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Composition and orientation dependent annealing of ion tracks in apatite - Implications for fission track thermochronology

A. Nadzri [a], D. Schauries [a], P. Mota-Santiago [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 Helmholtzzentrum, 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

The annealing behaviour of swift heavy-ion tracks in apatite from different origins is studied as a function of their crystallographic orientation and the mineral composition. The tracks were generated by irradiating the apatite samples with 2.3 GeV Bi ions, which have a comparable rate of energy loss to fission tracks in this mineral. The track radius was investigated using synchrotron-based small-angle x-ray scattering (SAXS) combined with *ex situ* annealing. Results indicate that tracks parallel to the c-axis are initially larger and anneal slower than those perpendicular to the c-axis. Natural variation in the mineral composition shows stronger annealing resistance of ion tracks with higher chlorine content. The SAXS results are consistent with previous studies on etched tracks and provide evidence that the orientation and composition effects are directly linked to the property of the un-etched track and not to preferential etchability. The study helps to connect the empirical studies on etched fission tracks to more fundamental solid-state processes.

1. Introduction

Price and Walker (1963) first discovered that the damage zone created by the passage of a fission fragment can be enlarged by suitable chemical etching such that it is visible in an optical microscope. In nature these damage zones, also called 'fission tracks', are formed in minerals such as apatite as a result of the passage of high energetic nuclear fragments generated by spontaneous fission of uranium impurities. The energy released of around 170 MeV is split between a heavy and a light particle with energies of about 70 and 100 MeV, respectively. Using statistical analysis of etched tracks, the geological age of a given sample can be determined by measuring the areal density of surface-intersecting tracks accumulated over time (Gleadow et al., 2002; Wagner and Van den Haute, 1992) and the track-length distribution yields information on its thermal history (Gallagher et al., 1998; Gleadow et al., 2002; Tagami and O'Sullivan, 2005). A detailed understanding of the damage of un-etched tracks in minerals (often denoted as "latent tracks") and its dependence on geologically relevant conditions is of fundamental importance for the application of etched tracks in thermochronology (Fleischer, 2004; Gallagher et al., 1998), but so far the relationship between etched and un-etched track behaviour has received only limited attention.

The same processes that are responsible for the formation of fission tracks are operational when heavy ions with kinetic energies in the MeV to GeV range pass through a solid. Such ions can cause permanent material modifications in small volumes surrounding the virtually straight ion paths in many materials, so called 'ion tracks'. These often cylindrical ion tracks are only a few nanometres wide and, depending on the energy, several tens of micrometres long, thus showing extremely large aspect ratios exceeding 1000:1 (Fleischer et al., 1975). Ions with sufficient energies to produce tracks can be generated in large ion accelerator facilities with precise control over ion species, energy and fluence (number of ions per unit area) and are thus very well suited to simulate fission tracks under controlled conditions.

Un-etched tracks consist of highly disordered (often amorphous) material and are known to shrink over time when exposed to elevated temperatures (Fleischer et al., 1965). The crystal lattice undergoes a process of self-repair or recrystallization, whereby displaced atoms are able to be restored to their original positions. The extent of damage recovery depends on the temperature and time. The same degree of annealing can be obtained by heating a sample to a high temperature for a short time or to a low temperature for a long time. For example, apatite will lose all of its tracks in 1 h at approximately 350–400 °C, whereas it will take over a million years (~10^6 years) to achieve the same effect if the sample is held at ~100 °C (Naeser and Faul, 1969). This is important as laboratory based experiments require reasonable time scales but need to be extrapolated to geological time scales to assess the impact

* Corresponding author.
E-mail address: patrick.kluth@anu.edu.au (P. Kluth).

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of the temperature on fission track thermochronology. On geological time scales, fission tracks in apatite are sensitive to comparatively low temperatures so that the maximum temperature at which fission tracks are useful for thermochronology over geological time scales for apatite varies around 110 °C depending on the mineral composition. The current models used in fission track thermochronology predict annealing temperatures from earth-surface temperatures to 110 °C, in the so called 'partial annealing zone' to ~ ±10 °C on time-scales between 10^6–10^8 years (Lisker et al., 2009; Wagner and Van den Haute, 1992)

The majority of the studies conducted on annealing of induced fission tracks in apatite are performed by means of chemical etching (Carlson et al., 1999; Crowley et al., 1991; Donelick, 1991; Donelick et al., 1999; Green et al., 1986; Ravenhurst et al., 2003) where the average lengths of etched confined tracks are investigated. It has been demonstrated that fission track annealing in apatite shows different behaviour depending on the chemical composition of the mineral but also on the crystallographic orientation of the tracks (Crowley et al., 1990; Donelick, 1991; Donelick et al., 1999; Gleadow et al., 2002; Ketcham, 2003; Sandhu et al., 1987). In particular, slower annealing rates were attributed to higher chlorine content (Barbarand et al., 2003a; Carlson et al., 1999; Crowley et al., 1991; Gleadow and Duddy, 1981; Green et al., 1986). The earliest study that observed this effect was Gleadow and Duddy (1981) using apatite from deep wells in the Otway Basin. They attributed the variability in the annealing rate to compositional differences. With regard to track orientation, Green and later Donelick found that the length of fission tracks decreases with increasing azimuth angle between the track and the c-axis measured in the prism plane of (hexagonal) apatite. Tracks parallel to the c-axis are thus longest and perpendicular to the c-axis shortest (Green et al., 1986; Donelick, 1991).

In this work, swift heavy-ion tracks in apatite were investigated regarding their thermal stability. Parallel, identical tracks were produced by using collimated ion beams of well-defined energy. This enables accurate characterisation of the track morphology and damage recovery by synchrotron-based small-angle x-ray scattering (SAXS). SAXS measures the x-ray scattering of a sample into small angles, which results from fluctuations in the electron density on nanometre to micrometre length scales. The electron density is directly related to the mass density and as such the scattering can be used to obtain information on the size, shape and spatial arrangement of ensembles of objects on these length scales as long as there is a difference in mass density. In the following we refer to the 'density' as the mass density. SAXS has been explored for the study of nuclear track already more than three decades ago (for example see Albrecht et al., 1985 and Dartyge et al., 1981). Compared to transmission electron microscopy (TEM), where direct imaging of the damaged zones is possible, SAXS requires a model assumption for the density distribution in the scattering object, or in relation to the work here for the track morphology. When using ions with energies exceeding hundreds of MeV, the energy loss does not vary significantly over most of the length of the tracks. Thus, for continuous ion tracks in most materials a cylinder model has been found to be appropriate (Eyal and Saleh, 2007; Zhang et al., 2015). The simplest of these models consists of a cylinder with constant density different to that of the surrounding undamaged material. This has been found to describe tracks in apatite and quartz particularly well and is consistent with the formation of amorphous material in the tracks (Afra et al., 2011, 2013). The amorphous material usually has a lower density than the crystalline state with abrupt boundaries to the crystalline matrix. The expansion of the material related to the different density in the tracks may lead to strain fields around the tracks such as in the case for quartz which can often not be resolved by SAXS (Afra et al., 2014b). The track radius obtained by SAXS is the radius of the cylinder in which the density is changed and is a measure of the volume weighted average track radius over the entire length of the tracks. While TEM can provide more detailed information about the structure of short sections of individual ion tracks using SAXS it is possible to measure track radii in minerals with extremely high precision given the results provide an average over ~10^6 tracks (Afra et al., 2011). For the amorphous tracks, the radii obtained by SAXS are in excellent agreement with those from TEM yet due to the large number of tracks measured it provides better statistics and thus much smaller uncertainties (Li et al., 2014; Afra et al., 2011). SAXS is a non-intrusive method that does not require elaborate sample preparation. We have previously demonstrated that it is well suited to analyse the morphology and annealing behaviour of unetched ion tracks in a variety of materials, including minerals such as apatite and olivine, synthetic quartz and amorphous SiO_2 (Afra et al., 2012, 2014a, 2014b, Kluth et al., 2008a, Schauries et al., 2015a, 2015b).

Here, we investigate the effects of the crystallographic orientation of the tracks and the chemical composition of the mineral on the track radius and the thermal annealing behaviour of un-etched tracks in apatite. We found that the track radius is sensitive to the orientation of the tracks and tracks parallel to the c-axis anneal slower than tracks perpendicular to the c-axis. We also observed that tracks in fluorine rich (F-rich) apatite anneal faster than in chlorine-rich (Cl-rich) samples. In contrast to the ion tracks studied in this work, fission tracks vary in their radius along the track axis and start to shorten at their ends upon annealing where the radius is smallest. This, however, suggests that the track radius and its variation upon annealing is of fundamental importance for the annealing behaviour of fission tracks the study of which is the main contribution of the present work to the topic.

2. Experimental techniques

2.1. Sample preparation and irradiation

Natural apatite samples from Durango, Mexico (DA), Otter Lake, Canada (OLA), Dashkesan, Azerbaijan (DKA), Mud Tank, Australia (MT), and Snarum, Norway (SC), were used for this study. Apatite refers to a group of minerals with the general chemical formula of $Ca_5(PO_4)_3$(F, Cl, OH). It is a common mineral found mostly as an accessory phase in a wide variety of geological settings. Fluorapatite has a hexagonal lattice structure of space group $P6_3/m$ while hydroxyapatite and chlorapatite can have either a hexagonal or monoclinic structure depending on the nature of the order/disorder of $(OH)^-$ and $(Cl)^-$ ions along the c-axis (Wu et al., 2004). The F and Cl contents of the five apatite samples determined by electron microprobe analysis (EMPA) are listed in Table 1. Partial analyses were carried out on major elements plus F and Cl using an accelerating voltage of 15 kV, a beam current of 35 nA, a spot size of 8 μm and counting time of 10 s to minimise problems of F migration. Other trace elements, such as Sr and Mn, that might also influence fission track annealing in apatite (e.g. Barbarand et al., 2003a), were not measured as the importance of these is considered secondary to the dominant influence of the halogen anions.

DA, OLA and DKA were cut along two crystallographic orientations yielding samples with the surface normal perpendicular (⊥) and parallel (∥) to the c-axis. For MT and SC, they were cut in random orientations, as no well-defined crystal forms were available. The samples were then polished to thicknesses between 60–80 μm to minimise x-ray absorption and parasitic scattering from the substrate during the SAXS measurements.

Subsequently, samples were irradiated at room temperature with 2.3 GeV Bi ions normal to the polished surface at the UNILAC accelerator at the GSI Helmholtzzentrum in Darmstadt, Germany. An ion fluence of 1×10^{11} ions/cm^2 was applied in order to minimise the amount of track overlap yet yield sufficient statistics for the measurements. According to the overlap model described in Riedel and Spohr (1979) the area of track-covered, i.e. modified, material per unit area is $d = 1 - \exp(-\pi R^2 n)$, where R is the track radius and n is the ion fluence. The fraction of overlapping track cross-sections with respect to d is then given by $(\pi R^2 n - d)/(\pi R^2 n)$. Assuming a track radius of 5.6 nm there is <5% overlap at a fluence of 1×10^{11} ions/cm^2. The