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Solid Inclusions in a Fluorite Variety from the Wölsendorfer Range (Bavaria, Fed. Rep. Germany)

By *Renaud F. C. Vochten**) and *Joris F. Geys***)

Abstract

Solid inclusions in the dark purple variety of fluorite, commonly known as “Stinkfluss”, mainly consist of U and Fe compounds. These inclusions are concentrated along cleavage planes in the fluorite. They are often surrounded by halo's and radiation belts, which diameters show to correspond with the ranges of α -particles, originating during the decay of uranium.

1. INTRODUCTION

The occurrence of solid as well as gaseous and fluid inclusions in many fluorite varieties is well known.

Fluid inclusions in fluorite generally consist of aqueous solutions of NaCl and KCl, in which the salinity can vary considerably. F. SMITH (1973) characterized some fluorite samples considering the Na/K-ratio's in their fluid inclusions.

A well known dark purple to almost black variety of fluorite from the Wölsendorfer range contains large amounts of gaseous inclusions. Crushing or breaking of the fluorite releases gases; their smell suggests the presence of halogenides.

R. VOCHTEN and E. ESMANS (1976) investigated these gaseous inclusions by high resolution mass spectrometry. The presence of H_2S , SO_2 , SOF , SOF_2 , S_2F_2 , S_2F and SF was detected, as has been stated in their paper.

The genesis of these fluor containing compounds is closely related to the occurrence of solid radioactive inclusions.

Through radiation the fluorite lattice may be locally destroyed and F_2 -gas could be released. Almost instantly this gas can react with other substances

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already present to form the higher cited products. The nature and the distribution of these solid inclusions were investigated and are discussed in this paper.

2. DESCRIPTION OF THE SAMPLES

Samples were taken in the fluorite mine "Marienschacht" at Wölsendorf, Oberpfalz, Bavaria, Federal Republic of Germany. The analyses were carried out exclusively on the dark purple or almost black variety, famous for its smell when crushed, and which, for that reason is called "Stinkfluss" by the local miners.

Accessory minerals recorded were quartz, galena, barite, autunite and iron-oxydes. In many cases quartz forms a separate phase, sometimes intensely interwoven with the fluorite phase. Sometimes fluorite is so completely supplanted by quartz that a pseudomorphosis is observed.

3. GEOCHEMICAL CONSIDERATIONS

Most semi-quantitative analyses were carried out by means of UV-emission spectrography. The yttrium content of the samples however, was determined by X-ray fluorescence.

All the samples contain considerable amounts of Fe and Si. Both attain 1% each. The bulk of these elements must be contributed to impurities of quartz and hematite.

Table I summarizes the data obtained for some important elements. The relatively low Y-grade of this fluorite variety is striking, when compared to other fluorites. Indeed F. SMITH and D. HIRST (1974) mention Y-contents of 75 to 325 ppm in Cornish fluorites and 120 to 815 ppm in fluorite samples from the Pennines, England. The Y-content of the Wölsendorfer fluorites are rather comparable to those of fluorites from Derbyshire (0-38 ppm), Durham (22-53

Table I. *Semi-quantitative geochemical composition of the Wölsendorf fluorite*

Element	content in ppm
Al	600-2000
U	100-500
Mg	100-300
Pb	30-150
Mn	30-100
Be	30-100
Cu	20-80
Bi	10-30
Ca	10-30
V	5-20
Y	3-10

ppm) or the Belgian Ardennes (9–25 ppm) (F. SMITH and D. HIRST, 1974), though it is obvious that the mean Y-content at Wölsendorf remains inferior to all others mentioned.

4. OPTICAL MICROSCOPY

To enable the investigator to study the inclusions microscopically, some thin sections were made.

The radioactive solid inclusions mainly occurred in the fluorite phase. They are surrounded by distinct radiation belts.

Most of these inclusions have an estimated diameter of $\pm 3 \mu\text{m}$. Many of them are located along cleavage planes in the fluorite. This permits to state, agreeing with R. HOFMANN (oral communication), that the radioactive inclusions are younger than the fluorite itself.

A photograph of such solid inclusions, surrounded by their circular, concentric radiation belts, is shown in fig. 1.

The dark purple tone of the fluorite could be due to the presence of stable colour centers, possibly induced by radioactive radiation. This subject will be more amply discussed in § 6. Parts of the lattice, which are intensely irradiated, can be isotropized. This can frequently be seen around the radioactive inclusions as paler or even colourless halo's.



Fig. 1. Concentric radiation belts, surrounding a radioactive solid inclusion in the fluorite phase.
Dash = $10 \mu\text{m}$.

In this context, a remark of K. PRZIBRAM (1953) can be cited, who stated that, as a consequence of the damage to the lattice, internal stresses are generated which cause a slight double refraction. Increased damage can lead to a complete destruction of the lattice, creating isotropic, spherical zones surrounding radiocative inclusions. Such isotropic spheres could indeed be observed in the studied samples.

The concentric radiation belts correspond to the ranges of the different α -particles, which originate during the decay of uranium. These belts are a little diffuse, owing to the fact that the range of α -particles, with the same amount of energy, is never exactly the same. This phenomenon is known as the stragling of α -particles ranges, caused by statistical fluctuations in their amount of collisions, and by a certain loss of energy in each collision.

Table II. *The range R of the α -particles emitted by different isotopes of the U decay series, in air, at 15°C, compared with the relative radii of the observed radiation belts in the Wölsendorf fluorites*

Data partly according to I. PERLMAN and T. YPSILANTIS (1950)

Isotope	E_{α} 10 ⁶ eV	λ sec ⁻¹	R_{air} cm	R_{fluorite} μm
U_{92}^{238}	4.25	$4.8 \cdot 10^{-18}$	2.67	11.7 ± 1
U_{92}^{234}	4.75	$7.4 \cdot 10^{-14}$	3.12	14.6 ± 3
Th_{90}^{230}	4.67	$2.6 \cdot 10^{-13}$	3.19	
Ra_{88}^{226}	4.88	$1.4 \cdot 10^{-11}$	3.39	
Po_{84}^{210}	5.40	$5.7 \cdot 10^{-8}$	3.87	19.7 ± 1.5
Rn_{86}^{222}	5.59	$2.1 \cdot 10^{-6}$	4.12	
Po_{84}^{218}	6.11	$3.8 \cdot 10^{-3}$	4.72	23.4 ± 1
Pb_{82}^{214}	7.83	$4.1 \cdot 10^5$	6.96	35.1 ± 1

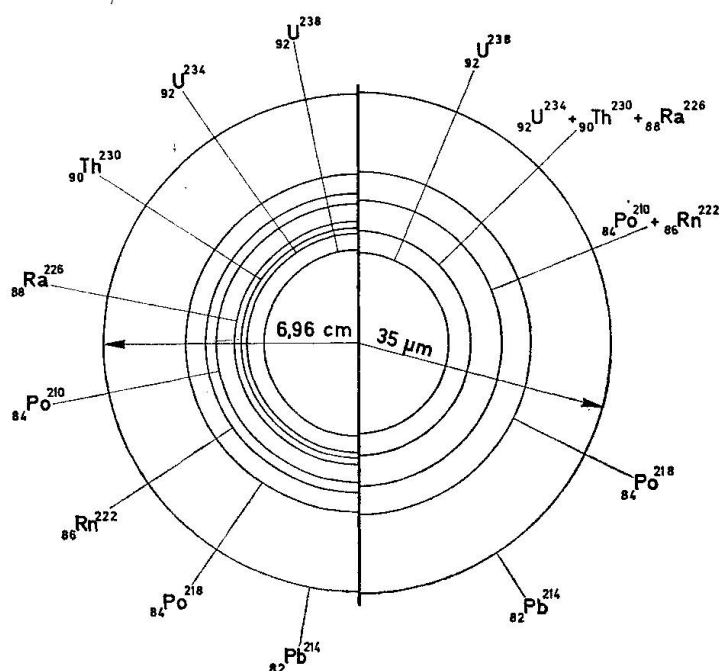


Fig. 2. Ranges of α -particles, emitted by the different isotopes of the U-decay series in air, at 15°C (left half), compared to those observed in fluorite (right half). The right half of the figure is exaggerated 2000 \times in size, with respect to the left half.

In table II, the range R of the α -particles from the different isotopes of the U decay series, in air, at 15°C , is compared to the relative radii of the observed radiation belts in the Wölsendorfer fluorites. Fig. 2 illustrates graphically the data from this table.

Plotting the energy E_α against the ranges R_{air} and R_{fluorite} , linear relationships can be observed. From the slope of both straight lines, the loss of energy per unit of distance can be calculated for air and fluorite respectively:

$$\begin{aligned} -\left(\frac{dE_\alpha}{dl}\right)_{\text{fluorite}} &= 1.5 \cdot 10^5 \text{ eV} \cdot \mu\text{m}^{-1}, \\ -\left(\frac{dE_\alpha}{dl}\right)_{\text{air}} &= 81 \text{ eV} \cdot \mu\text{m}^{-1}. \end{aligned}$$

These data demonstrate that α -particles lose 1850 times more energy crossing the same distance in fluorite than in air.

5. ELECTRON MICROPROBE ANALYSIS

In some samples the elements Ca, Si, U, Fe, Ba and Pb were examined by means of an electron microprobe apparatus JEOL J-XA-50 A. The goal of this analysis was to evaluate the distribution of these elements through the fluorite and the quartz phases.

The specimens were thus prepared: trim sawed slabs were embedded in araldite resin, which was allowed to harden for 24 hours. After polishing the surface it was coated by a coal layer of a few Angströms, to render it conducting.

The energy of the electron beam remained constant at 25 kV, while the absorbed current was $2 \cdot 10^{-8}$ A. P.E.T. was used as a diffraction crystal while recording Ca, Fe and U, and R.A.P. while measuring Si.

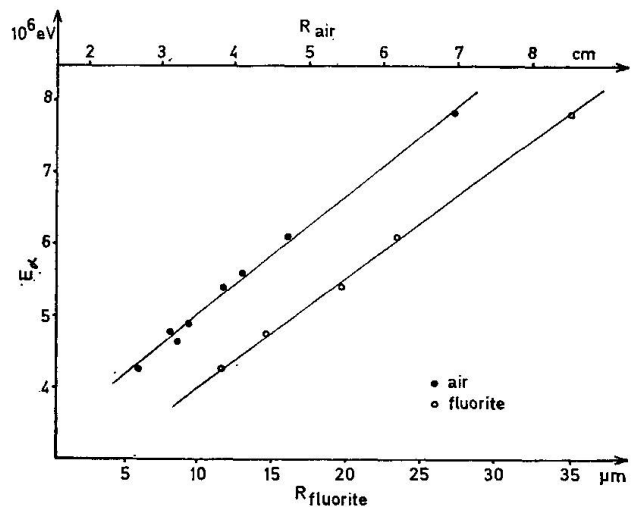


Fig. 3. Combined E_α -R-plots for air and fluorite.

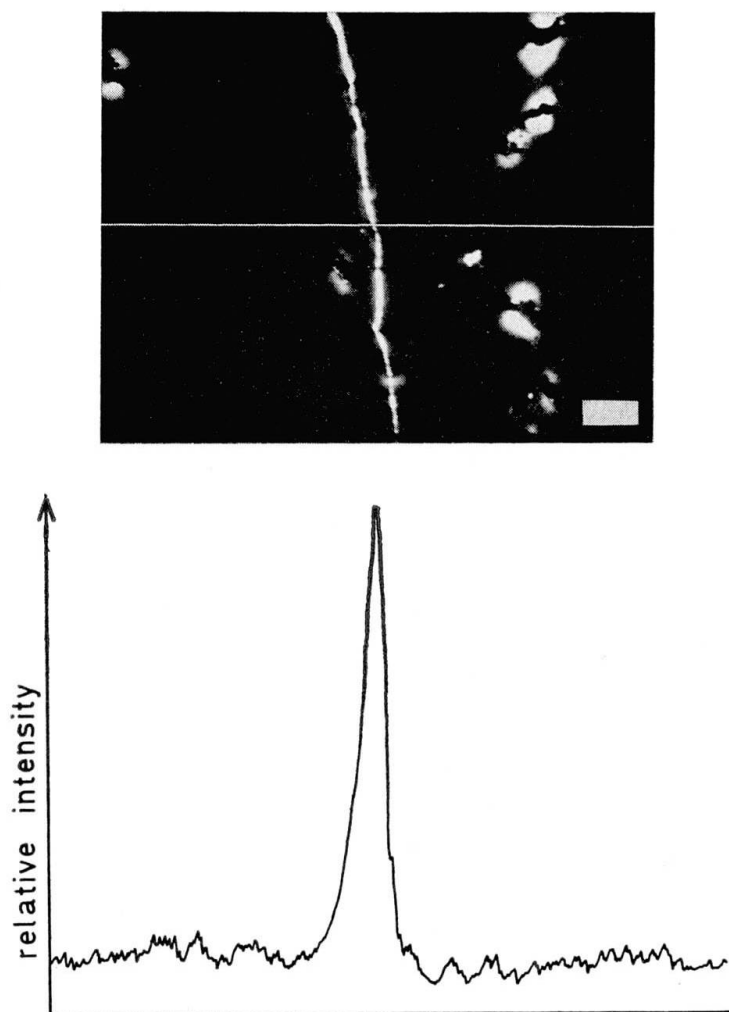


Fig. 4. Back scattered electron image of a U-Fe-strip in the fluorite phase (upper part), showing the distribution of relatively heavier elements as brighter area's. The lower part of the figure shows a continuous X-ray scan, across the U-Fe-strip, along the white line, showing its response for U. Dash on the photograph = $10\ \mu\text{m}$.

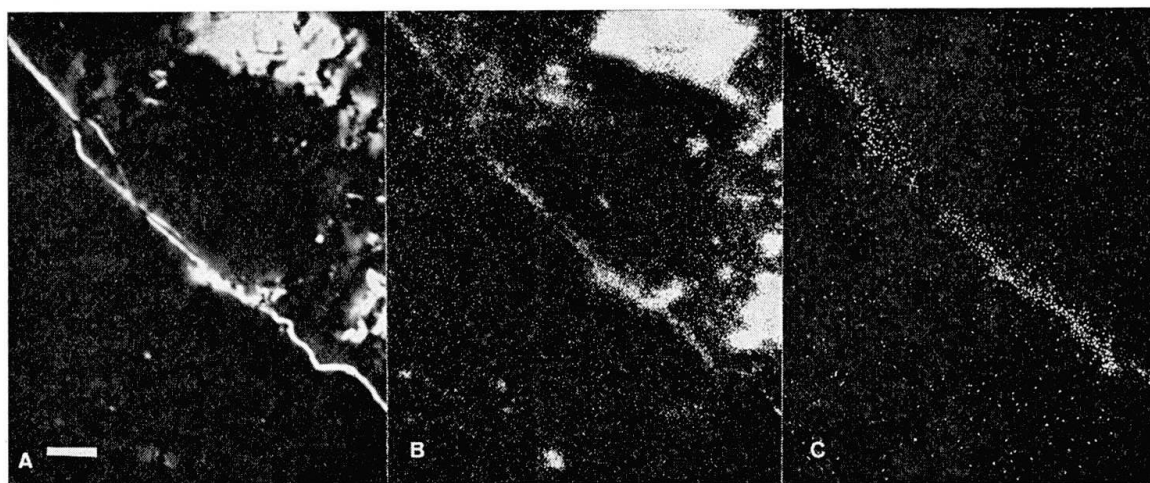


Fig. 5.

- A. Back scattered electron image of a U-Fe-strip in the quartz phase. Dash = $10\ \mu\text{m}$.
- B. X-ray beam scan photograph of Fe-distribution in the same area. Same scale.
- C. X-ray beam scan photograph of U-distribution in the same area. Same scale.

Uranium and iron are not always randomly distributed in the fluorite phase. Strong concentrations of uranium, associated to ironoxydes can often be found along cleavage planes in the fluorite (fig. 3).

Uranium-iron strips, which are very alike to those found in the fluorite phase, can be observed in the quartz phase (fig. 4 and 5).

Besides these strips, U, Pb, Si, Ca, Fe and Ba are randomly distributed in both the fluorite and the quartz phases.

6. THE COLOURATION OF FLUORITE IN A HYPOTHETICAL PERSPECTIVE

The numerous current hypotheses about the colouration of fluorite, can be classified in two groups. According to some authors the colour is due to chemical factors, such as inclusions, colloids or trace elements. In other papers physical factor are stressed upon: colour centers, possibly induced by radiation.

Two absorptionbands, α and β , were found by E. MOLLWO (1934) in natural crystals of fluorite. Though this author suggested the α -band to be analogous to the one found in alkali halides, and thus due to F-centers, J. SCHULLMAN, R. GINTHER and R. KIRK (1952) showed its connection with oxygen and hydroxide ions. Hence, the presence of impurities seems to play a prominent role in the colouration of some fluorites.

According to E. MOLLWO (1934) some kinds of colouration can be due to the presence of Ca colloids. This theory is considered as plausible by K. PRZIBRAM (1953), but strong evidence seems to be lacking.

H. HABERLANDT and A. SCHIENER (1935) try to explain the banded colouration of some fluorites by adsorption of radioactive and sulfide components during the crystals growth.

J. O'CONNOR and J. CHEN (1963) have suggested that all of the colour induced by irradiation is a result of the absorption by Y^{+2} -ions, which have been converted from Y^{+3} by trapping an electron. This hypothesis is however difficult to accept for the Wölsendorfer fluorite, which contains only minor traces of Y, notwithstanding its extremely dark tone.

Also F. HENRICH (1920) states that the dark colour of the Wölsendorfer "Stinkfluss" is caused by damage to the fluorite lattice, due to radioactive irradiation.

It is quite clear that considerable amounts of work remain to be done, before a clear picture of the colouration of fluorite will be available.

7. CONCLUSIONS

In the fluorite as well as in the quartz phases, solid inclusions mainly consist of iron and uranium compounds.

According to their random distribution in the fluorite mass, the elements U, Pb, Si, Ca, Fe and Ba must have been present during the primary phase of the fluorites genesis.

Concentrations of U and Fe along cleavage planes in the fluorite must however be younger.

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