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Composition dependent thermal annealing behaviour of ion tracks in apatite

A. Nadzri [a,*], D. Schauries [a], P. Mota-Santiago [a], S. Muradoglu [a], C. Trautmann [b,c], A.J.W. Gleadow [d], A. Hawley [e], P. Kluth [a]

[a] Department of Electronic Materials Engineering, Research School of Physics and Engineering, Australian National University, Canberra, ACT 2601, Australia
[b] GSI Helmholtz Centre for Heavy Ion Research, Planckstrasse 1, 64291 Darmstadt, Germany
[c] Technische Universität Darmstadt, 64287 Darmstadt, Germany
[d] School of Earth Science, University of Melbourne, Melbourne, VIC 3010, Australia
[e] Australian Synchrotron, 800 Blackburn Road, Clayton, VIC 3168, Australia

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ABSTRACT

Natural apatite samples with different F/Cl content from a variety of geological locations (Durango, Mexico; Mud Tank, Australia; and Snarum, Norway) were irradiated with swift heavy ions to simulate fission tracks. The annealing kinetics of the resulting ion tracks was investigated using synchrotron-based small-angle X-ray scattering (SAXS) combined with *ex situ* annealing. The activation energies for track recrystallization were extracted and consistent with previous studies using track-etching, tracks in the chlorine-rich Snarum apatite are more resistant to annealing than in the other compositions.

1. Introduction

Minerals such as apatite often contain trace amounts of radioactive ^{238}U. Spontaneous fission of these U impurities can produce two highly charged fission fragments [1]. The radioactive decay releases energies around 170 MeV that is split between a heavy and a light fragment of about 100 and 70 MeV, respectively [2,3]. Due to the high energy of the fragments they penetrate the crystalline material interacting with it predominantly through inelastic interactions with the material electronic system [1,3]. Coupling of this energy into the atomic system leads to the formation of amorphous cylinder-like damage trails the so-called 'fission track'. These tracks are typically a few nanometres wide and about 10 μm long. Upon exposure to elevated temperatures, these tracks are known to shrink in size as a consequence of the gradual recovery of the crystalline structure [4,5].

Fission tracks are used to determine the age of archaeological and geological samples as well as their thermal history by studying the number and length distribution of chemically etched tracks [3,6]. The specific chemical etchant used preferentially attacks the damaged region, enlarging the track diameter to allow imaging them by optical microscopy. Etching however removes the material inside the ion tracks as well as inside other local damaged zones that may exist in the mineral, erasing all information about the primary track damage and its dependence on the geological and material parameters [1].

In this work, tracks of comparable diameter were created by irradiation with swift heavy ions to simulate fission track damage. Controlled irradiation leads to the formation of parallel identical tracks. This enables accurate characterisation of the 'latent' un-etched tracks by synchrotron-based small angle X-ray scattering (SAXS). We have previously demonstrated that SAXS is a powerful, non-intrusive method to analyse the morphology and annealing behaviour of un-etched ion tracks [4,5,7–9].

Studies using chemical etching show that the annealing behaviour of fission tracks in apatite is dependent on the halide ratio and apatites richer in fluorine annealed faster than those richer in chlorine [10–14]. We now investigate the effects of thermal annealing on latent tracks in apatite from different geological locations with different halide composition. We study the reduction in track radii upon partial annealing of the ion tracks. This is an important step for determining the correlation between the primary damage in the mineral and relevant geological parameters.

* Corresponding author.
E-mail address: allina.nadzri@anu.edu.au (A. Nadzri).

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2. Experimental techniques

2.1. Sample preparation and irradiation

This study was carried out using natural apatite samples from three different regions with different halogen composition. Apatite is a mineral group with the chemical formula of $Ca_5(PO_4)_3X$ with X representing the halide composition such as F (fluorapatite), OH (hydroxyapatite) or Cl (chlorapatite) [15]. Apatite is anisotropic, with an hexagonal lattice structure of $P6_3/m$ [16]. Table 1 lists the locality and the Cl and F contents for the three apatite samples used in this study, based on electron microprobe and wet chemical analyses.

The samples were pre-annealed at 450 °C for 24 h to remove all natural tracks present in the apatite crystals. Thin slices of the crystal were then prepared by cutting and polishing to thickness between 80–120 μm to minimise X-ray absorption during the SAXS measurements. Subsequently, samples were irradiated at the UNILAC accelerator at the GSI Helmholtz Centre in Darmstadt, Germany using 2.3 GeV Bi ions at room temperature. Samples were irradiated with the ion beam normal to the polished surface.

As estimated by SRIM-2010 [19], the projected ion range is roughly 78 μm and the electronic energy loss dE/dx on the sample surface is 29.1 keV/nm for apatite, independent of halide composition. This value is of comparable magnitude as natural fission fragments (100 MeV) where the dE/dx is approximately 15 keV/nm. In order to minimise track overlap, an irradiation fluence of 1×10^{11} ions/cm^2 was used. For this value, less than 5% of the surface is covered with ion tracks with negligible overlap [8].

2.2. SAXS measurement

For characterisation of the ion tracks, transmission SAXS measurements were performed at the SAXS/WAXS beamline at the Australian Synchrotron in Melbourne, Australia. The experiments were carried out with an X-ray energy of 11 keV and a sample-detector distance of approximately 1.6 m. Measurements were taken with exposure times of 1, 2, 5 and 10 s, producing images with sufficient intensity for accurate data analysis. Different exposure times were used to ensure that measurements were well within the linear regime of the detector. The tracks were tilted by 10° with respect to the X-ray beam using a three-axis goniometer.

To study the recovery kinetics of the ion tracks in apatite, *ex situ* annealing was performed in a conventional furnace under ambient atmosphere. Samples were annealed at temperatures between 200 and 410 °C with an initial increment of 50 °C that was later reduced to 20 °C to better resolve reductions in track radii near the closure temperature. Samples were annealed for 30 min at each temperature and SAXS measurements were recorded between annealing steps at room temperature. An unirradiated sample was measured for background removal.

3. Results and discussion

Fig. 1 shows selected SAXS detector images for the three apatite samples before and after annealing at 310 °C and 390 °C. Before annealing, all samples display a strong scattering signal from the tracks concentrated in the oscillating narrow bent streaks. These streaks result from the high aspect ratio of the aligned, tilted ion tracks and contain information about their radial density [3,4,8]. At 390 °C the scattering signal from the tracks is significantly reduced in intensity and the oscillations in the streak intensity 'washed out' for all three apatite compositions, indicating a partial recovery of the crystalline structure.

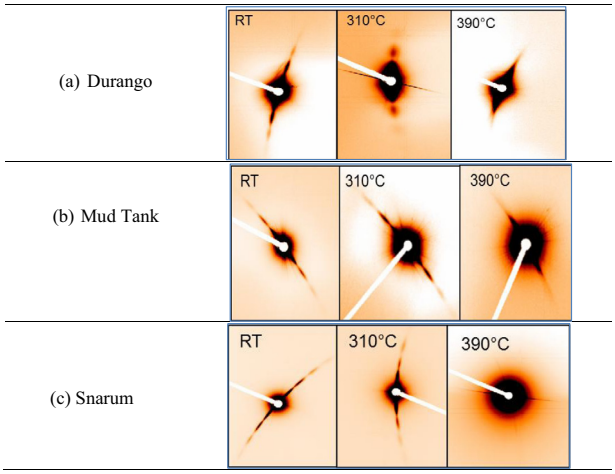

Fig. 1. Selected SAXS detector images of ion tracks in apatite from (a) Durango, Mexico (b) Mud Tank, Australia, and (c) Snarum, Norway. The images are shown for tracks before annealing (left column), and after annealing at 310 °C (middle column) and 390 °C (right column).

The scattering intensities as a function of the scattering vector q from the SAXS images observed are shown in Fig. 2(a–c) for all annealing temperatures. The oscillations in the scattering intensities suggest monodisperse radii and sharp boundaries between the track and matrix material, consistent with amorphous tracks [4]. All compositions display a shift of the first minimum to higher q with increasing annealing temperature. This indicates a reduction in the track radius. At higher temperatures, the oscillations become noticeable washed out for most samples. To best describe the experimental results, a simple cylinder model is used [4]. The model assumes parallel almost identical tracks [5]. A narrow Gaussian distribution of track radii is used to account for deviations from this idealistic model. The fits to this model are represented by the solid lines in Fig. 2. The width of the Gaussian distribution (polydispersity) is increasing from approximately 5% of the ion track radius at room temperature to ~10% at higher temperatures for all apatite compositions. The observed increase in the polydispersity can possibly be related to a softening of the track boundaries due to diffusion processes during recrystallization.

Fig. 2(a) shows the SAXS patterns for ion tracks in Durango apatite. As mentioned before, at room temperature, the sample shows strong scattering from tracks with clear oscillations. Traces of the tracks remain evident for temperatures above 390 °C, however the extraction of useful data becomes difficult due to the low scattering intensity and the absence of oscillations. Similar to Durango apatite, Fig. 2(b) and (c) show the SAXS patterns for Mud Tank and Snarum apatite, respectively, for each annealing step. For the latter, slight deviations of the model fits and the data are apparent, that may be caused by deviations from the simple cylindrical model for this apatite composition. While we are currently investigating other suitable models, the relative changes in the track radii are unlikely to be influenced by the model choice.

Fig. 3 shows the ion track radii as a function of the annealing temperature for all three compositions studied. Durango apatite shows the highest track radius (5.5 nm) at room temperature

Table 1
Geographical origin and halide composition of the studied apatite samples.

Apatite name	Locality	F (wt.%)	Cl (wt.%)
Durango	Durango, Mexico	3.40–3.53 [17,18]	0.43
Mud Tank	Mud Tank Mine, NT, Australia	2.93	0.040
Snarum	Snarum, Norway	1.01	2.49