Chemical Geology 404 (2015) 52–61

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

The densities and dimensions of recoil-track etch pits in mica

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ARTICLE INFO

Article history:
Received 2 July 2014
Received in revised form 17 March 2015
Accepted 23 March 2015
Available online 2 April 2015

Editor: K. Mezger

Keywords:
Track etching
Recoil track
Fission track
Ion track
Phlogopite
Recoil-track dating

ABSTRACT

Measurements of alpha-recoil-track densities in mica as a basis for geological dating depend on an etch model relating the number of tracks per unit volume (N_{RT}) to the counted number of etched tracks per unit area (ρ_{RT}). The model of Gögen and Wagner (2000) implies that ρ_{RT} increases linearly with etch time (t_E), so that N_{RT} can be calculated from the slopes or intercepts of step-etch functions $\rho_{RT}(t_E)$. This model rests on the assumption that the etch rate of the mica surface (v_V) and the horizontal etch pit growth rate (v_H) are both constant, in contradiction with experimental results and computer simulations of mineral dissolution. We present results of four different experiments aimed at relating etch pit densities to volumetric track densities. Step-etch data are vulnerable to observation-related artefacts at increasing t_E and lack the resolution to confirm or refute the supposed linear increase of ρ_{RT} with t_E. The intercepts of regression lines fitted to step-etch data are imprecise and perhaps inaccurate. Intercept estimates based on mirror-image counts and (etch)–anneal–etch experiments indicate that v_V increases during the initial etching stages. The (etch)–anneal–etch results show that no pre-etch is in fact required, implying that surface tracks are more resistant to annealing than tracks in the bulk of the mineral. Track-size measurements confirm that v_H is also not constant but decreases with increasing etch-pit size. The results show that no recoil-track etch pit in phlogopite etched in 40% HF grows larger than ca. 7 μm and that the track-size distribution becomes quasi-invariant at >6 min etching. This signifies that there exist accessible etching conditions at which the etch-pit size distribution becomes a fixed, distorted reflection of the size distribution of latent recoil tracks. It is not improbable that track addition and loss also cancel each other out in this equilibrium state, in which case both the etch-pit size distributions and densities ρ_{RT} become independent of etch time.

1. Introduction

Natural crystals incur various forms of metastable damage to their atomic lattice and electron shells from the disintegration of radioactive constituents. The accumulated damage can serve as a measure of the time elapsed since they last experienced conditions at which the damage repair rate exceeded its production rate. This is the basis of radiation-damage methods (luminescence, electron spin resonance, fission-track) used for archaeological, geographical, and geological dating. It is perhaps surprising that recoil tracks resulting from alpha disintegration are not yet used for dating. Alpha recoils are the main contributors to the lattice damage in high-actinide minerals and the dominant factor in their metamictization. Moreover, etching of mica cleavage planes reveals discrete recoil-track etch pits that can be counted with an optical microscope (Huang and Walker, 1967; Huang et al., 1967; Fig. 1). The fact that recoil-track production is ~2 10^6 times faster than that of fission tracks ($^{238}\lambda_\alpha = 1.55\ 10^{-10}\ a^{-1}$; $^{238}\lambda_f = 8.5\ 10^{-17}\ a^{-1}$) is an advantage for dating young and low-actinide samples.

Experiments on muscovite (Katcoff, 1969; Garrison et al., 1978; Wolfman and Rolniak, 1978; Hashemi-Nezhad et al., 1979; Hashimoto et al., 1980a, b), biotite (Gentry, 1968, 1973; Hashemi-Nezhad and Durrani, 1981, 1983), phlogopite (Unger, 1993), and lepidolite (Kasuya et al., 1989; Coleman et al., 1993) established that (1) a single α-recoil is enough to form an etchable track but that consecutive connected or overlapping recoils starting from a single parent nucleus also produce just one etch pit, (2) a recoil-track excess could nevertheless result from diffusion between successive decays, and (3) recoil tracks anneal at lower temperatures than fission tracks. Research at the Max-Planck Institute for Nuclear Physics in Heidelberg (Wagner, 1995, 1998; Gögen, 1999; Gögen and Wagner, 2000; Jonckheere and Gögen, 2001; Wagner et al., 2002) led to an etch model that implies the number of recoil-track etch pits per unit surface (ρ_{RT}) increases as a linear function of etch time (t_E; Gögen, 1999; Gögen and Wagner, 2000):

$$\rho_{RT} = N_{RT} D_{RT} + N_{RT} v_V t_E - \Delta\rho_{RT} \qquad (1)$$

The remaining variables in Eq. (1) are the number of recoil tracks per unit volume (N_{RT}), their etchable size (D_{RT}), the etch rate perpendicular to the etched surface (v_V), and the track deficit due to the optical limit of

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http://dx.doi.org/10.1016/j.chemgeo.2015.03.023
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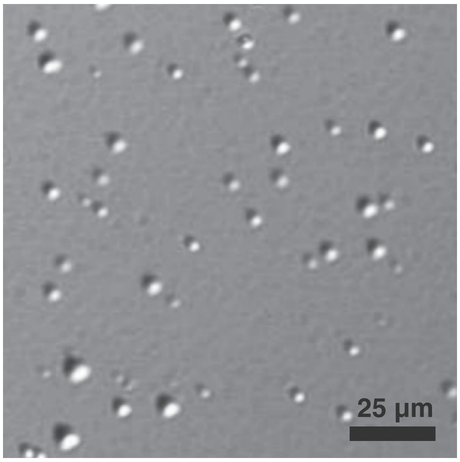

Fig. 1. Recoil-track etch pits (40% HF; 60 s) in the cleavage plane of phlogopite; the surface was carbon-coated and photographed with incident-light Nomarski differential interference contrast.

the microscope ($\Delta\rho_{RT}$), all of which were assumed constant. It follows that if these constants are known, N_{RT} can be calculated from the intercept ($\kappa = N_{RT}\, D_{RT} - \Delta\rho_{RT}$) or from the slope ($\lambda = N_{RT}\, v_V$) of a regression line fitted to a ρ_{RT} *versus* t_E plot. If D_{RT} and $\Delta\rho_{RT}$ are not known, N_{RT} can still be calculated from its slope, needing only a measurement of v_V.

Glasmacher et al. (2003) combined measurements of ρ_{RT} *versus* t_E with measured etch rates parallel (v_H) and perpendicular (v_V) to the cleavage plane of phlogopite (Lang et al., 2002a,b, 2003, 2004) and LA-ICP-MS measurements of U and Th to calculate an age of ca. 6 Ma for a sample from the Kerguelen, consistent with geological data. The recoil-track method has since attracted the attention of other researchers, who (1) confirmed earlier results obtained through step-etch experiments (Dong et al., 2005a,b; Gao et al., 2005a; Stübner et al., 2005; Yuan et al., 2008) and (2) determined the closure temperature of recoil tracks in phlogopite in annealing experiments (ca. 30 °C; Gao et al., 2005b; Yuan et al., 2009). Recoil-track age determinations using Eq. (1) are based on a simple etch model that assumes constant values of v_V and v_H. Experimental data on etching and etch pit evolution in crystalline materials from atomic force microscopy (Lang et al., 2002a, 2003; Aldushin et al., 2006; Kurganskaya et al., 2012) and vertical scanning interferometry (Lasaga and Lüttge, 2001, 2003) and numerical simulations (Meakin and Rosso, 2008; Stübner et al., 2008; Kurganskaya and Luttge, 2013) led to much more complex models of mineral dissolution, which suggest that constant etch velocities along given crystallographic orientations are insufficient for accurately describing the etching process. Etching is accomplished by interaction of different mechanisms (e.g., step retreat, surface alteration, and decomposition; Lasaga and Lüttge, 2001; Aldushin et al., 2006), which depend on intrinsic (chemical composition, bond strength, lattice defects) and extrinsic (pH, temperature, saturation state, etc.) parameters and lead to variable and non-constant etch rates.

The etchable size (D_{RT}) of recoil tracks is unknown but doubtless related to the size of the latent (unetched) tracks. Latent recoil tracks in samples less than a few Ma can have complex, bimodal size distributions that depend on the time interval since crystallization and cooling below the closure temperature (Jonckheere and Gögen, 2001; Stübner and Jonckheere, 2006). This implies that D_{RT} is not a constant for a given mineral, although a meaningful effective etchable size that is independent of the etch time t_E can still be defined for a specific sample. In mica, typical recoil tracks (~30–180 nm) are of the order of several to several tens of sheet silicate layers. Several mineral dissolution studies investigated the development of etch pits at point defects or dislocations (e.g., Lasaga and Lüttge, 2003; Aldushin et al., 2006; Meakin and Rosso, 2008; Kurganskaya and Luttge, 2013). Numerical simulations of pits developing from recoil-track sized defects (Stübner et al., 2008) show that the lateral growth rate of an etch pit varies not only with etch time but also depends on the initial size of the defect, in agreement with observations of etched phlogopite surfaces under an optical microscope (Stübner et al., 2005).

If the etch rates v_V, v_H are not constant under constant etching conditions, estimates of N_{RT} based on a ρ_{RT} *versus* t_E plot must be viewed with caution. This contribution presents statistics related to the areal densities and sizes of etched recoil tracks and evaluates the estimates of the intercepts (κ) and slopes (λ) of step-etch functions. Four experiments demonstrate that N_{RT} can be obtained from ρ_{RT} on the basis of a simple, phenomenological etch model based essentially on v_V and evading many of the complexities inherent in mineral dissolution kinematics.

2. Experiments

Four experiments (Stübner et al., 2005) aimed at determining κ and λ were carried out on a single phlogopite from the Laacher See tuff, collected at Maria Laach (German Eifel) and part of the collections of the *Universiteit Gent*: (1) a step-etch experiment, (2) mirror-image counts, (3) an etch–anneal–etch experiment, and (4) track-size measurements. For the first experiment, a sample was etched for 60 s in 40% HF at room temperature, rinsed in ethanol, and placed on a microscope slide. The tracks were counted at 500× and 1000× magnification with a Zeiss Axioplan 2 microscope equipped with incident-light Nomarski differential interference contrast (N-DIC). The sample was then re-etched for 30 s and counted again. In this manner, t_E was increased from 60 s to 420 s in 30 s increments. If the sample became damaged, it was replaced by a new one, etched in a single step, without discernible effect on the results. Except for one etch step, >1000 tracks were counted, so that the statistical (Poisson) counting errors are around 2%.

Five mica flakes were cleaved for a mirror-image experiment. The facing surfaces were etched for 60, 90, 120, 150, or 180 s in 40% HF at room temperature, rinsed in ethanol, dried, and carbon coated. A composite image of each of the facing surfaces was constructed from digital photomicrographs taken at 200× magnification using N-DIC. One image was mirrored, translated, and rotated to coincide with that of the facing surface, with dislocations, inclusions, and surface steps serving as reference points. The etched recoil tracks were marked on the covering (upper) image. Marks that also coincided with an etched track in the covered (lower) image when the upper image was removed were counted as paired etch pits. The lower microscope magnification (200×) compared to the step-etch experiments (500×, 1000×) was required for constructing images with enough track etch pits and other surface features to yield significant numbers of paired etch pits and helped by the greater surface reflectance from the carbon coating.

The etch–anneal–etch method was proposed by Green et al. (1978) for measuring the etch velocities (v_T) along ion tracks in meteorite minerals. Here, it was used to avoid the increase of ρ_{RT} due to surface etching, i.e., to achieve experimental conditions where $\lambda = 0$. A first set of five samples was pre-etched for $t_P = 5$ s in 40% HF and rinsed in ethanol, and a second set for $t_P = 10$ s. All samples were annealed for 18 h at 350 °C (Gögen, 1999) to remove the unetched tracks in the bulk. The pre-etched tracks were thereupon enlarged in a second etch step of $t_E = 60$, 120, 180, 240, or 300 s. The recoil track counts were performed on images captured with a CCD camera at a microscope magnification of 200×. Carbon coating and N-DIC produced crisp images. In the same manner, sets of two samples each were prepared that were pre-etched for $t_P = 1$ s and 0 s, annealed under the same conditions, re-etched for $t_E = 240$ s or 300 s and carbon coated.

The aim of the track-size measurements was also to obtain ρ_{RT} estimates corrected for surface etching, reasoning as follows. According to the model of Gögen and Wagner (2000), tracks intersecting the mica surface are etched for a time t_E whereas those exposed by bulk etching are etched for a variable shorter time. Assuming constant rates of surface etching (v_V) and etch pit growth (v_H) (Gögen and Wagner, 2000; Aldushin et al., 2006), then surface-intersecting tracks grow to a size