Autoradiography of geological fluorite samples for determination of uranium and thorium distribution using nuclear track methodology

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In this paper we present the uranium and thorium distribution analysis of several samples of the "La Azul", an epithermal fluorspar deposit in southern Mexico, using nuclear track methodology (NTM), in the alpha-autoradiography mode, by placing the mineral sample in contact with a polycarbonate detector. This constitutes a non-destructive analysis, with sufficient sensitivity to provide valuable information about textural and paragenetic characteristics of the geological samples. The selected nuclear track detector was CR-39 (Landauer®). The region of interest of the geological samples was polished and put in contact with the detector material surface for 45 days in a vacuum chamber (10^{-3} torr). After this period of time, the detectors were chemically etched, revealing the autoradiograph of the radioactive material. The results show a clear distribution of bands of uranium and thorium in the fluorite samples. This is valuable information for the genetic or geochronological studies of the ore deposits.

Keywords: Geochronology; autoradiography; alpha particles; fluorite; nuclear track detectors.

En este trabajo se presenta el análisis de la distribución de uranio y torio en varias muestras del depósito de fluorita de tipo epitermal denominado "La Azul", del sur de México, usando la Metodología de Trazas Nucleares (MTN), en la modalidad de autoradiografía por contacto entre la muestra del mineral y el material detector de policarbonato. Este procedimiento es un análisis no destructivo, con sensibilidad suficiente para aportar información valiosa acerca de la textura y características paragenéticas de las muestras geológicas. El material detector seleccionado fue el CR-39 (Landauer®). El área de interés de las muestras geológicas fue pulida y puesta en contacto con la superficie del material detector por 45 días en una cámara de vacío (10^{-3} Torr). Después de este tiempo, los detectores fueron atacados químicamente para revelar la autorradiografía del material radiactivo. Los resultados muestran una clara distribución de las bandas de uranio y torio en las muestras de fluorita. Esta información es muy valiosa para los estudios genéticos y geocronológicos de los depósitos minerales.

Descriptores: Geocronología; autoradiografía; partículas alfa; fluorita; detectores por trazas nucleares.

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1. Introduction

Several dating methods of geological samples are based on the natural radioactive disintegration of uranium and thorium [1]. This is the case of U-Pb and (U-Th)/He geochronometers. When selecting samples for dating with these methods, we need to know if the uranium and thorium of the minerals are distributed homogeneously as well as which are the zones in the sample with greater or lesser concentrations of these elements.

In the present work we use autoradiography with a CR-39 nuclear track detector to characterize the uranium and thorium distributions in fluorites that we want to use as a (U-Th)/He geochronometer from a fluorspar deposit in southern Mexico [2]. The samples used were all of fluorite in which the uranium and thorium were previously measured with Induced Coupled Plasma Mass Spectrometry (ICP-MS).

Uranium and thorium are found in the lattice of the fluorite (CaF_2) structure (Fm3m) due to the similarity of the ionic radius of these elements and calcium (Ca^{2+}: 0.99 Å, U^{4+}: 0.97 Å, Th^{4+}: 1.02 Å). However, when the fluid from which the fluorite precipitates contains tens of μg/g quantities of U and/or Th, these cannot be accommodated in the fluorite structure and inclusions of (U, Th)-rich minerals crystallize in fractures and growth faces.

The earlier solid state nuclear track detectors (SSNTD) were used in geological samples [3], but they were only able to record heavy particles such as those emitted by the fission of unstable isotopes and required the use of a thermal neutron reactor to induce fission of the ^{235}U isotope. In the seventies, the organic-based detectors were developed. They are able to detect neutrally charged, lighter particles. Basham and Easterbrook [4] considered that alpha autoradiography was better than the classical photographic methods. Duane and Williams [5] used nitrate–based nuclear track detectors to study the distribution of uranium in uranium-bearing samples. At the beginning of the eighties it was discovered that CR-39, used in the optics and the aerodynamics industry, was an excellent detector material for α-particles from the radioactive decays of U, Th and Rn with high efficiency in the range of 0.3 to 13 MeV, which is the range of energies of these natural radioisotopes. The applications and possibilities of the CR-39 have been increasing: in autoradiography it is one of the commonest, cheapest and most useful materials as Nuclear Track Detector (NTD) [6-8].

2. La Azul fluorite deposit

The La Azul deposit and other fluorite sources are located 10-15 km NE of the city of Taxco (Guerrero state, Mexico), at the eastern limit of the famous mining district (Fig. 1, Geology simplified from Morán-Zenteno *et al.* [9], Rivera *et al.* [10] and Alaniz-Álvarez [11]), which is one of the oldest localities mined since Hispanic colonial times in the Americas. The deposit is located in the vicinity of a fault that juxtaposes a Late Eocene-Early Oligocene volcanic succession and Cretaceous carbonate rocks from the Morelos Formation [12,13]. The main mineralization is related to the replacement of carbonates and is largely composed of fluorite, with variable amounts of calcite and quartz, and minor ones of barite, pyrolusite, pyrite and uraninite. The La Azul deposit is characterized by a great textural variety. The primary texture comprises several types of banded, massive and colloform fluorite in contact with carbonate. Breccias, nodules and fine layers of yellow or colourless fluorite are found as the latest generations.

3. Methodology

This method is based on the detection of the alpha particles from the natural radioactive decay products of ^{238}U and ^{232}Th.

TABLE I. Description of the polished hand samples used for autoradiography analysis.

Sample	Colour	Description	U μg/g	Th μg/g
A20	Purple	Sample with oriented and massive texture formed by dark purple fluorite. It presents porosity filled with late fluorite and clay minerals. With optical microscopy silica is found locally associated with fluorite as small inclusions.	68.5	0.68
Az5	Purple and brown	Sample with colloform and botryoidal texture. The fluorite is associated with carbonate replacement.	3.63	0.1
Az7	White and black	Sample with alternating centimetric bands of black and white fluorite.	4.83	0.34
T3	Purple	Calcite-cemented hydraulic breccia with angular clasts of early purple fluorite.	26.9	0.06

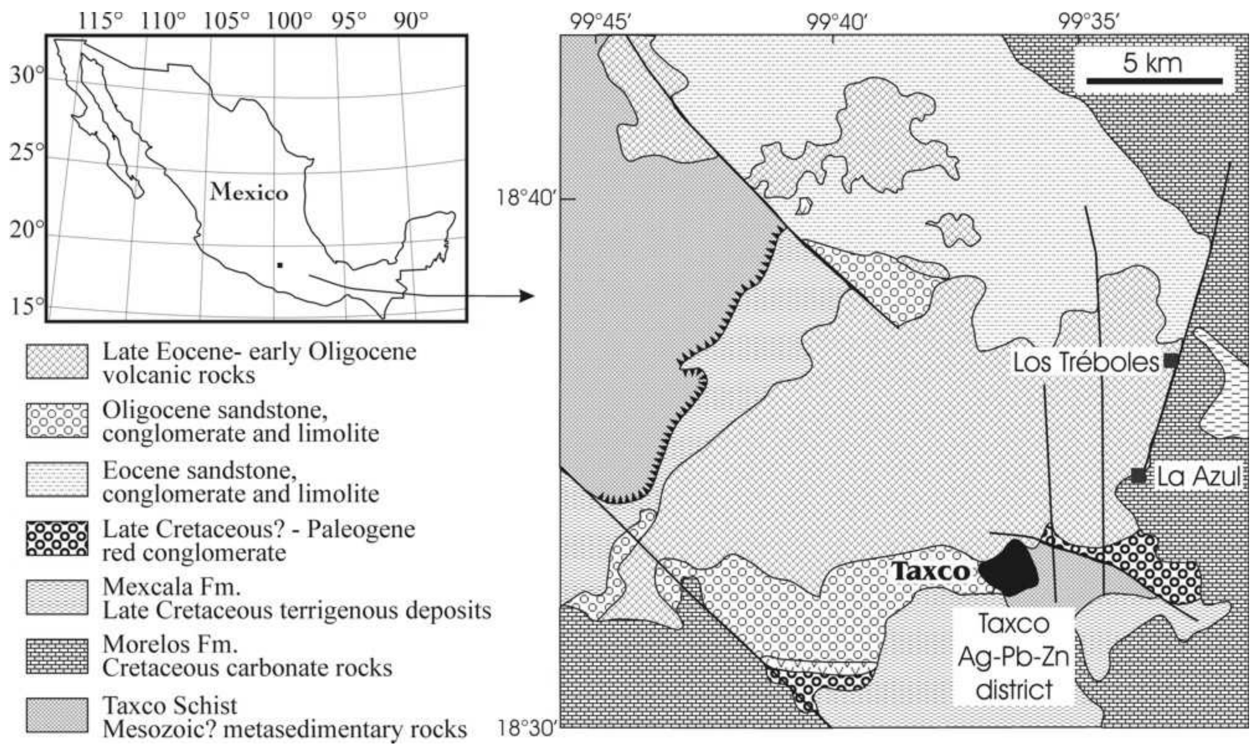

FIGURE 1. Geological map of the Taxco area. The deposits studied are located and named in the map.

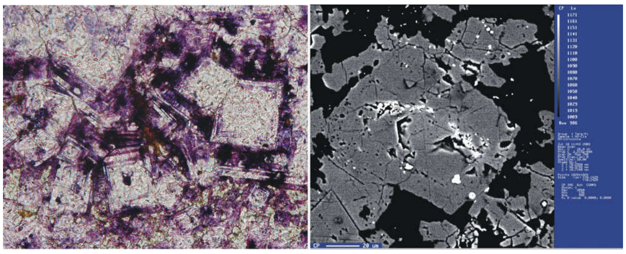

FIGURE 2. Uraninite crystals as shown by optical microscopy (left) and electron microprobe (right). Purple fluorite in optical image acquired its colour by the damage induced from radioactive uraninite. Bright spots on right image are uraninite (backscattered electron photograph).

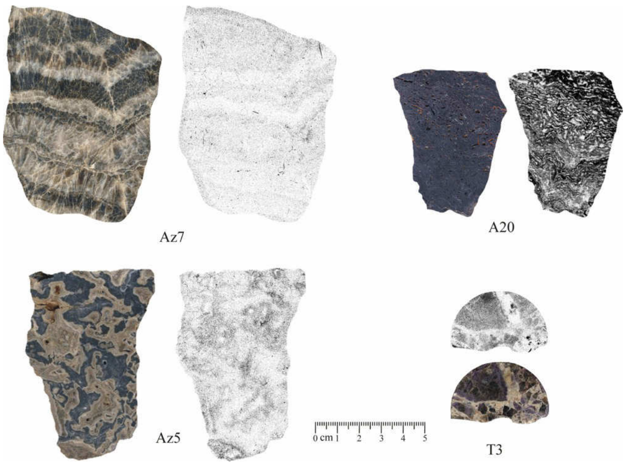

FIGURE 3. Photographs of hand specimens (left) and autoradiograph (right) of each sample after chemical etching (see text for explanation). White spots in photographs indicate the points where fluorite has been extracted and analyzed with ICP-MS for U and Th. The higher α-track densities appear as dark areas, and low α-track densities as light areas in the photographs.

Geological sample preparation: The selected fluorite samples need to be cut in order to show the natural bands of distribution of the U and Th. After the procedure, the cut surfaces need to be polished until they have a smooth surface. The CR-39 is cut in a convenient size and shape for each sample, a very important advantage of the nuclear track detectors. The detector material is placed in contact with the prepared sample surface. Later on, the samples together with the detectors are placed in a vacuum chamber at 10^{-3} torr, for a period of 45 days. After the exposure to radiation, the detectors are chemically etched in a 6M-KOH solution at 60$\pm$1°C. The time of etching was selected in five-hour intervals up to twenty hours. At each step the detectors were washed with distilled water for fifteen minutes and dried with absorbent paper, avoiding any mechanical damage to the detectors. The method was applied to rock samples with different concentrations of uranium. The results can be illustrated through the figures of the plastic detectors, showing very well-defined zones where the U and Th were deposited. This information is very valuable for the geological analysis of the rocks.

4. Results and discussion

Using optical microscopy and electron microprobe we determined that several inclusions in purple fluorite of La Azul are uraninite (UO_{2+x}, x between 0.25 and 0.3, see Fig. 2). The distribution of uraninite and the uranium found in the fluorite lattice can be mapped with the autoradiography samples and compared to macroscopic textures. In this work, four samples were analysed, and each one presents a very different kind of texture (breccias, massive, oriented and banded bodies). The samples analyzed are characterized by variable contents of uranium in the range $\sim$4μg/g to $\sim$70 μg/g and in all cases very low contents of thorium. The samples are described in Table I and shown in Fig. 3. All photographs are to the same scale. We can see that the autoradiograph reproduced the texture of every sample.

5. Conclusions

Fluorite is a common mineral in many classes of ore deposits of low and high temperature, and it is sometimes rich in uranium. Uranium and thorium distributions of the rock formations from alpha-autoradiography on geological samples, can give genetic information and the information for localization of adequate areas of isotopic dating sampling.

The use of autoradiography with plastic detectors is simple, low in cost, and do not require high technological facilities. The information of the radioactive material distribution is very valuable for the geochemical analysis in geological samples.

1. T. Pi, Unpublished PhD thesis, Universidad Nacional Autónoma de México (2005).
2. T. Pi, J. Solé, and Y. Taran. *Mineralium Deposita* **39** 976 .
3. J.D. Kleeman and J.F. Lovering, *Atomic Energy in Australia* **10** (1967) 3.
4. I.R. Basham and G.D. Easterbrook, *Inst. Mining Metallurgy Trans B* **86** (1977) 96.
5. M.J. Duane and C.T. Williams, *Econ. Geol.* (1980) 766.
6. K. Azkour, A. Nourreddine, J.C. Adloff, and A. Pape. *Radiat. Meas.* **31** (1999) 223.
7. F. Castillo, I. Gamboa, G. Espinosa, G. Somogyi, and A. Tapia. *Nuclear Tracks Radiat. Meas.* **8** (1984) 487.
8. K. Ogura, H. Yanagie, M. Eriguchi, T. Matsumoto, and H. Kobayashi. *Radiat. Meas.* **31** (1999) 389.
9. S.A. Alaniz-Álvarez, A.F. Nieto-Samaniego, D.J. Morán-

Zenteno, and L. Alba-Aldave *J. Volcanol. Geotherm. Res.* **118** (2002) 1.

10. D.J. Moran-Zenteno *Rev. Mexicana Cienc. Geol.* **15** (1988) 167.

11. E. Rivera *et al.*, *Carta Geológico-Minera Cuernavaca E14-5,* Consejo de Recursos Minerales, México, (1988).

12. K.F. Clark, *Geology and mineral deposits of the Taxco mining district. SEG guidebook series, Mexican Silver Deposits* **6** (1990) 281.

13. Z. De Cserna and C. Fries, Jr. *Carta Geológica de México,* hoja Taxco 14Q-h(7), scale 1:100,000, Instituto de Geología, Universidad Nacional Autónoma de México, 1981.