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Alpha-recoil tracks in natural dark mica: Dating geological samples by optical and scanning force microscopy

U.A. Glasmacher [a,*], M. Lang [b], S. Klemme [c], B. Moine [d], L. Barbero [e], R. Neumann [b], G.A. Wagner [a]

[a] *Forschungsstelle Archäometrie der Heidelberger Akademie der Wissenschaften, Max-Planck-Institut für Kernphysik, Postfach 103980, D-69029 Heidelberg, Germany*

[b] *Gesellschaft für Schwerionenforschung (GSI), Planckstr. 1, D-64291 Darmstadt, Germany*

[c] *Mineralogisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 236, D-69120 Heidelberg, Germany*

[d] *Laboratoire de Géochimie des Systèmes Volcaniques, Université P.M. Curie, F-75005 Paris, France*

[e] *Dpto. Geología, Universidad de Cádiz, Apto 40, E-11510 Puerto Real, Spain*

Abstract

Alpha-recoil tracks (ART) are lattice defects caused by the α-decay of ^{238}U, ^{235}U, ^{232}Th, and daughter products. Visualization of etched ARTs in dark mica by phase-contrast microscopy allows dating of Quaternary geological as well as archaeological materials. Visualization of etched ARTs by Nomarski-differential-interference-contrast microscopy (NDICM) and scanning force microscopy (SFM) enables the access to areal densities (ρ_a) of ART etch pits beyond 10^4 mm^{-2} and thus the extension of the new ART-dating technique to an age range >1 Ma. The successful application of SFM as a new tool in geochronology could open the way to a field to be characterized as nanogeochronology. In order to visualize ARTs by NDICM and SFM, dark mica was etched with 4% HF at 21 °C for 5–107 min. A linear relationship between ρ_a and etching time (t_e) was observed for phlogopites from the Kerguelen Islands (French territory, Indian Ocean), and the Kovdor magmatic complex (Russia). The volume density (ρ_v) of ART is a function of etching speed (v_{eff}) and slope of the ρ_a-growth curve. The ART-age equation allows the calculation of an individual ρ_v-growth curve for the phlogopite analysed by us using the uranium and thorium content. The ART-ages were determined by combining the experimentally obtained volume density with the individual ρ_v-growth curve.

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1. Introduction

Alpha-recoil tracks (ARTs), lattice defects in natural minerals, were first visualized by etching and phase-contrast microscopy in mica [1,2]. Huang and Walker [1] discovered a background of small and shallow etch pits as they tried to etch

* Corresponding author. Tel.: +49-6221-516-321; fax: +49-6221-516-633.
E-mail address: ua.glasmacher@mpi-hd.mpg.de (U.A. Glasmacher).

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spontaneous fission tracks in mica. The lattice defects are caused by the alpha decay of ^{238}U, ^{235}U, ^{232}Th, and daughter products. An α-disintegration releases energy of several MeV, part of which is transferred to the daughter nucleus as recoil energy ($\sim 10^2$ keV). The alpha-recoil nucleus slows down when interacting with the lattice atoms and produces 10^3–10^4 lattice defects, which represent one single ART [3,4]. The size of latent ARTs in dark mica is in the range of 30–100 nm. Within the decay cascade, the first α-disintegration already forms an ART [5]. Subsequent α-emission processes do not produce additional ARTs, but modify shape and diameter of the already existing ART left by the initial parent nucleus. It was proposed that the quantification of ART-densities, combined with the analysis of uranium and thorium could provide a dating technique [1,2].

Methodological problems and difficulties related to the shallow and faint appearance of ARTs hampered the development of a practicable dating technique. Hashemi-Nezhad and Durrani [6,7] addressed shortcomings of the ART system in dark mica and improved the understanding of the physical model. Based on phlogopite (dark mica) from Quaternary volcanic rocks (10^4–10^5 a) of the Eifel region Germany, Gögen and Wagner [8] proposed an etching model for the increase of etch pit areal density at the 0 0 1-plane of phlogopite with increasing etching time (ART-growth). The volume density (ρ_v) of ARTs, which is necessary to evaluate an age, is a function of the slope of the linear ART-growth and the effective etching rate (v_{eff}) [5]. Furthermore, Gögen and Wagner [8] presented an age equation that allows calculating a ρ_v vs. age growth curve for the phlogopite for given uranium and thorium contents. Combining the experimentally determined ρ_v to the calculated ρ_v-growth curve leads to the age of the phlogopite. The uranium and thorium contents of phlogopite are in the range of 1–10 ng g^{-1}. Therefore, the use of laser ablation-induced coupled plasma-mass spectrometry (LA-ICP-MS) is required to quantify the contents [9]. The interpretation of the ART-age has to consider that all crystal defects caused by the radioactive decay in minerals are metastable. The retention characteristics of ART are essentially controlled by temperature and time. When phlogopite is kept at 500 °C for 15 min, all tracks are annealed [3]. Extrapolating the experimental data to geological time implies that the ART density is reduced to 50% at a constant temperature of 50 °C for a period of 1 Ma. In the case of volcanic rocks with rapid cooling, the ART-retention temperature is passed within hours or days after eruption, so that the ART-ages represent the rock formation.

In the present contribution, we attempt to extend the ART-dating technique to pre-Quaternary ages (1–100 Ma) by calibration with samples of independently determined age and known thermal history.

2. Experimental

An optical microscope (Olympus BX-50) was used to quantify the areal density (ρ_a) of two phlogopite samples (OB-93-214, AGL-91-29) from volcanic rocks of the Kerguelen Islands (French territory, Indian Ocean). On the basis of geological knowledge and field evidence, the formation age of the samples is in the range of 6–10 Ma. Phlogopite surfaces exposed by cleavage were etched at different etching times (29–107 min) in a 4% HF-solution at 21 °C. The etch pits on the cleavage planes (0 0 1-planes) were imaged using an optical microscope with Nomarski-differential-interference-contrast technique (NDIC), a 20× objective together with a double magnification lens, a video camera (Panasonic F15 HS), the analySIS® software, and the 3-D Autoscan® stage. A mean ρ_a was determined by evaluating the etch pit densities with 10 images of size 209×157 μm^2 each.

Three phlogopite samples (Kovdor magmatic complex, Kola Peninsula, Russia; Erzgebirge, Germany; Triassic dike, Central Spain) of formation or $^{40}Ar/^{39}Ar$ cooling ages in the range of several 10–100 Ma were used to test the SFM as a tool for quantifying ρ_a. Again, cleavage planes were etched at different etching times (5–20 min) in a 4% HF-solution at 21 °C. The etch pits were imaged with SFM. All micrographs were acquired in the constant-force mode. ρ_a was determined by counting the etch pits in five images of size 3×3 μm^2. All errors given for the resulting data are 1σ of the mean.

3. Results

3.1. Visualization

3.1.1. Optical microscopy

Etching two phlogopites of the Kerguelen Islands shows a homogeneous distribution of shallow triangular etch pits (Fig. 1). As a function of etching time, ρ_a increases linearly (Fig. 2). An etching time of 107 min resulted in $\rho_a = 2.4 \times 10^4$ ART/mm^2. As discussed by Gögen and Wagner [8], based on a linear model, a straight line was fit to the data. The slope (*m*) of the areal growth of OB-93-214 is 233(5) ART/mm^2 min and the slope of AGL-91-29 is 247(2) ART/mm^2 min. Three techniques have been applied to determine the etching velocity that is responsible for the accumulations of the ART etch pits with etching time on the 0 0 1-plane (Table 1) [3]. Applying a

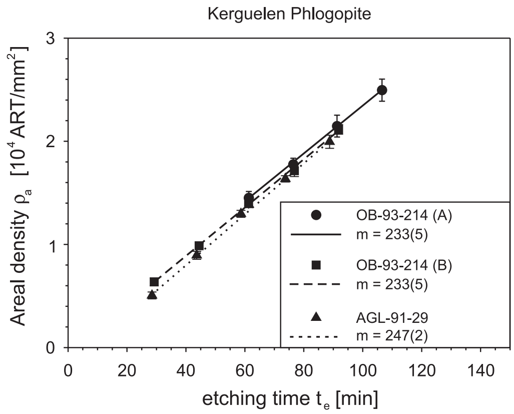


Fig. 2. Areal density of ART etch pits versus etching time of phlogopites from the Kerguelen Islands. The error bars are 1σ of the mean. Assuming a linear model, straight lines are fitted to the data points. The *m* values represent the slopes in units of ART/mm^2 min. Each data point results from evaluating 10 micrographs of 206 × 156 μm^2.

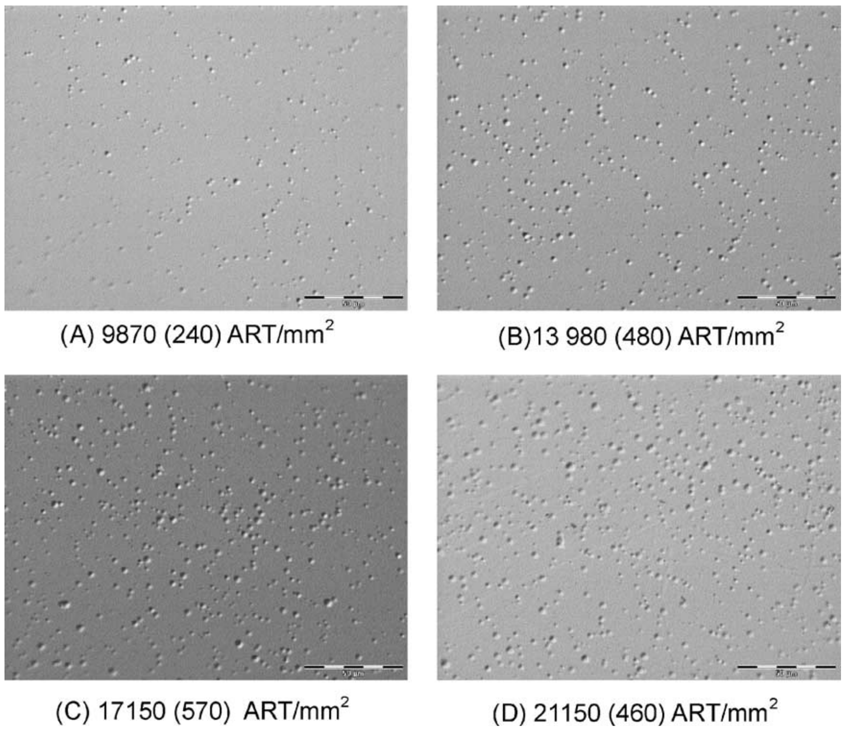
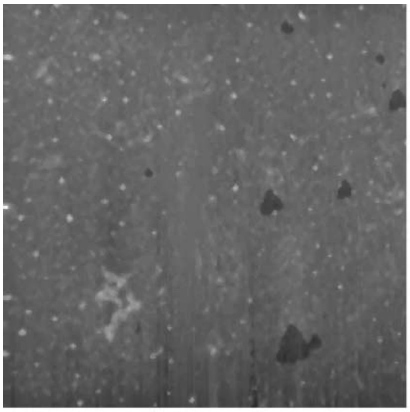


Fig. 1. Optical microscopy images (206 × 156 μm^2) displaying ART etch pit distributions at different etching times on the 0 0 1-plane of phlogopite from the Kerguelen Islands (OB-93-214). The numbers below each image display the areal densities, the errors representing 1σ of the mean. Etching was performed with 4% HF at 21 °C and etching times: (A) 45 min, (B) 61 min, (C) 77 min, (D) 92 min.

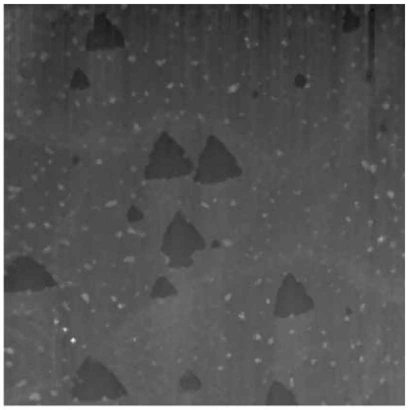
Table 1
Etching velocity (v_{eff}) measured for the phlogopite OB-93-214 with three different techniques (OM: optical microscopy; PM: profilometry; SFM: scanning force microscopy)

	OM	PM	SFM
v_{eff} [10^{-6} mm/min][a]	5.8 (0.3)	6.3 (1.5)	3.3 (2.0)
ρ_v [10^7 ART/mm^3][b]	4.0 (0.2)	3.7 (0.9)	7.1 (4.3)
ART-age [Ma][c]	6.1 (+0.2, −0.5)	5.8 (+0.7, −1.0)	11.3 (+5.3, −6.6)

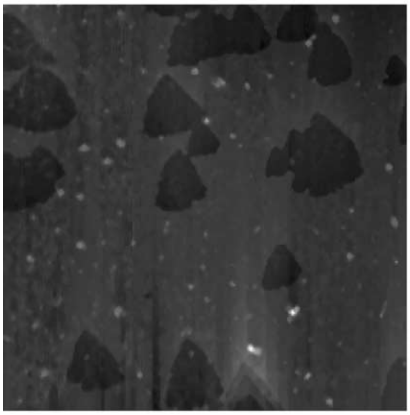
The slope (m) of the areal-density growth curve and the etching velocity were used to calculate the volume density. The ART-age was determined as described in the text and shown in Fig. 5.
[a] Experimental.
[b] Calculated.
[c] Determined as illustrated in Fig. 5.



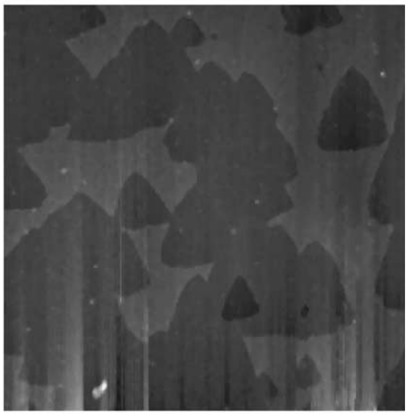
(A) 1.0 (2) 10^6 [ART/mm^2]



(B) 2.5 (1) 10^6 [ART/mm^2]



(C) 3.4 (2) 10^6 [ART/mm^2]



(D) 4.4 (3) 10^6 [ART/mm^2]

Fig. 3. SFM images (3×3 μm^2) displaying ART etch pit distributions at increasing etching times on the 0 0 1-plane of phlogopite from the Kovdor magmatic complex. The numbers below each image display the areal density. The errors of the areal densities are 1σ of the mean. Etching was performed with 4% HF at 21 °C and etching times of: (A) 5 min, (B) 10 min, (C) 15 min, (D) 20 min.

$v_{eff} = 5.8(3) \times 10^{-6}$ mm/min for OB-93-214 and $v_{eff} = 7.6(3) \times 10^{-6}$ mm/min for AGL-91-29, which were measured by optical microscopy [3], the volume density (ρ_v) results in $4.0(2) \times 10^7$

ART/mm^3 for OB-93-214 and $3.3(1)\times10^7$ ART/mm^3 for AGL-91-29. The values $v_{\text{eff}} = 6.3(1.5)\times10^{-6}$ mm/min for OB-93-214 determined by profilometry and $v_{\text{eff}} = 3.3(2.0)\times10^{-6}$ mm/min for OB-93-214 determined by SFM lead to a volume density $\rho_v = 3.7(9)\times10^7$ ART/mm^3 and $\rho_v = 7.1(4.3)\times10^7$ ART/mm^3 for OB-93-214 respectively.

3.1.2. Scanning force microscopy

Etching the phlogopite of the Kovdor magmatic complex reveals homogeneously distributed, shallow triangular etch pits. Previous results by Lang et al. [10,11] indicate that ART etch pits visualized by SFM differ in shape and size from etch pits of dislocations and fission tracks. ρ_a increases with etching time (Fig. 3). At an etching time of 20 min, $\rho_a = 4.4\times10^6$ ART/mm^2 was obtained. A straight line was fit to the data. The slope (m) of the areal growth is $2.2\ (2)\times10^5$ ART/mm^2 min (Fig. 4).

3.2. Age determination

In order to determine the age of the Kerguelen phlogopite analyzed in this work, the calculated volume density vs. age growth curve based on the mean U and Th contents is used. This function is plotted in Fig. 5 as a bold straight line, the thin

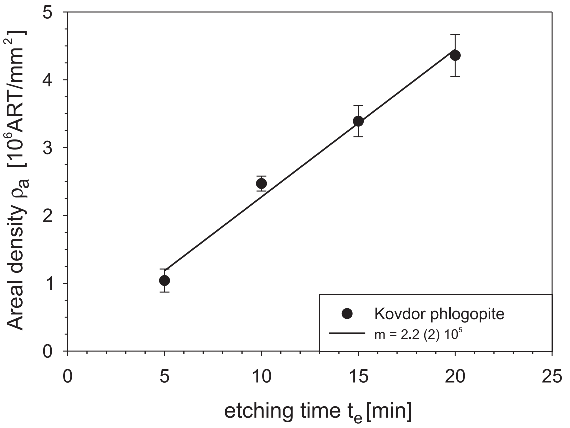


Fig. 4. Areal density of ART etch pits as a function of etching time of the Kovdor deposit. The error bars are 1σ of the mean. Assuming a linear model, a straight line was fitted to the data. The m value represents the slope in units of ART/mm^2 min. Each data point results from evaluating five micrographs of 3×3 μm^2.

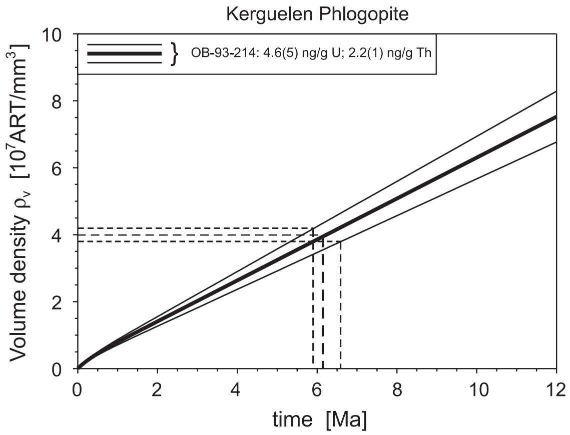


Fig. 5. Volume–density growth curves (bold continuous line) calculated by using the age equation of Gögen and Wagner [8] and the mean of the uranium and thorium content of the Kerguelen phlogopites. The thin continuous lines representing 1σ of the mean. The experimentally determined mean volume density and the resulting mean age value are connected by a bold dashed line (uncertainties indicated by thin dashed lines).

lines taking into account the uncertainties of the U and Th contents. By means of this diagram, the experimentally determined volume density can be directly related (dashed lines) to an age value of 6.1 (+0.2, −0.5) Ma (OB-93-214). The asymmetric error of the age value comprises the uncertainties of both the volume density and the U and Th contents, as indicated by the dotted lines. In the same way, the age volume was obtained for the second Kerguelen phlogopite samples (AGL-91-29, $U = 2.8(4)$ ng g^{-1}, Th $= 1.4(3)$ ng g^{-1}) providing an age of 8.5 (+1.6, −1.1) Ma. Both ages are in agreement with the crystallization age. The volume densities that were calculated by using v_{eff} from SFM and profilometry resulted in ART-ages of 11.3 (+5.3, −6.6) Ma and 5.8 (+0.7, −1.0) Ma, respectively (Table 1). The upper uncertainty of the age determined by using the SFM measured v_{eff} is of no geological meaning.

Calculating the ART-age of phlogopite from the Kovdor deposit revealed unexpected problems: Uranium and thorium values determined by LA-ICP-MS exhibited very inhomogeneous distributions on a scale $\leqslant 10$ μm. The distributions vary parallel and perpendicular to the c-axis. In contrast to this procedure, the areal density of ART etch pits recorded by SFM originated from a bulk layer of thickness ~200 nm. Based on the LA-ICP-MS findings, it must be expected that the SFM-technique would provide strongly varying results, when measuring the etch pit density for bulk layers in different depths on a micrometer scale. Therefore, numerous measurements distributed on this scale, taking into account the inhomogeneous U and Th distributions, will be required in order to provide a reliable mean age of this phlogopite.

4. Conclusion

Etched ARTs were successfully visualized by optical microscopy with NDIC-technique and by scanning force microscopy. It was shown that the areal density ρ_a of older samples (Ma) increases linearly with etching time. The gradient of this increase is a product of the ART volume density ρ_v and the effective etching velocity v_{eff}.

The ART-ages of the Kerguelen phlogopites determined by us are in the expected age range that is based on the geological evolution of the Kerguelen Islands. The successful application of the SFM opens the way towards a novel field to be characterized as nanogeochronology.

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