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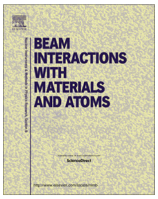

BEAM INTERACTIONS WITH MATERIALS AND ATOMS

Annealing behaviour of ion tracks in olivine, apatite and britholite

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ABSTRACT

Ion tracks were created in olivine from San Carlos, Arizona (95% Mg_2SiO_4), apatite ($Ca_5(PO4)_3(F,Cl,O)$) from Durango, Mexico, and synthetic silicates with the apatite structure: $Nd_8Sr_2(SiO_4)_6O_2$ and $Nd_8Ca_2(SiO_4)_6O_2$ using 1.6 and 2.2 GeV Au ions. The morphology and annealing behaviour of the tracks were investigated by means of synchrotron based small angle X-ray scattering in combination with *ex situ* annealing. Tracks in olivine annealed above ~400 °C undergo a significant change in track radius due to recrystallisation of the damage tracks. At temperatures higher than 620 °C, the scattering images indicate fragmentation of the track cylinders into smaller subsections. Ion tracks were annealed at elevated temperatures up to 400 °C in the Durango and Ca-britholite, and up to 560 °C in Sr-britholite. While there was a significant change in the track radii in the Durango apatite, tracks in the two synthetic samples remained almost unchanged.

1. Introduction

When heavy ions with energies in the range of tens of MeV to GeV penetrate a solid, they lose their energy predominantly through inelastic interactions with the electrons of the target material and leave a narrow, cylindrical trail of damage called an ion track [1,2]. Ion tracks are typically a few nanometers in diameter and can be up to tens of micrometers long. When these tracks are annealed, they shrink in size until eventually the damaged material recovers.

Ion tracks in olivine provide a record of cosmic rays that have passed through the minerals in meteorites [3]. Chondritic meteorites typically contain olivine ($(Fe,Mg)SiO_4$), which is susceptible to ion track formation from high energetic cosmic particles. Information on the annealing behaviour of ion tracks in olivine can be used to estimate the temperature before and after track formation. Previous investigations of the annealing behaviour of irradiation damage in olivine have been mainly conducted to investigate the charge spectrum of ancient cosmic rays [4,5]. Discrepancies in results on the variation of the track etch velocity with the primary ionization rate or the variation of etchable track length with the atomic number of the incident ion has been attributed to partial annealing of the cosmic ray tracks over time-scales of 10^7 years [6–9].

In apatite, track formation results from the spontaneous fission of naturally incorporated traces of uranium. Etched tracks of fission fragments are used for dating and constraining the thermal history of geological samples [10–13]. Likewise, fission tracks have been observed from spontaneous fission of ^{244}Cm in $Nd_8Ca_2(SiO_4)_6O_2$, a potential host phase for immobilization of minor actinides [14]. Since the discovery of fission tracks, considerable research effort has focused on investigating the annealing behaviour of natural and induced tracks in minerals with a wide range of beam energies [11,12,15,16]. Studies of etched tracks have shown that the annealing rates depend on the chemical composition of the apatite [17–20].

Recently, we have shown that small angle X-ray scattering (SAXS) is capable of resolving radii of un-etched (latent) tracks with high precision and is well suited to study their recovery kinetics using *in situ* and *ex situ* annealing experiments [21,22]. Preliminary SAXS measurements of ion tracks in the San Carlos olivine combined with *in situ* annealing revealed that their track morphology is very similar to that of natural apatite with

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approximately the same density change of 1% within the tracks compared to the matrix [21,22]. However, unlike in apatite, tracks in olivine do not show any substantial change after annealing at 350 °C for approximately 6 h [21].

In this work, we combined synchrotron based SAXS with *ex situ* annealing in order to study the annealing behaviour of unetched swift heavy ion tracks in two minerals: San Carlos olivine and Durango apatite, as well as two synthetic silicates with apatite structure, $Nd_8Sr_2(SiO_4)_6O_2$ and $Nd_8Ca_2(SiO_4)_6O_2$. The synthetic silicates (britholite) allow for the systematic study of the effect of composition on track annealing behaviour as well as their potential use for nuclear waste immobilization [23–25]. Tracks are generated with ion energies in the range of GeV, as the focus of this report is to elucidate differences in annealing behaviour and compare the effects of different composition and material structure. While these energies may be different to those of fission tracks and cosmic rays, the energy loss mechanisms (electronic) are the same and thus the damage structure can be expected to be similar.

2. Experiment

Olivine (95% Mg_2SiO_4) from San Carlos, Arizona, apatite ($Ca_5(PO4)_3(F,Cl,O)$) from Durango, Mexico and synthetic apatites: $Nd_8Sr_2(SiO_4)_6O_2$ and $Nd_8Ca_2(SiO_4)_6O_2$ were polished to thicknesses of 40–60 μm and irradiated with ^{197}Au ions to a fluence of 5×10^{10} ions/cm^2 at the UNILAC accelerator at the GSI Helmholtz Centre in Germany. The low irradiation fluence yields well-separated tracks. The olivine was irradiated with a beam energy of 2.2 GeV while the apatite samples were irradiated with 1.6 GeV ions. In both minerals the projected ion range exceeds the sample thickness as estimated by the SRIM-2008 [26]. Irradiations were performed at room temperature under normal incidence. The olivine and the natural apatite were annealed at 450 °C for 24 h before irradiation to remove any natural tracks pre-existing in the minerals. Sample specifications and irradiation parameters are listed in Table 1.

Transmission SAXS measurements were performed at the SAXS/WAXS beam line of the Australian Synchrotron with X-ray energies of 12 and 20 keV and camera lengths of approximately 1600 and 2000 mm for measuring ion tracks in olivine and the apatites, respectively. Samples were mounted on a three-axis goniometer and tilted such that the axis of the tracks had an angle between 5° and 10° to the incoming X-ray beam. The spectra were collected with a Pilatus 1 M detector with exposure times of 5 and 10 s for the X-ray energy of 12 keV and 20 and 30 s for 20 keV, the latter in order to compensate the lower flux delivered at higher energies. Scattering from un-irradiated samples was measured as a reference for background removal.

In order to study the annealing behaviour of the ion tracks, the irradiated samples were annealed *ex situ* in a conventional furnace under ambient atmosphere. The furnace was heated to the desired temperature and the sample was then inserted. During the insertion, the temperature of the furnace only dropped by a maximum of ~50 °C and equilibrated in less than a minute. After each 30 min annealing step, SAXS measurements were performed. Each given sample was sequentially annealed from room temperature up to a maximum of 950 °C for the San Carlos olivine, 560 °C for Sr-britholite, and 400 °C for Ca-britholite and Durango apatite. A second Durango apatite was annealed only at 380 and 400 °C in order to investigate the effect of thermal history on the annealing behaviour of tracks. Additionally an unirradiated San Carlos olivine was annealed at 1050 °C and measured for comparison.

3. Results and discussion

3.1. Tracks in olivine

SAXS images from ion tracks in olivine at room temperature and after annealing are shown in Fig. 1(1–6). The tracks are tilted by ~10° with respect to the X-ray beam. The anisotropy in the scattering signal is caused by the high aspect ratio of the tracks that are only a few nanometers in diameter and up to tens of micrometers in length. The presence of strong oscillations in the un-annealed sample is consistent with monodisperse track radii and a sharp density change between the track and the matrix material. With increasing annealing temperature, the spacing of the oscillations gets larger as compared with the room temperature image; thus, the track is expected to be reduced in radius [22]. The image at 650 °C reveals the appearance of a new feature in the scattering signal in the form of a "bulging" of the scattering signal. This effect starts at ~620 °C, increases in size with increasing annealing temperature, and is most likely a consequence of fragmentation of the tracks. Fragmentation into smaller subsections of various lengths can occur due to Rayleigh instabilities of the narrow, initially cylindrical tracks [29,30]. These fragments naturally reduce the aspect ratios of the now separated track features, washing out the oscillations and resulting in scattering contributions normal to the originally confined streaks. Additionally, at such high temperatures oxidation of the olivine that occurs in air above 600 °C [31] may also affect the track structure and the observed scattering signal. While we cannot quantify the contribution of oxidation or separate this effect from the scattering signals of the tracks, we have annealed an unirradiated olivine sample at 1050 °C for 30 min and the SAXS image from this sample also shows an anisotropic scattering signal as shown in Fig. 1(7), which further complicates the SAXS analysis at these temperatures and needs to be investigated in the future.

For SAXS data analysis below 530 °C, the scattering intensities are extracted by masking and radially integrating the intensity from the streaks of the anisotropic images. The X-ray scattering intensities of radial sectors perpendicular to the streaks (e.g. small arc sectors in the area between the two streaks that do not overlap with either of the streaks) are used as the background intensity as

Table 1
Sample specifications and irradiation parameters including the surface and average electronic energy loss calculated using SRIM-2008. The average energy loss gives the mean energy loss over the length of the sample or the projected range of the ion, whichever is smaller. We note that SRIM calculations include at least 10% uncertainty. Track radius is from SAXS measurements.

Material	Density (g/cm^3)	Sample thickness (μm)	Au ions energy (GeV)	Fluence (ions/cm^2)	Ion beam projected range (μm)	Surface energy loss (keV/nm)	Average energy loss (keV/nm)	Track radius (nm) at room temperature
San Carlos olivine (95% Mg_2SiO_4)	3.32	40	2.2	5×10^{10}	90	26.2	30.3	4.6 ± 0.1
Durango apatite ($Ca_5(PO4)_3(F,Cl,O)$)	3.19	50	1.6	5×10^{10}	63	28.8	29	5.1 ± 0.1
Synthetic britholite $Nd_8Sr_2(SiO_4)_6O_2$	5.62 [27]	60	1.6	5×10^{10}	53	36.8	29	5.5 ± 0.2
Synthetic britholite $Nd_8Ca_2(SiO_4)_6O_2$	5.47 [28]	60	1.6	5×10^{10}	54	36.5	29	5.1 ± 0.1