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Novel etching protocol for epidote fission tracks

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ABSTRACT

Along the years, etching for fission tracks was a major issue in the development of the epidote fission track dating. It was not a consensus in the scientific community. As an attempt to mitigate it, we present a novel etching protocol (HF 40% at 15 °C for 80 min) and test it in ten different natural samples etched with HF 40% at 15 °C for 80 min (nine epidotes and one clinozoisite). The samples had their chemical compositions determined, forming a database for epidote chemical compositions. Fission tracks were observed in five samples. The uranium content in the remaining four samples was too low and hence tracks could not be observed. Further analyses, Raman and uranium concentration, confirm this observation. Fission tracks were not observed in clinozoisite sample. The proposed etching protocol showed to be less hazardous and efficient to etching fission tracks in epidote.

1. Introduction

There are three processes leading to epidote formation (Bar et al., 1974): deuteric action during the late phase of magmatic crystallization, low-grade regional metamorphism and hydrothermal activity. When the temperature of formation is below the closure temperature for fission track system in epidote, the age of magmatic crystallization, low-grade regional metamorphism, formation or reactivation of geological faults may potentially be obtained by epidote fission track dating (FTD). Epidote was one of the target mineral investigated in the early years of fission track dating (for instance, Naeser et al., 1970, Bar et al., 1974, Haack, 1976). Between 1970 and 1983 several etching procedures were proposed for the revelation of fission tracks in epidote (Table 1). Initially, epidote fission tracks were etched with hot sodium hydroxide (NaOH) in several controlled conditions. Bal et al. (1982) used 48% hydrofluoric acid (HF) at 40 °C for various times. Chakranarayan and Powar (1982) revealed epidote fission tracks with NaOH followed by HF etching. Lal and Waraich (1983) proposed a combination of HF and HCl at 25 °C. The disagreement among laboratories on a standard etching condition led to the discontinuance of the epidote fission track studies in the mid-eighties. Two decades later, Curvo et al. (2005) resumed the efforts to set chemical etching conditions. After failing to reveal fission tracks in epidote on a Brazilian sample using 25N NaOH, for 100 min at 75 °C they succeeded employing 48% HF for 12.5 min at 35 °C. This latter condition proved to effective in etching fission tracks, however, the high concentration of the etchant as well the relatively elevated temperature at which the chemical treatment is carried out, makes this procedure more laborious and potentially unhealthy.

Based on Curvo et al. (2005) findings, we propose a safer and more effective chemical etching for the epidote fission track. A set of 10 epidote samples (8 samples from Brazil and 2 samples from Peru) were characterized in detail by energy dispersive x-ray spectroscopy (SEM-EDS), to obtain the concentrations of major elements and then they are tested for the proposed etching.

2. Sample

All samples were donated by fellow researchers (CLI, BD485, BD495/2, N336/2, Brejui, P and EV) or purchased (Diamantina, Capelinha and EQ). Samples CLI to Brejuí, are originally from Rio Grande do Norte State, NE-Brazil, whereas samples P and EV came from Peru. Epidote samples from Diamantina and Capelinha are named after their cities of origin in Minas Gerais State, SE-Brazil. The geographical location of the EQ is unknown.

The samples are in two forms: ~0.5 mm grains size and 3 cm × 2 cm phenocrysts dimension.

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Table 1
Summary of several etching protocols used for epidote fission-track dating over the years.

Author	Etching conditions
Naeser et al., 1970	50N NaOH, 150 °C, for 60–180 min
Bar et al., 1974	37.5N NaOH, 159 °C for 150 min
Haack 1976	75N NaOH, boiling for 30 min
Saini et al., 1978	100N NaOH, 200 °C for 40 min
Bal et al., 1982	48% HF, 40 °C for different times
Chakranarayan and Powar, 1982	25N NaOH, 150 °C for 120 min + 48% HF, 30 °C for 15 min
Lal and Waraich, 1983	HF:HCl (1:1), 25 °C, for 20–25 min
Curvo et al., 2005	HF 48%, 35 °C for 12.5 min

3. Experimental procedure

3.1. Step-etching experiments

To build a step-etch curve, we chose the epidote phenocryst from the Brejuí Scheelite Mine, located in the Borborema Province, Rio Grande do Norte State-NE, Brazil. This is a well-known sample and has already been used in a previous etching study and dated with the FTD (Curvo et al., 2005).

A piece of the Brejuí sample was broken into smaller parts of ~1 mm in diameter. The grains were mounted in epoxy resin, polished and etched. The etching parameters were chosen to make chemical treatment less hazardous than the one proposed by Curvo et al. (2005): 40% HF at 15 ± 1 °C. The solution was placed in a circulating water bath in which the temperature is constant and controlled within ± 1 °C. The track density and confined tracks parallel to the surface were measured under a regular microscope, with a nominal magnification of 1000 × (100 × dry objective and 10 × ocular lenses).

The step-etch curve was built with etching times of 30, 40, 50, 60, 70, 80, 90, 100 and 110 min. A different mount (~100 grains each) was used in each experiment. Fossil confined fission track lengths and fossil fission track densities were measured in all mounts.

3.2. Sample characterization

The sample chemical compositions were determined by SEM-EDS. The equipment used was a SEM model LEO 430i coupled with an EDS system. The equipment settings were: 108 eV, 15 kV accelerating voltage, 19 mm working distance, 3 nA beam current, and vacuum of 1×10^{-5} Torr.

The Raman spectra were recorded using a micro-Raman spectrograph Renishaw model in-Via equipped with a Leica microscope model DMLM and couple with an air-cooled CCD detector. Single-point spectra were recorded with 633 nm helium-neon laser line with 10s accumulation time and 1800 grooves/mm grating.

3.3. Etching experiments

A total of ten epidote samples were analyzed. From those, five were phenocrysts and five were composed of grains. The phenocrysts were sliced in ~1 mm thick slices and the grains were hand-picked under a stereomicroscope. Each sample was mounted in epoxy resin, grounded with sandpaper, polished with diamond suspension and etched with 40% HF at 15 ± 1 °C for 80 min, which was the etching time selected for the step-etch experiments (see Section 4.2).

3.4. Uranium content determination

After the etching procedure, we could not find tracks in five samples (CLI, EV, Diamantina, Capelinha and EQ). This could be either because of variations in the chemical composition, that could imply in different etching responses, or just because uranium content was too low. To check the latter possibility, these samples were sent to the nuclear reactor with a muscovite mica juxtaposed to them. Irradiation was performed with a nominal thermal neutron fluence of 3×10^{15} neutrons/cm^2 at the IPEN/CNEN reactor, Brazil. To estimate the ^{238}U concentration in μg/g, the equation relating the induced fission track density, ρ_i, with the thermal neutron fluence was applied (Wagner and Van den haute, 1992):

$$\rho_i = gN_{235}R_i(\eta q)_i\sigma\phi \quad (1)$$

where g is the geometry factor, N_{235} is the number of ^{235}U atoms per unit of volume, R_i is the mean length of etched fission tracks in the muscovite mica, $(\eta q)_i$ is the efficiency of the etching and observation under optical microscopy (Jonckheere and Van den haute, 1999), σ is the cross section for fission of ^{235}U by thermal neutron capture and Φ is the thermal neutron fluence.

The geometry factor, g, of the pre-etched sample surface is 0.5 for an external surface (Wagner and Van den haute, 1992). We adopted the value of 20.50 ± 0.25 μm for R_i (Jonckheere, 2003). According to Soares et al. (2013) the $(\eta q)_i$ parameter is 0.92 ± 0.02 and σ is 584.33 b (Carlson, 2011).

The number of ^{238}U atoms per unit of volume, N_{238}, can be regarded to the natural abundance of ^{238}U/^{235}U (~137.88) by (Steiger and Jäger, 1977):

$$N_{238} = N_{235}\cdot 137.88 \quad (2)$$

The uranium content can be estimated by (Hasebe et al., 2004):

$$238U = \frac{N_{238}\cdot M}{N_A\cdot 10^{-6}\cdot d} \quad (3)$$

where ^{238}U is given in (μg/g), N_A is the Avogadro's number, M is the molar mass of ^{238}U and d is the muscovite mica density.

4. Results and discussion

4.1. Chemical characterization

A database of chemical compositions for 10 epidotes samples was built. The major element contents, determined by SEM-EDS, are shown in Table 2. Only one sample, CLI, turned out not to be epidote. The lack of iron in its chemical composition indicates that CLI is a clinozoite.

4.2. Step-etch experiments

Photomicrographs of tracks in various stages of etching (30–110 min at 40% HF at 15 ± 1 °C) are shown in Fig. 1. Visually, some tracks etched for 30, 40, 50 and 60 min are very thin showing an under-etch of the tracks. For 110 min, tracks are very thick, making more difficult distinguish individual tracks due to track overlapping. Tracks at 70, 80 and 90 min are comfortably distinguished. They are not

Table 2
Chemical composition (wt%) obtained through SEM-EDS. Nine samples are epidotes and one (CLI) is a clinozoisite. The Brejuí sample, in bold, has been used in other works (Curvo et al., 2005) and is used as our reference sample.

Samples	C	Al	Si	Ca	Fe	O	Cr	Mn
CLI	10.27	9.99	12.68	10.96	0.02	55.15	0.02	0.01
BD485–1	9.97	7.46	12.62	9.41	4.07	53.63	0.02	0.08
BD495–2	9.13	8.72	12.43	11.32	5.92	52.47	–	–
N336–2	9.54	7.83	13.80	9.94	4.36	53.77	0.02	0.03
P	9.97	7.29	16.29	6.24	3.67	56.03	0.02	0.05
Brejuí	**9.68**	**8.16**	**11.93**	**10.85**	**6.36**	**52.84**	**0.05**	**0.13**
Diamantina	9.93	8.09	11.83	10.76	6.08	53.21	0.01	0.06
Capelinha	9.34	8.65	12.30	11.11	5.77	52.73	0.02	0.04
EQ	9.49	7.82	12.07	10.94	7.16	52.44	0.01	0.05
EV	9.34	9.58	12.40	11.19	4.20	53.24	0.02	0.02