Eq. 2), provides an important physical form that has long been recognized as needed (Carlson 1990; Gleadow et al. 2002; Jonckheere and Chadderton 2002) for the development of physical models of FT formation and annealing. Besides the precise picture of morphologies of FTs, as demonstrated in this study, the combination of ion-irradiation with TEM and SAXS can be readily used in order to obtain a deeper understanding of the gradual recovery of radiation damage during annealing at the atomic-scale.
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References cited


Figure Captions

Figure 1. The electronic energy loss per unit length, \(-dE/dx\) = \(S_e\), as a function of target depth, \(x\), for the irradiations of 2.2 GeV Au ions in zircon, 2.2 GeV Au ions in apatite, and 80 MeV Xe ions in apatite, respectively.

Figure 2. Transverse cross section HRTEM images of tracks induced by exposure to 2.2 GeV Au ions || \(c\) or \(\perp c\) of apatite and zircon. The track orientation (or the zone axis of the target material) was determined by indexing the inset of fast Fourier transform image for each figure.

Figure 3. Conventional transverse cross section TEM images (under focus and bright-field) show multiple tracks in (a) apatite and (b) zircon. The areal densities of the 2.2 GeV Au ions induced tracks for both materials are consistent well within the nominal ion density (5\(\times\)10\(^{10}\) ions/cm\(^2\)). The track orientation (or the zone axis of the target material) was determined by indexing the inset of diffraction pattern for each figure. A track in b marked with the white arrows and square as a guide to the eye, is a representative of multiple square tracks with diagonals pointing in the <100> directions.

Figure 4. Conventional TEM images (under focus and bright-field) show tracks (viewed in longitudinal cross section) induced by exposure to 2.2 GeV Au ions || \(c\) or \(\perp c\) of apatite or zircon, as marked in each image.

Figure 5. SAXS measurements showing scattering intensities of 2.2 GeV Au ion induced tracks || \(c\) or \(\perp c\) of apatite and zircon as a function of the scattering vector \(q\), and corresponding fits with the hard cylinder model (solid lines). The errors of track radii correspond to the uncertainty of the fitting.
**Figure 6.** A comparison of variations in radius at each point along the tracks induced by the irradiation of 80 MeV Xe ions $\parallel c$ and $\perp c$ of apatite. (a) to (c) show three examples of conventional TEM images (under focus and bright-field) of tracks $\perp c$, taken at different depths from the ion irradiated surface along the whole length of a microtome section, as marked in a lower magnification image (d) A thin layer of gold was deposited on the irradiated surface as a surface marker. (e) Mean track radii, $R$, almost overlap along the tracks of the two directions. $R \sim S_c^{1/2}$ at smaller target depths. (f) Variations in track radius versus $S_c$ normalized to the threshold value of $S_{ct}$ can be understood in terms of the Szenes Model.
Fig. 1
Fig. 2
Fig. 3
Fig. 5

Scattering Intensity (a.u.)

- Apatite, $\parallel c$
- Apatite, $\perp c$
- Zircon, $\parallel c$
- Zircon, $\perp c$

- $R = 4.81 \pm 0.03$ nm
- $4.72 \pm 0.03$ nm
- $4.43 \pm 0.03$ nm
- $4.32 \pm 0.03$ nm

$q$ (Å$^{-1}$)
Fig. 6