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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

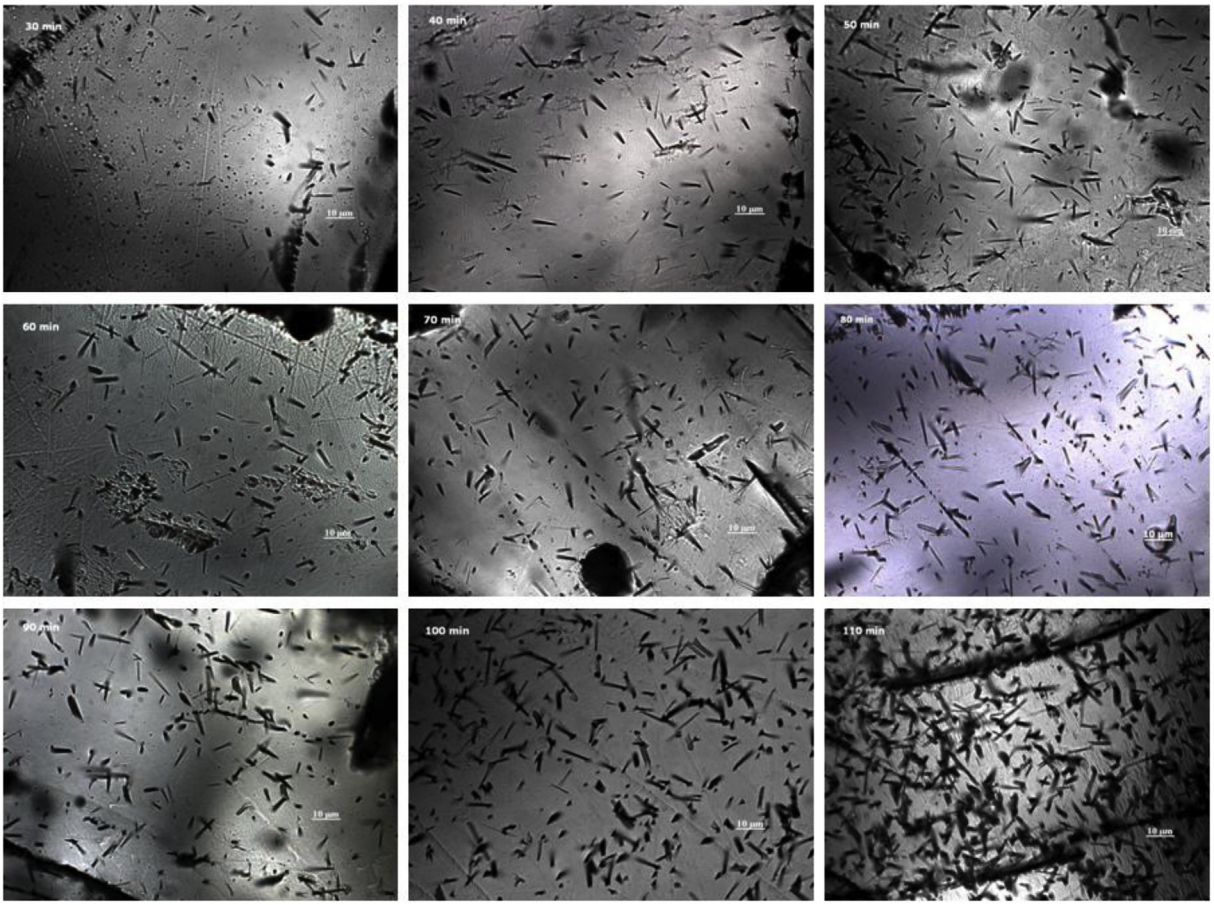

Fig. 1. Photomicrographs for epidote fission-track etching times of 30, 40, 50, 60, 70, 80, 90, 100 and 110 min, respectively, with HF 40% at 15 °C. The microscope magnification used was 1000×.

Table 3
Data for the step-etch curves of fission track densities and lengths for different etching times.

Time (minutes)	N	x	Track density (× 10^6 tracks/cm^2)	N_c	L (μm)
30	100	591	0.66 ± 0.03	23	9.15 ± 0.51
40	100	889	0.99 ± 0.03	32	9.87 ± 0.44
50	100	1221	1.36 ± 0.04	52	9.76 ± 0.30
60	100	1247	1.39 ± 0.04	65	10.98 ± 0.25
70	100	1584	1.76 ± 0.04	100	11.73 ± 0.19
80	100	1671	1.86 ± 0.05	101	11.53 ± 0.18
90	100	1812	2.01 ± 0.05	104	11.67 ± 0.16
100	100	1854	2.06 ± 0.05	100	11.68 ± 0.18
110	100	1670	1.86 ± 0.05	100	12.29 ± 0.20

N: fields counted; x: number of tracks; N_c; number of measured confined tracks and L: mean confined tracks length. The error related means the standard deviation of the mean (1σ).

so thin, neither so thick. The results of the step-etch experiments are shown in Table 3. The step-etch curves for fission track densities and lengths are shown in Fig. 2. Track-in-tracks and track-in-cleavage confined fission tracks were measured to determine the mean confined track lengths.

The definition of optimal time of the fission track density step-etch curve for fission track densities (Figure 2A) demands some consideration, since the etching time at which track density stop growing is uncertain. In addition, at 110 min, track overlap start affecting the counting efficiency as it is shown in Fig. 1. Track length, however, seems to stop increasing from 70 min etching time (Figure 2B). Pulling together the above information, we can situate the optimal etching time between 70 and 100 min. In principle, any of these preselected etching times could be adopted. The last criterion applied was the ease of counting, which lead us to choose 80 min.

4.3. Etching experiments and analysis

The remaining nine samples were etched with the chosen conditions (HF 40% at 15 ± 1 °C for 80 min). Only four of them fission tracks were observed (four grain samples): BD485, BD495/2, N336/2 and P. Photomicrographs of the etched tracks in these samples are shown in Fig. 3. The samples CLI, Diamantina, Capelinha, EQ and EV did not show fission tracks. All of them are phenocrysts, except the CLI, as commented above. Although the CLI is not an epidote it is part of epidote group and was prepared and etched together with the other samples.

Chemical compositions (Table 2) indicate that the phenocrysts are epidote. There are no significant differences in chemical compositions among samples, including Brejuí. In addition, the Raman spectra of these samples were compared to the Brejuí epidote Raman spectrum (Fig. 4). All spectra have the peaks at the same Raman shifts of Brejuí. Differences in peak intensity appear because we did not find the way to analyze the samples at the exact same crystallographic orientation, due to difficult to manipulate a monoclinic mineral with many crystallographic faces. Thus, we can conclude that chemical composition was not the cause we did not find tracks in these samples.

The muscovite micas juxtaposed with the epidote phenocrysts samples (EV, Diamantina, Capelinha and EQ) during thermal neutron irradiation presented lower surface fission track densities ($\sim 10^4\ cm^{-2}$, Table 4) when compared with the Brejuí sample irradiated with similar

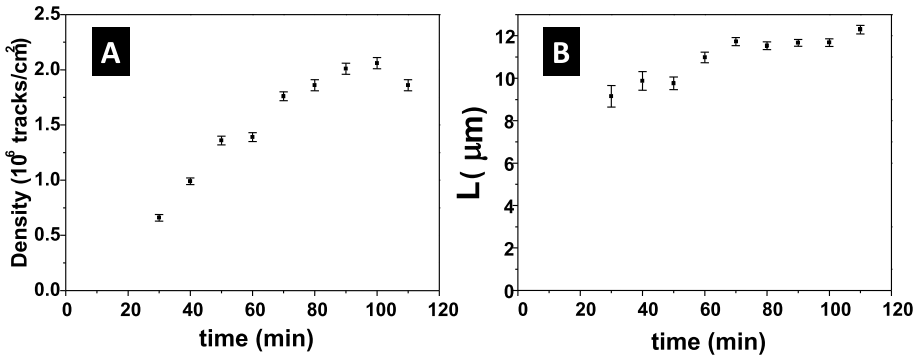

Fig. 2. Etching curve: A) Fission-track density and B) Confined fission-track length.

neutron fluence ($\sim 10^6$ cm^{-2}, Curvo et al., 2007). According to Nakasuga (2010), the uranium content of Brejuí sample is 10 µg/g and Curvo et al. (2007) found a track density of $\sim 10^6$ tracks/cm^2 when Brejuí was irradiated with a fluence of 1.95×10^{15} neutrons/cm^2 (approximately the same neutron fluence used in this work). Only for the sake of discussion, the ^{238}U content in these samples was estimated using equations (1), 2 and 3. The results are shown in Table 4. In addition to the small number of counted tracks, a major source of uncertainty is the value of the neutron fluence. The nominal value was used for calculation. Our experience with this reactor, shows that the actual value is frequently about 30% lower than the nominal one. In this way, the presented ^{238}U concentration values are rough, probably underestimated values. The valuable information, however, is that the uranium concentrations in these samples are below 1 µg/g, too low to yield a significant number of fossil fission tracks, even in a period of millions of years.

It was difficult to polish the CLI and P samples. The CLI sample is opaque, making the observation by optical microscope impossible in the transmitted light mode. At the polishing step, both samples were fragmented and after etching were totally (CLI) or partially (P) destroyed. However, as shown in Fig. 3, the P sample revealed fission tracks. These two samples are the ones that showed a greater divergent chemical composition compared with other samples of epidote (Table 2).

5. Conclusion

We set a new etching protocol (HF 40% at 15 °C for 80 min) and tested it in ten samples, whose chemical compositions were determined by SEM-EDS. Nine of them were epidote and one turned out to be a

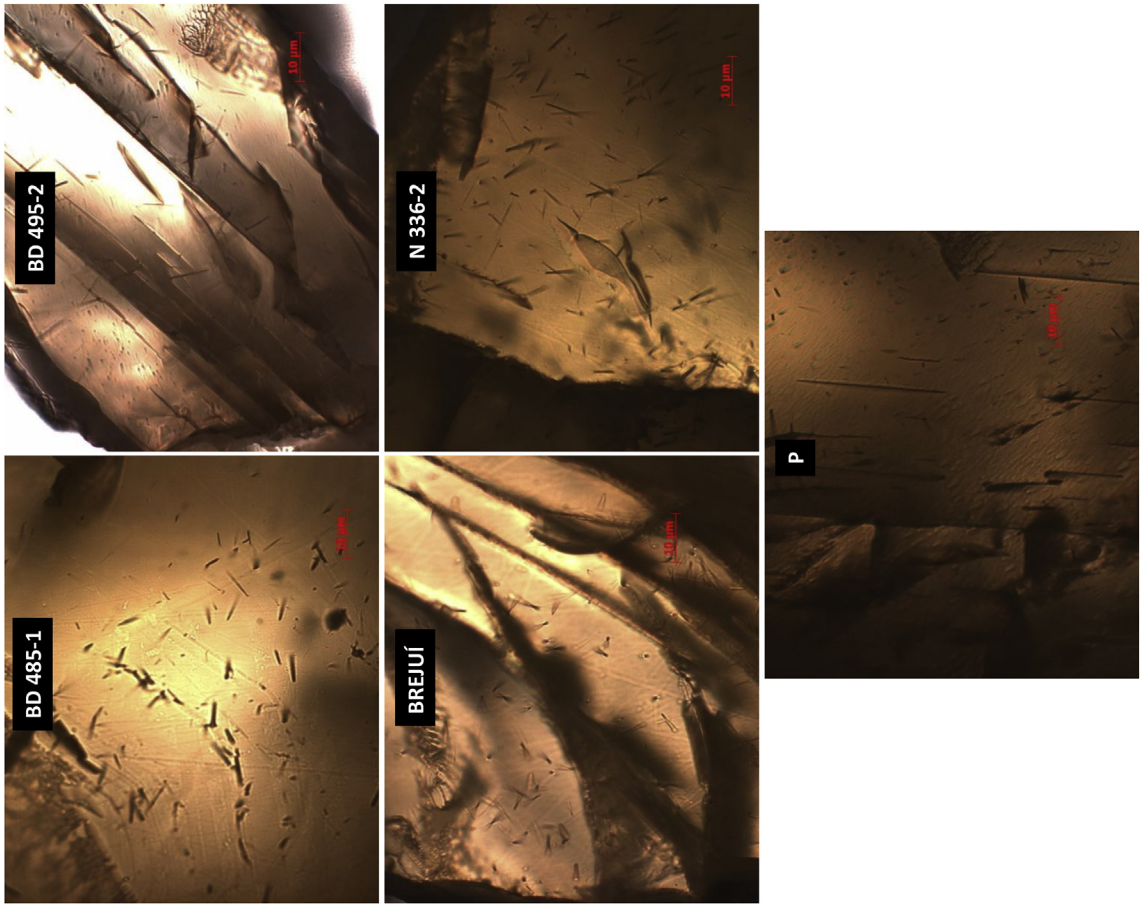

Fig. 3. Photomicrography of epidotes samples that revealed fission tracks using HF 40%, 15 °C for 80 min. The microscope magnification used was 1000×.

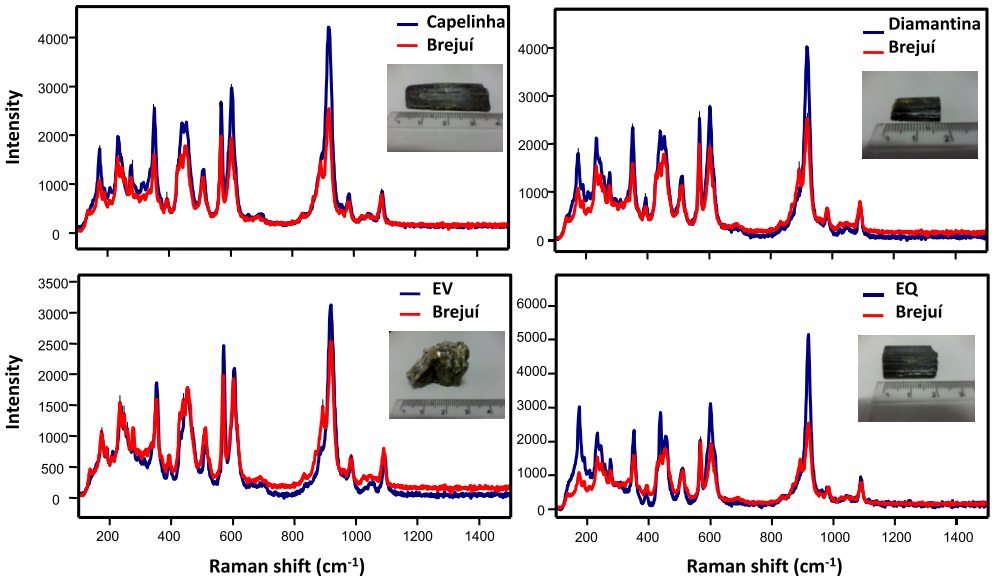

Fig. 4. Raman spectra of epidote samples. The blue line is the Brejuí sample, this one was used as a standard epidote and the red line are Capelinha, Diamantina, EV and EQ epidote samples. Photos of each epidote phenocrystal are presented in the insets. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4
Data for estimative of uranium concentration in some samples. The ^{238}U column is the estimative of uranium concentration in μg/g of the samples.

	N	Σ tracks	Induced density (× 10^4 tracks/ cm^2)	^{238}U (μg/g)
EV	25	17	4.3 ± 1.0	0.52 ± 0,20
Diamantina	25	9	2.3 ± 0.8	0.28 ± 0.13
Capelinha	25	3	0.8 ± 0.5	0.10 ± 0,07
EQ	25	7	1.8 ± 0.7	0.22 ± 0,11

N is the number of analyzed fields. The errors related to Induced density means the standard deviation of the distribution (1σ).

clinozoisite. We could not observe tracks in the clinozoisite and four of the epidote samples. Further analyses, Raman and estimative of uranium concentration, indicate that the low uranium content is the primary cause of failing observing tracks in these epidote samples.

The proposed protocol is less hazardous than a previous one (Curvo et al., 2005) and showed to be efficient for revealing tracks. As a secondary outcome, a database of epidote chemical compositions was initiated and can be valuable information for researchers working with epidote FTD.

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