

# Mineralogical and geochemical characteristics of uranium-rich fluorite in El-Missikat mineralized granite, Central Eastern Desert, Egypt

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## Abstract

A unique, highly radioactive variety of fluorite mineral has been recorded in the uranium occurrence of El-Missikat sheared granite pluton. In this occurrence, the uranium assumes different forms, including its presence as discrete, visible, secondary minerals, rare uraninite and its association with the jasperoid and silica veinlets. However, in some other parts of the sheared zone, the uranium was found to be solely incorporated with fluorite crystals, filling veinlets and fractures without any other manifestation. This paper focuses on the relevant mineralogical and geochemical characteristics of this unique fluorite variety. In addition to an investigation with binocular and polarizing microscopes, the separated fluorite grains were analyzed using an environmental scanning electron microscope (ESEM) and a field-emission scanning electron microscope. In addition to this, some fluorite crystals were subjected to electron microprobe analyses. While the fluorite accounted for as much as 20 % of the sheared granite samples studied, it was found to range from 82 to 96 % in the different size fractions of the separated heavy mineral content. In some parts of the separated fluorite crystals, uranium in quantities of up to 2200 ppm was found to be heterogeneously distributed in the fluorite lattice, regardless of its coloration.

## Introduction

Several uranium occurrences have been discovered within or near the peripheries of some younger granitic plutons in the Eastern Desert of Egypt (Fig. 1). In almost all of these occurrences, the uranium mineralization is structurally controlled and represented by visible secondary uranium minerals that are yellow in color. Among these occurrences, the El-Missikat, El-Erediya and Gattar plutons are actually related to the uranium vein-type deposits. The El-Missikat granite pluton is located in the central part of the Eastern Desert, midway between Safaga on the Red Sea coast and Qena in the Nile Valley, at about 85 km from each (Fig. 2). The uranium mineralization (mainly uranophane) in the El-Missikat occurrence is associated with jasperoid veins found along the faults and fractures that are mainly filled with silica in typical shear zones (BAKHIT, 1978; ABU DIF, 1985; HUSSEIN et al., 1986; ABU DIF et al., 1997 & RASLAN, 2004). In addition, uraninite was identified by MOHAMED (1995) in some of the silica veins of the El-Missikat occurrence.

The intimate association of blue-to-violet fluorite with the secondary uranium mineralization is clearly evidenced in all the U-bearing granites in Egypt. According to SARCIA (1958), the presence of fluorite suggests the epigenetic hydrothermal origin of the uranium mineralizations. In his study

of the highly sheared granites of Wadi Belih in the Gattar pluton, RASLAN (1996) ascertained that the granites rich in secondary uranium minerals are usually rich in fluorite with a deep-blue to violet colour (RASLAN, 1996). On the other hand, most of the previous studies on the El-Missikat uranium occurrence have attributed the radioactivity to the visible secondary uranium minerals associated with the siliceous veins. However, apart from these mineralized siliceous veins, visible deep-blue to violet fluorite crystals were recorded in other parts of El-Missikat, highly sheared mineralized granite that are very strongly radioactive, but without any visible uranium mineralization (Fig. 3A). In such parts, it was actually revealed that the fluorite crystals are responsible for the high levels of recorded radioactivity. These fluorite crystals do indeed occur as disseminations, veinlets, fractures and cavity filling in the sheared granite (Fig. 3B). This mode of uranium occurrence was recorded for the first time and must be considered during any prospecting for uranium in the granitic rocks of Egypt. At the same time, this behaviour should be taken into consideration for any elucidation of the uranium genesis in the granitic and related rocks. On the other hand, the presence of radioactive fluorite in the granitic and associated feldspar rocks that could be used in the ceramics industry in Egypt might have an environmental impact. Physical upgrading of the

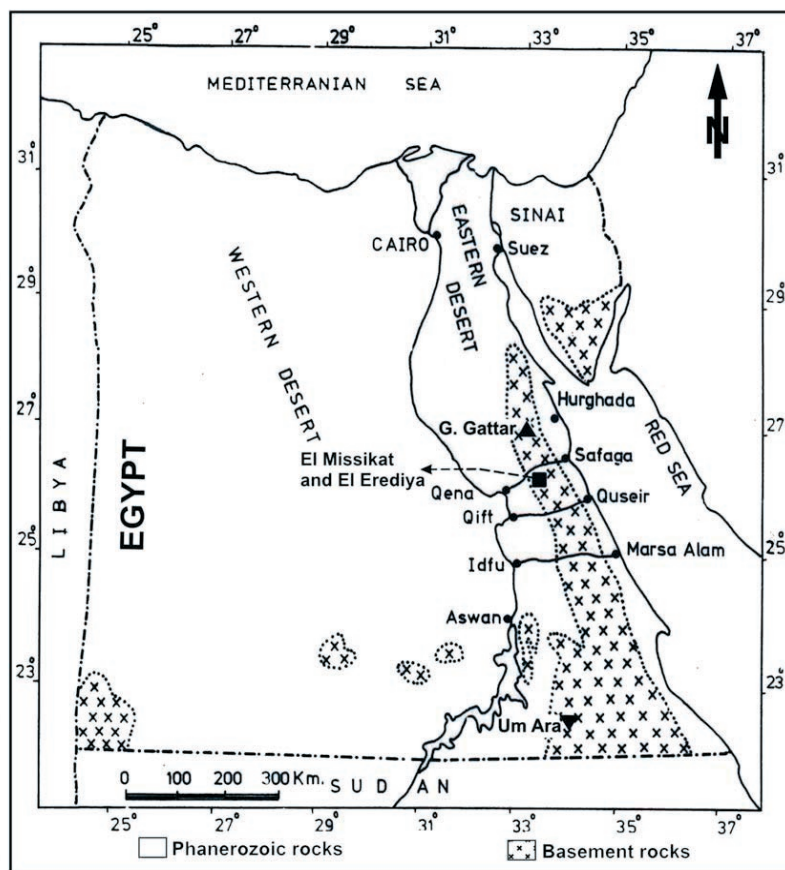


Fig. 1. Location map of the uranium occurrences in younger granites.

studied radioactive fluorite was carried out using gravitative and magnetic separation techniques (RASLAN, 2008).

A systematic study was thus undertaken to define the mineralogical and geochemical characteristics of the El-Missikat's highly radioactive,

fluorite-rich granite. For this purpose, field, petrographical and mineralogical as well as geochemical studies have been performed for the representative bulk rock samples as well as for the separated accessory heavy minerals.

### Sampling and techniques

Four grab samples representing the highest values of anomalous field radioactivity and visible deep-blue to violet fluorite were collected from the jasperoid shear zone of the El-Missikat granite pluton. The equivalent uranium and thorium contents of the collected samples (Table 1) were measured using a Gamma-ray spectrometric technique. The application of the alpha-tracks technique (autoradiography) was based on using  $\alpha$ -particle-sensitive films. The separation of the heavy accessory minerals from the radioactive fluorite-rich granite was carried out by bromoform (sp. gr. 2.85 gm/cm<sup>3</sup>) after proper crushing, desliming and sizing to estimate the distribution and abundance of the heavy minerals among the various grain size fractions. On the other hand, for the petrographic study, six

thin-polished sections were prepared (three for the rock and three for the separated heavy accessory minerals). The latter was achieved using a Nikon (Optiphot-Pol) polarizing microscope equipped with an automatic photo-micrographic attachment (Microflex AFX-II). The distribution of the

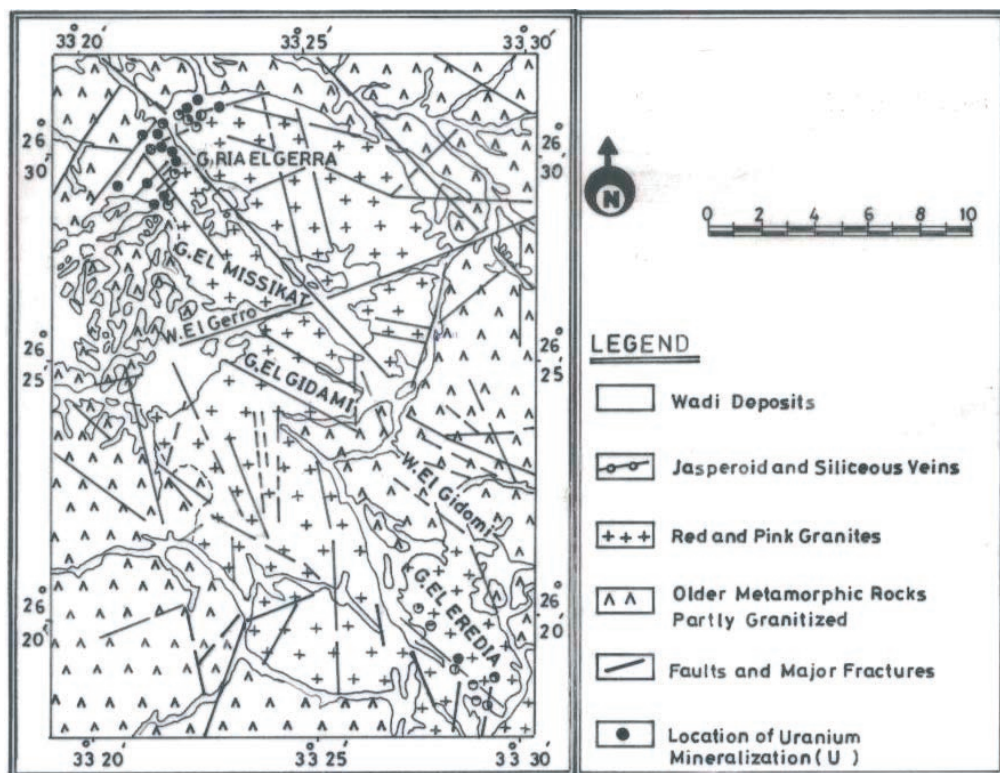


Fig. 2. The main granitic masses of El-Missikat-El Erediya area showing the radioactive veins and the major structural lines, after BAKHIT and EL KASSAS (1989)

Table 1. Equivalent uranium and thorium contents of El-Missikat fluorite bearing-granite

Sample No.	eU (ppm )	eTh (ppm)	eTh/eU	Description
1	1975	239	0.12	Highly radioactive channel grab samples collected from highly sheared granite with visible blue-violet fluorite crystals and without visible secondary uranium minerals.
2	1831	320	0.17	
3	1524	53	0.03	
4	925	80	0.09	

heavy accessory minerals among the various size fractions was determined using a counting technique under a binocular stereomicroscope.

The studied samples were then analyzed using a field-emission scanning electron microscope (JEOL 6335F). The JEOL 6335F can be described as a cold field-emission scanning electron microscope. Such cold field-emission microscopes have the advantage of a high level of brightness (large current density) and a small beam diameter (high resolution) at low accelerating voltages to allow the imaging of soft polymeric materials without causing any damage to the sample. The resolution of the instrument is around 15 Angstroms, depending on the particular sample. This instrument has an Oxford Instruments energy-dispersive X-ray spectrometer (EDS) for the elemental analysis of the micro-areas, a backscattered-electron detector that allows compositional analysis, and a cathode luminescence detector that can image complex, characteristic, visible spectra for detailed molecular structure information. The analytical conditions were a 0.5–30 accelerating voltage, 1.5 nm (at 15 kV) / 5.0 nm (at 1.0 kV). The magnification was 10X to 500,000X with a digital image up to 2048 x 2048 pixels, and 1280 x 1024 pixels for the display image. The imaging modes were secondary-electron imaging (SEI) and backscattered-electron imaging (BSI). The studied samples were also previously analyzed using an environmental scanning electron microscope (ESEM) in a laboratory of the Nuclear Materials Authority, Egypt. The latter is a Philips Model XL 30 that is supported by an energy-dispersive X-ray (EDAX) Unit.

Finally, the prepared thin-polished sections were analyzed using a JEOL SUPERPROBE 733 with an accelerating voltage of 15 kV and a beam size of approximately 1 micron. The crystals used for the elemental analyses were TAP (Thallium acid phthalate), PET (Pentaerythritol) and LiF (Lithium Fluoride). The standards were monazite (Th-Ce-La), uranium metal (U), fluorite (Ca-F), cubic zirconia (Y), europium fluoride (Eu), gadolinium (Gd), ytterbium (Yb) and lutetium fluoride (Lu).

### Petrography

In thin sections of the studied sheared granite, fluorite crystals were found in an abundant amount, distributed all over the sections and more so side by side with increasing shearing of the granites. They are characterized by high relief, cracking and isotropism. These crystals are distinguished by their deep-blue to violet color and are present in various grain sizes, ranging from fine to

coarse grains. Besides occurring as interstitial grains between the perthite, quartz and opaques, the fluorite crystals are mainly recorded as filling microfractures and cavities in the highly sheared granite, which reflects their late origin as a result of the hydrothermal alteration of the granites (Figs. 3C, D and E). The deep-violet fluorite crystals are closely associated with iron oxides (Fig. 3F) and show more intensive  $\alpha$ -tracks (Fig. 3G).

### Mineralogical investigation

A representative bulk sample was subjected to crushing, desliming, sizing and heavy liquid separation using bromoform to investigate the contents and the distribution of the heavy accessory minerals within the various size fractions. A microscopic examination was then carried out for the various size fractions.

A mineralogical investigation of the obtained accessory heavy minerals revealed that the radioactive fluorite represents about 20 %, by weight, of the original rock sample. The contents of heavy and accessory minerals were determined using the counting technique. The obtained results are presented in table (2), where the fluorite was found to range from 88.40 to 96.40 % in the different sizes of the obtained heavy fractions, with the rest represented by minor amounts of magnetite, hematite and mica.

The fluorite occurs as colored transparent crystals, and represents the main constituent of the bulk heavy minerals. They are present as cubes and are characterized by a vitreous luster. The majority of the fluorite crystals occur as multicolored or as blue to violet, to relatively black; however, some crystals are colorless and were noticed to have internal colored zones. On the other hand, some of the blue-violet to deep-blue-violet fluorite crystals were found to contain black inclusions (Fig. 3H). The presence of uranium in the investigated fluorite is clear from the intensive  $\alpha$ -tracks developed on the cellulose covers of the thin sections of that granite.

Table 2. Heavy mineral contents of the various size fractions of the highly sheared granite of El-Missikat

Mineral % Size (mm)	Fluorite	Hematite	Magnetite	Mica
- 0.800 + 0.600	88.40	4.20	3.75	3.65
- 0.600 + 0.400	90.20	3.10	3.90	2.80
- 0.400 + 0.200	94.00	2.20	2.00	1.80
- 0.200 + 0.045	96.40	1.00	1.30	1.30



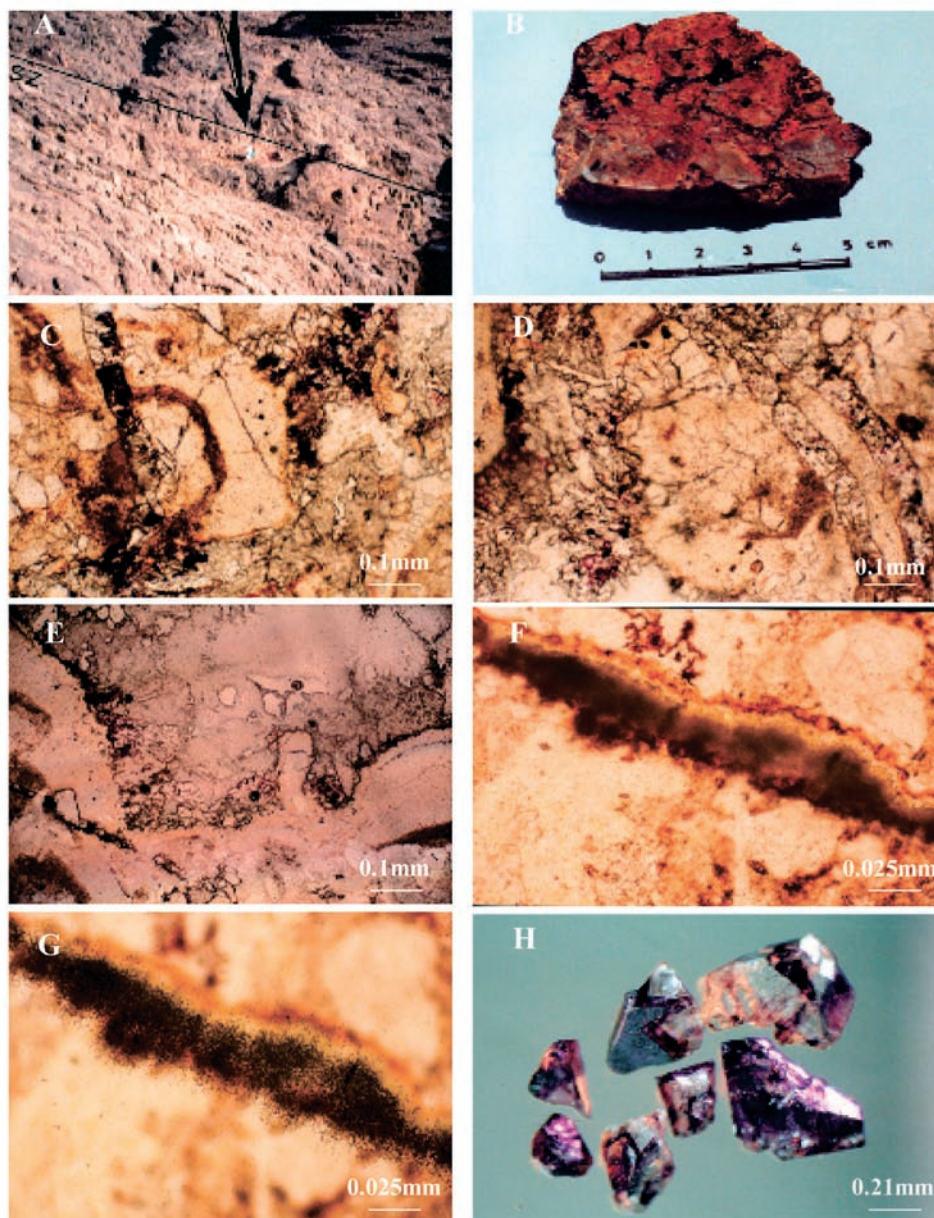


Fig. 3.

A - Trench dug along the shear zone in Gabal El-Missikat. N.B: The Arrow is pointing to the trench.

B - Close-up photograph showing El-Missikat radioactive granite with visible veinlets of blue fluorite crystals.

C, D & E - Deep-blue to violet fluorite occurs as a cavity and fracture filling, Polarized Light (P.L.), El-Missikat highly sheared radioactive granites.

F & G - Fracture filled with blue fluorite crystals, Polarized Light P.L., and its corresponding alpha tracks.

H - Blue-violet fluorite crystals with different gradation, and some with internal radioactive black inclusions. Binocular microscope.

#### Environmental Scanning Electron Microscope

Semi-quantitative analyses using the ESEM technique were carried out for both fluorite veinlets and the separated fluorite crystals containing black inclusions. The purpose was to determine the chemical composition of these inclusions as well as that of the fluorite in various color zones within the same crystal.

#### Radioactive fluorite disseminations and veinlets

The disseminated and veinlets of the deep-blue to violet fluorite in the studied rock samples (Figs. 4 A, B) were analyzed using ESEM. The obtained data (Fig. 4C) for these veinlets reflected the chemical composition of the fluorite together with the uranium, ranging from 3.11 to 4.99 wt. %. These results proved that fluorite is the main source of radioactivity in the studied rock and in agreement

with the intensive alpha-tracks that were microscopically found on the cellulose covers of thin sections of that granite.

#### Radioactive colored-fluorite crystals

Several radioactive colored-fluorite crystals containing black inclusions together with color bands (Figs. 4D, E) were subjected to ESEM microanalyses. An ESEM image (Fig. 4F) and two EDAX spectra for the black inclusion and in the deep-blue to violet zones within the same fluorite crystal are presented in (Figs. 4G, H) respectively. The analyses of the inclusions in the fluorite show the presence of a strong peak of iron (5.68, 44.82 and 7.94 wt.%) together with the elemental composition of the fluorite. The analyses of the colored and colorless zones in the fluorite show that it basically consists of Ca and F, with appreciable amounts of uranium (2.66, 3.13 and 3.31%).



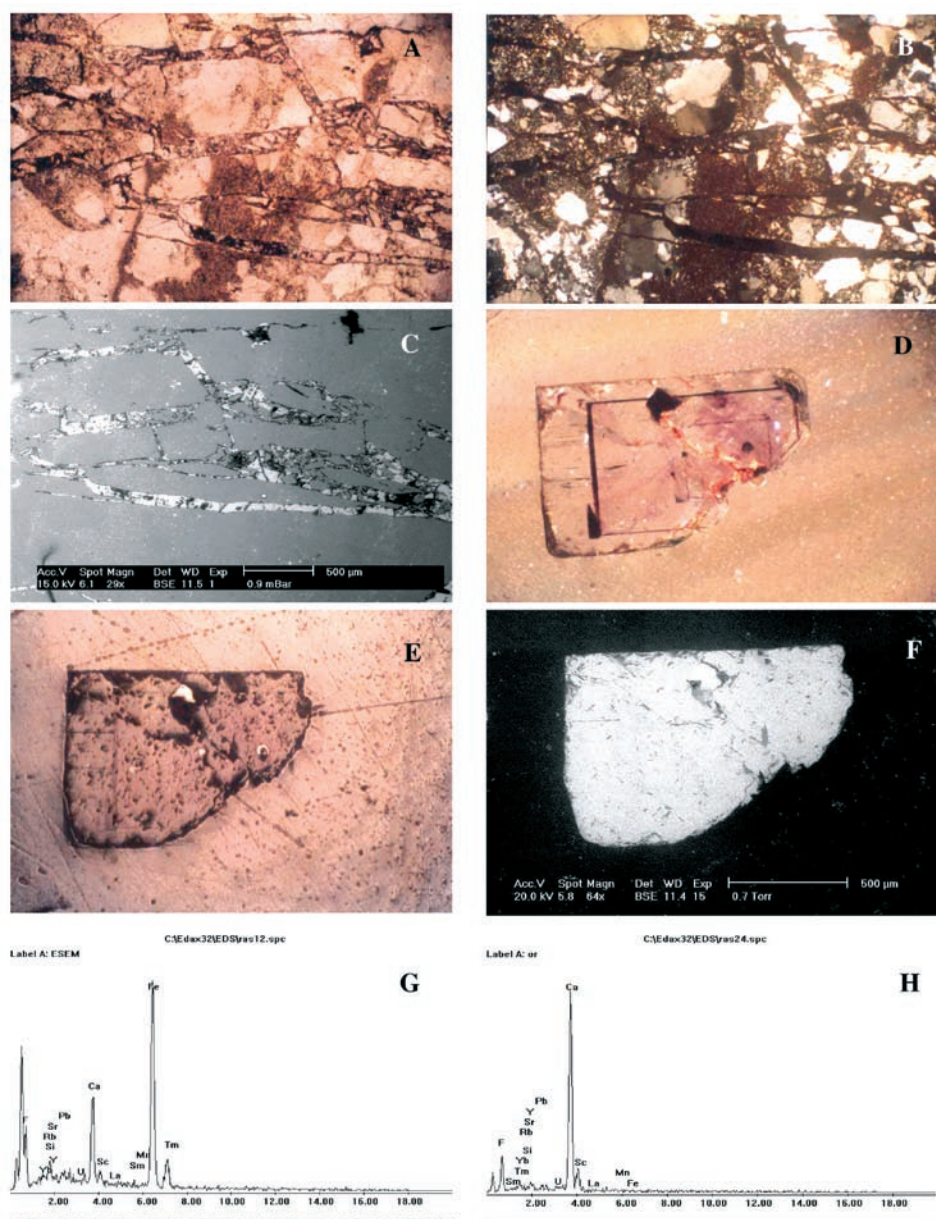


Fig. 4.

A - Deep-blue-violet fluorite found in the form of fissures and fracture fillings, Polarized Light PL.

B - The same as previous photograph but between the crossed nicols.

C - Back-scattered SEM image for the previous photograph.

D, E & F - Photomicrographs showing separated blue-violet fluorite crystal with different gradation, internal color zones and black inclusions in polarizing and reflected light respectively.

G & H - EDX spectra for inclusion and fluorite crystal.

### Field-Emission Scanning Electron Microscope

SEM analyses using the field-emission scanning electron microscope (JEOL 6335F) were carried out for the pale violet zones in the fluorite crystals and their inclusions (Figs. 5A-B). In addition, a scan map was obtained for the same crystals. These results confirm the chemical composition of the fluorite and reflect the nature of the inclusions inside the fluorite. It was found that the inclusion is basically composed of silicate, as indicated from the scan map and the EDX analyses (Figs. 5C, D, E and F). Accordingly, it is clear that the inclusions inside the fluorite are mainly free from uranium and composed mainly of Si or Fe.

### Electron Microprobe Analyses

The studied fluorite crystals were analyzed using a JEOL SUPERPROBE 733. The obtained

results (Figs. 5G&H) and Table (3) reflect the presence of uranium in the fluorite. The uranium content ranged from 0.10 to 0.22 wt.%, with an average of 0.06 %, and the thorium ranges from 0.25 to 0.75 wt.%, with an average of 0.25 %. These results indicate that the radioactivity in the fluorite results from the uranium and thorium atoms, and that the studied crystals are enriched with Th rather than U. The distribution of U and Th atoms is heterogeneous in the crystal lattice of the studied fluorite, regardless of the coloration. The average contents of rare-earth elements in the investigated fluorite were as follows: Y, (0.34 wt.%), La, (0.038 wt.%), Ce, (0.10 wt.%), Eu (0.15 wt.%), Gd (0.18 wt.%), Yb, (0.21 wt.%) and Lu (0.20 wt.%). The obtained EMPA data cannot support any direct relation between the rare-earth element contents and the origin of the coloration of the fluorite.

Concerning the origin of the blue-violet color in the fluorite, RASLAN (1996) revealed that the XRD data of the colorless, blue-violet and deep-blue-

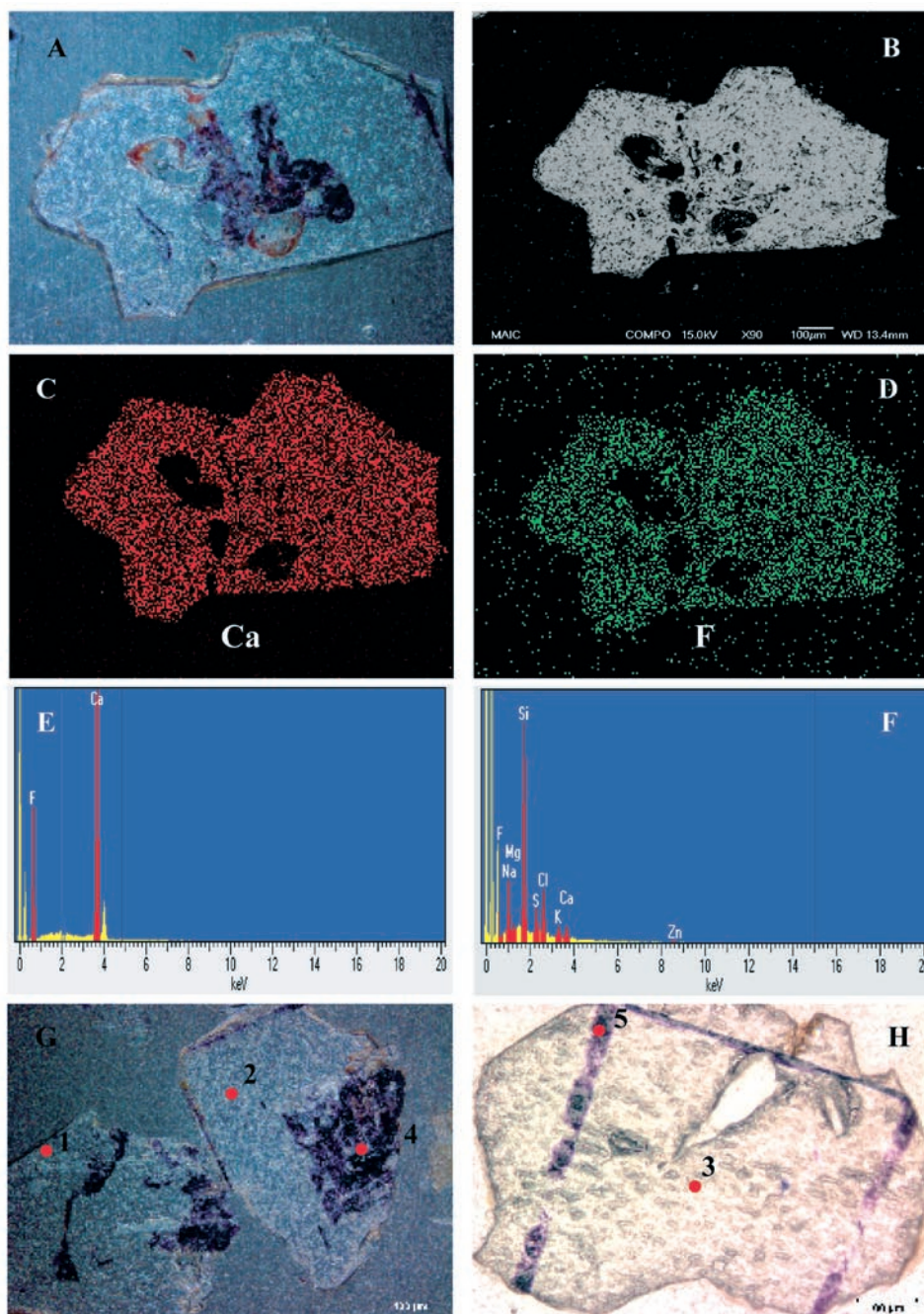


Fig. 5.

A - Blue to violet fluorite crystal with silicate inclusions, Polarized Light (PL).

B - SEM backscattered image for the same crystal.

C & D - Scan map for Ca and F respectively.

E & F - EDX spectra for fluorite and its inclusion.

G & H - Fluorite crystals with internal color bands and location of EMPA analyses within the crystals, Polarized Light (PL).

violet fluorite are usually very similar, indicating that the color is not affected by any organic or inorganic impurities, but mostly connected with the irradiation of the associated uranium minerals. Moreover, RASLAN (2000) indicated that a remarkable bleaching was noticed after annealing at 300 °C for 8 hours. Also, the XRD analyses for the blue-violet and deeply colored fluorite varieties after annealing confirmed a remarkable variation in some x-ray reflections, represented by an increase in the x-ray line intensity and the appearance of the doubling of some reflections (Fig. 6). This variation indicates an ordering of the crystal lattice (BERMAN, 1957). However, EL-KAMMAR et al. (1997) remarked that the change in the color in the fluorite is controlled by the Y content, in particular, and the Y group, in general.

Several workers attributed the color of the fluorite to the effect of radioactivity (DEER et al.,

1962; MACKENZI & GREEN, 1971; NASSAU & PRESCOTT, 1977; RASLAN, 2000 & EL-MANSI, 2000). The obtained EMPA analyses for the different shades of fluorite clearly indicate that the colors of the fluorite are mostly due to a disturbance in its crystal lattice, due to the radiogenic effect of the associated secondary uranium minerals present in the El-Missikat uranium occurrence, rather than as a result of any variations in their chemical composition.

### Origin of radioactive fluorite

Field, petrographic and mineralogical investigations as well as SEM and EMPA analyses for the fluorite in both the studied radioactive granite and the separated colored fluorite crystals resulted in the following points:



Analyses No.	Colorless 1	Colorless 2	Colorless 3	blue-violet 4	blue-violet 5
<b>U</b>	0.10	0.10	0.00	0.00	0.22
<b>Th</b>	0.00	0.25	0.75	0.00	0.00
<b>Y</b>	0.00	0.22	0.00	0.00	0.89
<b>Ca</b>	55.95	52.38	51.65	54.41	51.67
<b>F</b>	43.08	44.28	45.67	43.62	46.73
<b>La</b>	0.01	0.06	0.03	0.08	0.00
<b>Ce</b>	0.24	0.00	0.18	0.17	0.00
<b>Eu</b>	0.16	0.22	0.08	0.15	0.13
<b>Gd</b>	0.19	0.00	0.36	0.33	0.00
<b>Yb</b>	0.25	0.12	0.29	0.59	0.11
<b>Lu</b>	0.00	0.57	0.01	0.00	0.42
<b>Total</b>	99.98	98.20	99.02	99.35	100.17

Table 3.  
Selected EMPA  
analyses of  
El-Missikat  
radioactive  
fluorite

- 1 – It is quite clear that the studied fluorite crystals are strongly radioactive due to the presence of uranium and thorium in the crystal lattice of the fluorite.
- 2 – The lack of both secondary uranium minerals and uranium-bearing accessory minerals, such as zircon and monazite, in the studied radioactive granite as indicated from field observations and mineralogical examinations, proved that fluorite is the main radioactive mineral responsible for the strong radioactivity in the studied granite.

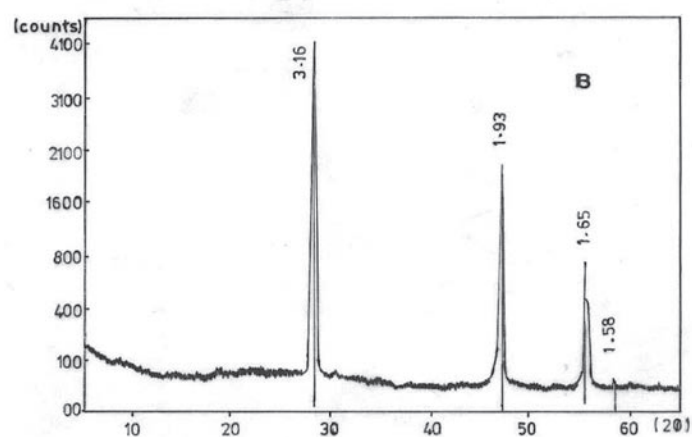
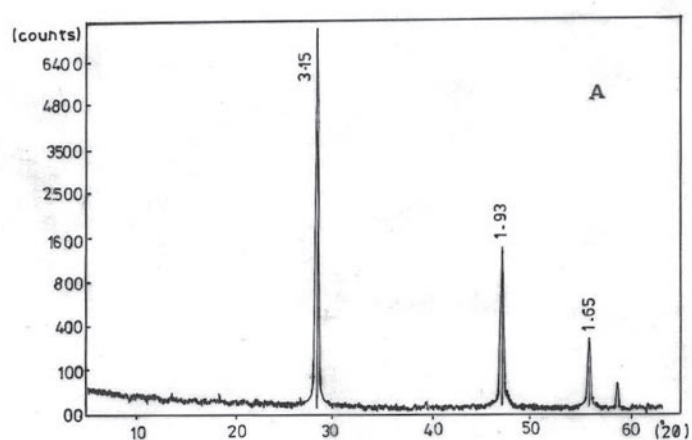


Fig. 6. XRD charts for separated blue-violet fluorite. (After RASLAN, 2000).

A - Before annealing,  
B - After annealing.

- 3 – It was found that iron is the main constituent in the chemical composition of the black inclusions in the fluorite together with the high uranium content and the normal elemental composition of the fluorite.
- 4 – The radioactivity in the fluorite is due to the presence of uranium and thorium elements in the crystal lattice of the fluorite and not due to the presence of primary radioactive mineral in the core of the fluorite.
- 5 – The presence of uranium in the fluorite is most probably the result of the ability of the fluorine ion to form an ionic complex with uranium as uranyl fluoride, which is important in the transport of uranium in acidic fluids. The presence of any available  $\text{Ca}^{+2}$  leads to the formation of fluorite; a matter which prevents uranium migration, as cited by LANGMUIR (1978).
- 6 – Also, uranium may substitute for calcium in the fluorite mineral structure due to the similarity of their ionic radii ( $\text{Ca} = 1.06\text{\AA}$ ,  $\text{U} = 1.05\text{\AA}$ ).
- 7 – The origin of the radioactive anomalies associated with fluorite-bearing granites in jasperoid veins can be interpreted in the scope of the hydrothermal origin, as indicated by: a) the presence of fluorite mineralization with jasperoid veins, which are mainly of hydrothermal origin; b) the presence of fluorite, which suggests the epigenetic hydrothermal origin of the mineralization (SARCIA, 1958).
- 8 – The absence of both uranium-bearing accessory minerals and secondary uranium minerals can be attributed to the lack of leached uranium in the circulating solutions and also to the absence of uranium leaching from the fluorite crystals.

## Conclusions

Highly radioactive fluorite-bearing granite was recorded in the jasperoid veins of the highly sheared granite of the El-Missikat pluton, but without any visible secondary uranium minerals. The studied fluorite occurs as blue-to-violet crys-

tals disseminated in the granite as well as in the form of veinlets, fractures and cavity fillings. Petrographic and mineralogical investigations revealed that the fluorite represents the main constituent of the total accessory heavy minerals in the studied radioactive samples. The presence of uranium and thorium in the crystal lattice of the fluorite is clear from the SEM and EMPA analyses. This mode of uranium occurrence must be considered during uranium prospecting in the granitic rocks of Egypt.

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