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Thermal annealing of fission tracks in synthetic apatites

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ABSTRACT

Synthetic analogues of poor-silicated natural apatites have been doped with uranium. These minerals have been irradiated with a thermal neutron dose in the aim to induce the ²³⁵U fission and to obtain a fission track population. Thermal annealing experiments have been performed on the fission track population and allow us to compare the ability of the synthetic minerals to anneal such nuclear damages with their natural analogues. The thermal of the fission tracks in the synthetic minerals need more time and/or higher temperature to reach the same annealing rate as in the natural analogues. The alpha damage present in the natural analogues seems to enhance the thermal annealing of fission tracks.

Keywords:
Apatite
Fission tracks
Thermal annealing
Alpha damage

1. Introduction

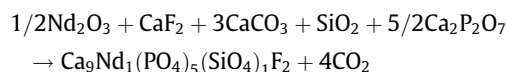
Silicated apatites, designed as britholites, have the general formula $\text{Ca}_{10-x}\text{Ln}_x(\text{PO}_4)_{6-y}(\text{SiO}_4)_y\text{Y}_2$. They belong to the Apatite group and crystallize in the hexagonal system (spatial symmetry group $\text{P6}_3/\text{m}$). They form a large family of compounds and have crystallized through a coupled substitution such as Ca^{2+} , $(\text{PO}_4)^{3-} \leftrightarrow \text{Ln}^{3+}$, $(\text{SiO}_4)^{4-}$. In natural ones, the structure is able to accept, over the lanthanides, a large array of cationic substitutions as Na, K, Cs, Mg, Sr, Pb, Mn, Fe, Mo, Ge, Cd, Al, Zr, U, Th, Pu [1–4].

Laboratory thermal annealing experiences in different natural mono-silicated fluor-britholite showed that these minerals are able to anneal fission tracks in low temperature thermal conditions [5]. In this work, our approach has been to elaborate the synthetic analogues of such apatites, to test their ability to repair nuclear fission tracks through laboratory thermal annealing experiments and to compare the thermal annealing behaviour of induced fission tracks in both synthetic and natural compounds.

2. Elaboration of the synthetic uranium-doped analogues

The uranium-doped synthetic apatites were synthesized by a high temperature solid–solid reactive sintering [6,7]. The uranium has been introduced by reacting crushed natural uraninite with an initial stoichiometric mixture made of $\text{Nd}_2\text{O}_3/\text{CaF}_2/\text{SiO}_2/\text{Ca}_2\text{P}_2\text{O}_7/\text{CaCO}_3$ to obtain an apatite. All these reagents were of analytical quality for the analysis and in stoichiometric proportions to obtain the synthetic compound. The uraninite UO_2 has been added to the

stoichiometric compounds and weighted to obtain an apatite with a total uranium content of about 10,000 ppm. The reaction of the apatite formation can be written:



Crystals with size of 0.1 mm were obtained after a rapid heating to 1773 K with a ramp rate of 300 K/h and a dwelling time of 2 h, then the temperature was let decreasing to ambient temperature at a rate of 50 K/min.

3. Crystallo-chemical characterization of the synthetic compounds

The synthetic compounds obtained consist of well crystallized acicular grains up to 0.1 mm, showing characteristic colour-less hexagonal prism with low birefringence in transmitted light under the polarizing microscope. SEM analysis of the synthetic crystals shows the well developed crystals (Fig. 1).

The X-ray powder diffraction pattern of the synthetic compound (Fig. 2) was recorded with a Siemens D 501 diffractometer ($\text{K}\alpha_1$ cobalt, internal standard: $\alpha\text{-Al}_2\text{O}_3$). The powder diffraction patterns confirm that the synthetic compounds are formed by an apatitic phase which crystallizes in the hexagonal system (space group $\text{P6}_3/\text{m}$). The experimental unit-cell parameters have been calculated. Crystallographic parameters are $a = 9.405 \times 10^{-1} \text{ nm}$ (9.405 Å) and $c = 6.906 \times 10^{-1} \text{ nm}$ (6.906 Å) for the synthetic apatite instead of $a = 9.431 \times 10^{-1} \text{ nm}$ and $c = 6.92 \times 10^{-1} \text{ nm}$ for the natural analogue apatite. Moreover, the introduction of a silicate groupment in the apatitic lattice has been controlled by mean of

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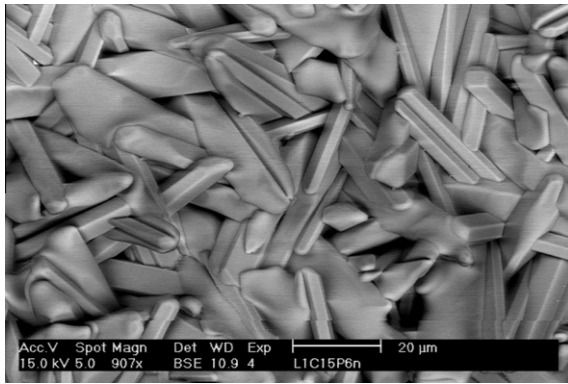


Fig. 1. Crystals of the synthetic apatite obtained by the solid-solid reaction (SEM Backscattered Electron image).

infrared spectroscopy (Perkin-Elmer FTIR 1600). Several crystals of the synthetic britholite were analyzed using an SX 50 Cameca microprobe. The mean composition of the crystals was determined as $\text{Ca}_{8.84} \text{Nd}_{0.93} (\text{SiO}_4)_{0.91} (\text{PO}_4)_{5.09} \text{F}_{1.28}$ with a calcium-content error of 0.06. This reported sample composition is the average of measures done on 20 synthetic crystals.

4. The annealing experiments on the induced fission tracks

The uranium-doped fluor mono-silicated apatites have been irradiated in the most thermalized column P1 of the Orphée reactor (Pierre Süe Laboratory, Commissariat Energie atomique, Saclay) so as to induce the fission of the uranium 235 isotope. The neutron dose was of $8.4 \times 10^{14} \text{ n/cm}^2$. After irradiation, the apatites samples were split into equal-sized aliquots and annealed isothermally at temperature of 300 and 310 °C for durations ranging from 30 min to 672 h. Each aliquot was mounted in epoxy resin, ground, polished using <1 mm diamond pastes and etched in 7% HNO_3

(weight %), at 21 °C. The etching time to reveal the uranium fission tracks was of 40 s at ambient temperature. The surface track densities were determined by using SEM at 5000× magnification. **Table 1** summarize the counting of tracks for each step of heating and the corresponding track densities (t/cm^2). The annealing rate of the tracks is presented as D_t/D_0 (with D_0 the initial track density before heating steps) in the last column. Different observations can be done. The **Fig. 3** shows that the induced track density is rather homogeneous even if some micro-inclusions of uranium oxide can be evidenced, however, preferentially etching occurred in relation with the different crystallographic orientations of the crystals. The initial induced track density (D_0 in the **Table 1**) allow to estimate an uranium content of about 3000 ppm. The uranium content included in the apatitic stoichiometry is lower than expected as some micro-inclusions of uraninite did not react completely.

5. Results and discussion

The annealing rate for each heating step is reported on the curves of the **Fig. 4** which show that fission tracks are progressively annealed with increasing temperature. The curves are similar to those of the natural analogue apatite as the mono-silicated fluoro-apatite from In Ouzzal (Hoggar, Algeria, [5], i.e. for an equivalent SiO_4/PO_4 ratio [8]). However, the thermal annealing rate of uranium fission tracks is still lower in the synthetic mineral, except in the beginning of the thermal annealing process. Except for this step, the natural sample systematically shows a higher sensitivity towards the thermal annealing of tracks (**Fig. 5**). As the fission tracks are induced tracks, freshly created in a reactor, it could be considered that the main parameter which would distinguish the natural apatites from the synthetic one could be the alpha damage cumulated in the mineral lattice. The synthetic apatite is free of any alpha damage. On the contrary, the lattice of the natural apatites has sustained high dose of alpha damage since several millions of years. Thus, if we state that the chemical composition –mainly the SiO_4/PO_4 ratio– of the two set of apatites is the same,

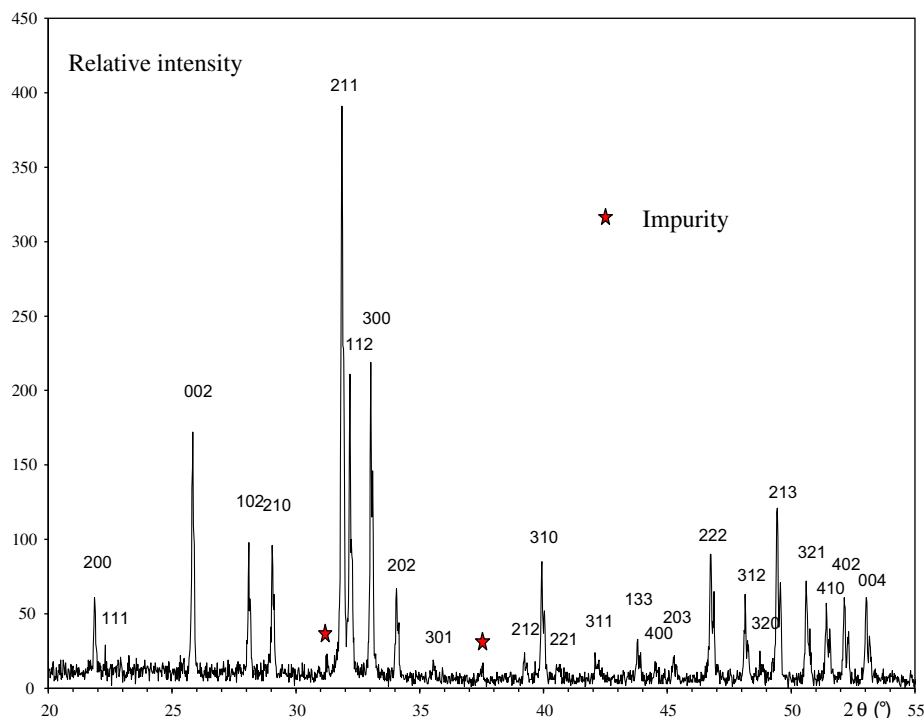


Fig. 2. XRD diagram of the synthetic apatite.

Table 1

Induced fission tracks densities and annealing rates in the synthetic apatites for different heating steps. The density of tracks D_t is calculated from the number of tracks counted and the area counted.

	Annealing time (min)	Number of tracks	Error ($2\sqrt{Nt}$)	Density of tracks D_t ($\times 10^6/\text{cm}^2$)	Annealing rate % (D_t/D_0)
Ambient temperature	0	3512	119	70.0 D_0	0
300 °C 0h30	30	6227	158	62.0	11.3
300 °C 1 h	60	5523	149	60.0	14.2
300 °C 7h30	450	7635	175	57.0	18.5
300 °C 24 h	1440	5701	151	56.8	18.8
300 °C 7 days	10,080	5684	151	56.6	19.1
300 °C 14 days	20,190	5907	154	50.1	28.4
Ambient temperature	0	3512	119	70.0 D_0	0
310 °C 1 h	60	3563	119	42.6	39.1
310 °C 2 h	120	4184	129	41.7	40.4
310 °C 5 h	300	4866	140	36.4	48.0
310 °C 8 h	480	2562	101	30.6	56.2
310 °C 1 day	1440	2391	98	28.6	59.1

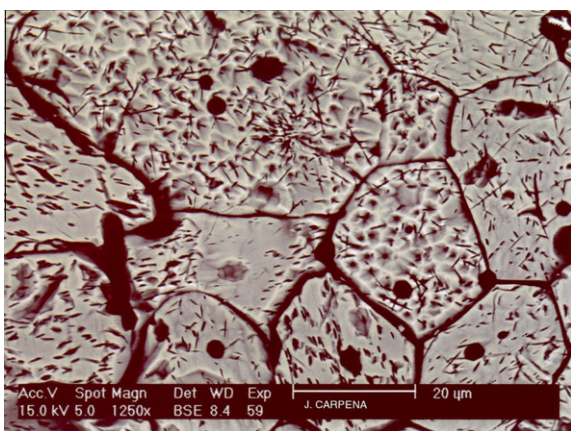


Fig. 3. Uranium induced fission tracks density D_0 in the synthetic apatite grains.

this result would evidence that the thermal annealing rate of fission tracks in apatites would be strongly dependant of the alpha-dose cumulated in the crystal lattice since its crystallization. The same hypothesis had been done [5,9] from the study of the activation energy for the thermal annealing of induced fission tracks in

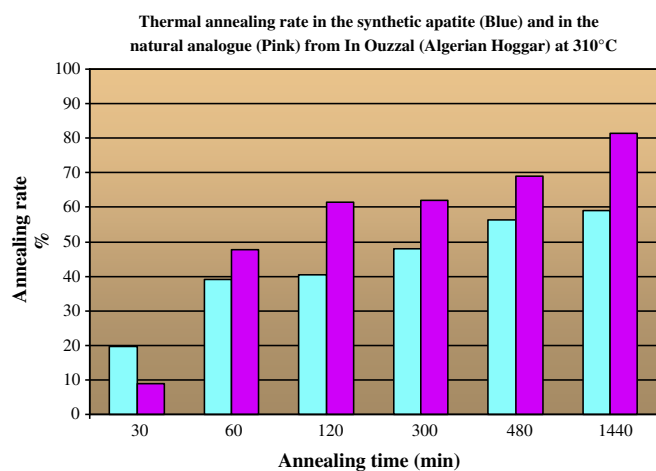


Fig. 5. Comparison of the thermal annealing rate of induced fission tracks in the synthetic analogue (in blue) of the natural apatite from In Ouzzal (Algerian Hoggar [2]) at 310 °C.

different natural apatites (i.e. different ages and different actinide contents). Fig. 6 shows that high actinide content in natural apa-

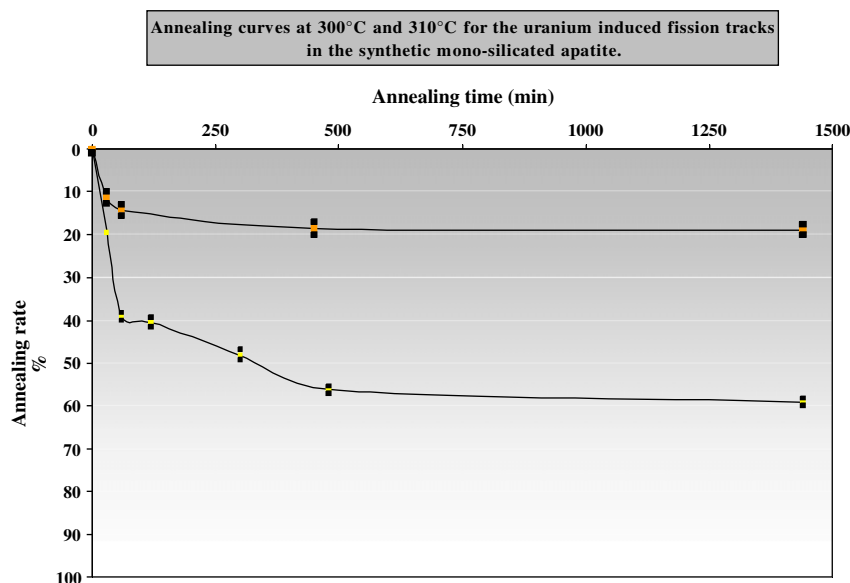


Fig. 4. Annealing curves for 300 (up) and 310 °C (down) of the induced fission tracks in the synthetic apatite.

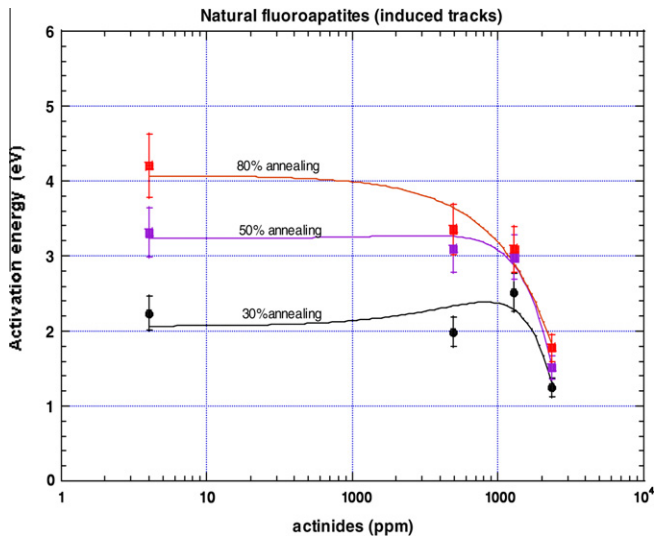


Fig. 6. Influence of the alpha dose from actinides (U and Th) in different natural apatites [5,9] on the activation energy for the thermal annealing of induced Fission tracks in natural apatites: when the actinide content is higher than 1000ppm, i.e. when the alpha damage is high, the activation energy is strongly lowered.

tites strongly lowers the value of the activation energy for the annealing of tracks. However, even if such a conclusion is plausible, we want to stay cautious as the two set of samples are not ideally similar.

6. Conclusion

Synthetic apatites have the ability to have their fission tracks annealed by thermal event as their natural analogues. From this work, we propose that the annealing rate of fission tracks in apatites is enhanced with the alpha damage sustained since their crystallization age. For a same thermal event, the annealing rate of the fission tracks in synthetic apatites, free of alpha damage, is lower than in natural apatites. This conclusion has to be taken into account by the fission tracks geochronologists, as it means that the

more the alpha dose sustained by the apatite lattice is high, the lower will be the closure temperature of the mineral, as observed in natural apatites with contrasted Fission Track ages in a same area [10]. From the point of view of the nuclear ceramist, the alpha damage sustained by the ceramic will be beneficial for a better behaviour towards irradiation damage from the wastes.

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