

## THE URANIUM MINERALIZED BELT OF UPPER TULGHES SERIES, EAST CARPATHIANS, ROMANIA

PAULINA HÎRTOPANU

Faculty of Geology and Geophysics, Bd. N. Bălcescu, No. 1, Bucharest, Romania

**Abstract.** The Crucea uranium deposit is situated in the proximity tectonic contact of old Precambrian Bretila Group with the youngest Tulghes Series (G4 level). Because of its complex tectonic setting, the host rocks of the Crucea deposit are strongly retromorphosed and highly carbonatated. The occurrence of uraninite/pitchblende gives rise to a strong alteration of the host rocks. A few other small uranium mineralization points occur near Crucea deposit. These small occurrences and the large Tulghes pitchblende occurrence (Tulghes Valley, at Grintieşu) in the south of Crucea deposit, could be evidence for it to be traced the fourth belt, the Uranium Belt (UB), situated in the east of the other three MnB, BaB, and SB, on the alignment Crucea-Grintieşu. The uranium mineralization of Crucea deposit presents three mineralogical compositions: a. Primary uranium oxide ore, constituted by uraninite/pitchblende enclosed in black carbonaceous matter; b. Primary and secondary coffinite/other U-silicates as veinlets; c. uraninite mineralization as octahedral and cubic crystals. All three U mineralization types are always accompanied by sulfides/arsenides, sometimes as constituent minerals. The U mineralization is a multistage type of genetic process which starts with the precipitation of a hydrothermal complexes on the Cambrian sea floor, its initial emplacement, followed by metamorphism, and finished with strongly remobilization from its original source (TG4), caused by the Alpine thrusting of Bretila Group, over the level four (TG4) of Tulghes Series. Then later the locally new hydrothermalism determined the occurrence of a new uraninite crystals/group of crystals.

*Keywords:* Tulghes Series, U-oxides, U-silicate, subduction zone, submarine hydrothermal, multistage genesis.

**Résumé.** Le gisement d'uranium de Crucea est situé à proximité du contact tectonique de l'ancien groupe précambrien Bretila avec la plus jeune série Tulghes (niveau G4). En raison de son cadre tectonique complexe, les roches hôtes du gisement de Crucea sont fortement rétro-morphosées et fortement carbonatées. L'apparition d'uraninite/pechblende donne lieu à une forte altération des roches hôtes. Quelques autres petites occurrences de minéralisation de l'uranium se trouvent près du gisement de Crucea. Ces petites occurrences et la minéralisation de pechblende de Tulghes (vallée de Tulghes, à Grintieşu) dans le sud du gisement de Crucea, pourraient être la preuve d'une quatrième ceinture, la ceinture d'uranium (UB), située à l'est des trois autres MnB, BaB et SB, sur l'alignement Crucea-Grintieşu. La minéralisation d'uranium du gisement Crucea présente trois compositions minéralogiques: a. minerai primaire d'oxyde d'uranium, constitué d'uraninite/pechblende enfermée dans de la matière carbonée noire; b. coffinite primaire et secondaire/autres silicates d'uranium sous forme de veinules; c. uraninite sous forme de cristaux octaédriques et cubiques. Les trois types de minéralisation d'uranium sont toujours accompagnés de sulfures/arséniures, parfois en tant que minéraux constitutifs. La minéralisation d'uranium est un type de processus génétique en plusieurs étapes qui commence par la précipitation d'un complexe hydrothermal sur le fond marin cambrien, son emplacement initial, suivi du métamorphisme, et se termine par une forte remobilisation à partir de sa source d'origine (TG4), causée par la poussée alpine du groupe Bretila, au-dessus du niveau quatre (TG4) de la série Tulghes. Puis, plus tard, un nouveau épisode d'hydrothermalisme local a déterminé l'apparition de nouveaux cristaux d'uraninite/ groupe de cristaux.

*Mots-clés:* Séries de Tulghes, oxides d'uranium, silicates d'uranium, sulfures, zone de subduction, genèse hydrothermale sous-marine, genèse en plusieurs étapes.

## 1. INTRODUCTION

The Crucea uranium deposit is situated at the proximity contact of the old Precambrian Bretila Group which thrusts over the younger Cambrian Tulgheş Series, just at the tectonic border between them. Geologically and structurally the Bretila Group belongs to a complex area, so called Eastern Central Carpathian Nappes (Săndulescu, 1984). Because of its complex tectonic setting, some host rocks of the Crucea deposit are strongly retromorphosed (Fig. 1 right) and highly carbonated (Fig. 2 left), such as in the shear zone. A few other small uranium mineralization points occur near Crucea deposit. These small occurrences and the large Tulgheş pitchblende occurrence (Tulgheş Valley, at Grințieşu) in the south of Crucea deposit, could be evidence for it to be traced the fourth belt, the uranium Belt situated in the east of the other three – Manganese Belt, Barium Belt, Sulfide Belt – on the alignment Crucea-Grințieşu.

## 2. THE COUNTRY ROCK OF URANIUM MINERALIZATION

The retromorphosed Pietrosu Bistriței porphyroide granite (Fig. 1 left) and some rocks which look as they belong to high Tulgheş Series (TG4) (Figs. 1 right, 2 left and 2 right) are the host of Crucea Uranium mineralization. In the proximity of mineralization, the country rocks are strongly hematitized, as can be seen in Figs. 3 left and 3 right. The occurrence of **uraninite/pitchblende** gives rise to a strong alteration of the host rocks. The presence of hematite extending around the pitchblende/uraninite/U-silicate veins is the most characteristic feature of this alteration (Hirtopanu *et al.*, 2005). The hematitized carbonate rocks host the uranium silicates. The Grințieşu pitchblende is hosted by Pietrosu Bistriței Precambrian retromorphosed porphyroid granite, but it came here through a strongly remobilization from its original source, TG4 level of Tulgheş Series.

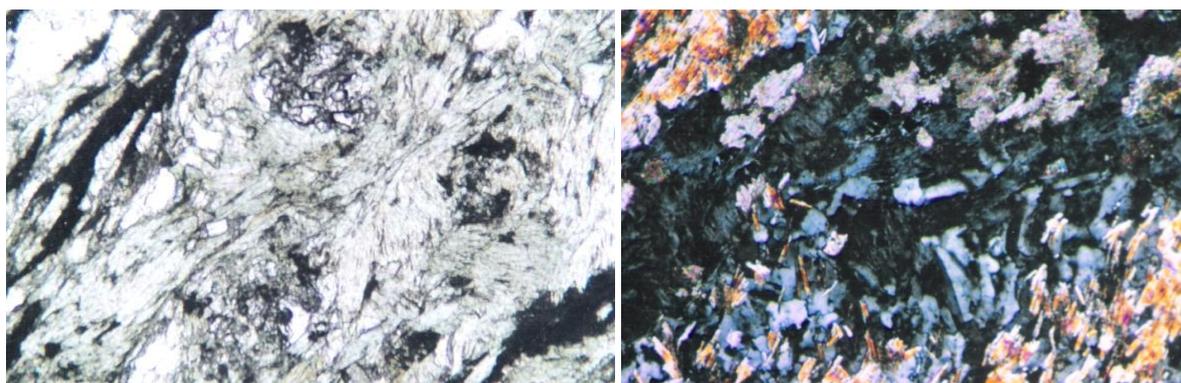


Fig. 1. Retromorphosed Pietrosu Bistriței porphyroide granite: almandine relics in quartz/chlorite/albite/graphite rock, TL, NII,  $\times 30$  (left); Retromorphosed rock of Bretila Group: muscovite (coloured), calcite (high birefringence), albite (twinned) and chlorite (low birefringence), TL, N+,  $\times 25$  (right).

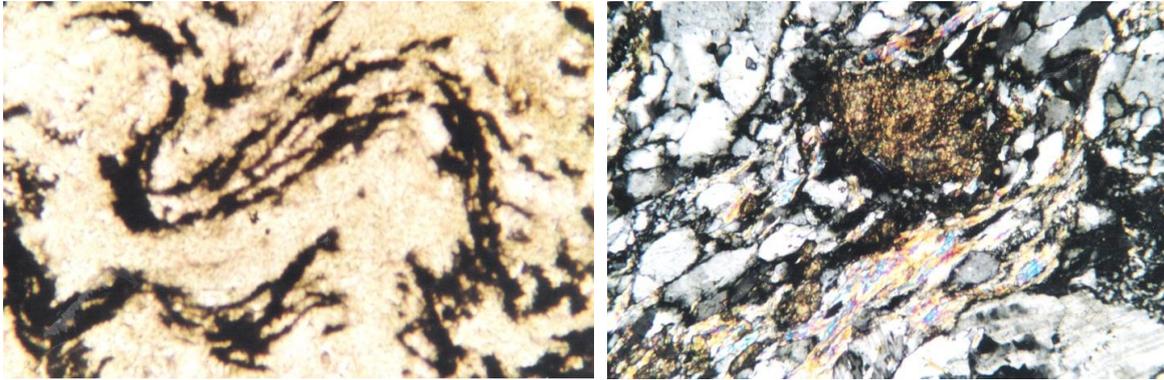


Fig. 2. “Kink texture” of folded titanite ( black) in quartz sericite rocks (white, yellow), TL, NII, sample 32G, (left); Titanite (large grain, centre) in quartz-muscovite rock, TL, N+, ×30, sample 18G.

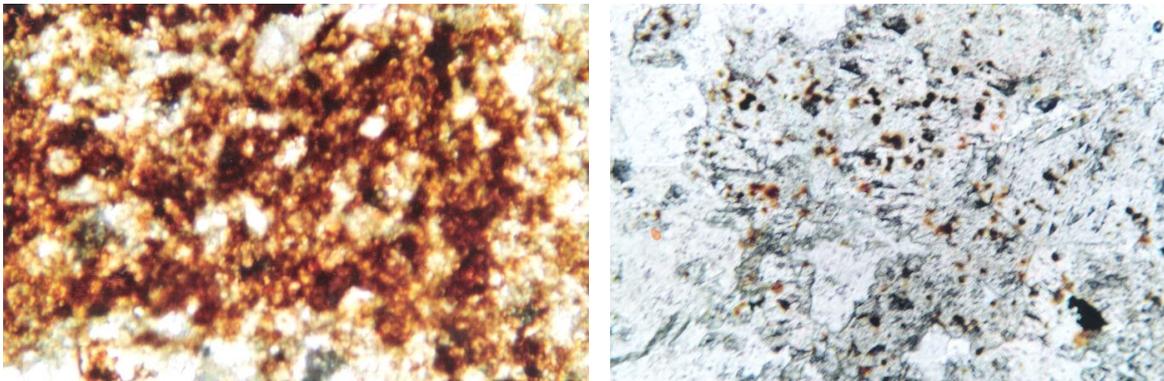


Fig. 3. Ferroan dolomite (grey) hematitized (black, red), TL, NII, ×30, sample 28G (left); Dolomite (white grey) (right) riddled by hematite (black, red, small grains), TL, NII, ×35 (right), sample 19G.

### 3. THE URANIUM AND SULFIDE MINERALIZATIONS

- A. The primary oxide uranium ore**
- B. The primary and secondary coffinite and other U-silicates**
- C. Associated sulfides to uranium ore**
- D. Later locally hydrothermal uraninite mineralization**

**A. The Crucea primary oxide uranium ore** is mainly constituted by pure uraninite (Fig. 4) grains enclosed in black carbonaceous matter (CM) as botryoidal/ bands/ angular grains, as can be seen in Figs. 4 and 6. The primary **Grințieșu pitchblende**, known by the synonym name **nasturane**, is generally massive, black, granular or forms veins/bands/nests with a botryoidal to reniform appearance of more than 1cm. The pitchblende is a primary, metamict, and impure variety of uraninite. It is an amorphous, pitchy form of the crystalline uraninite.

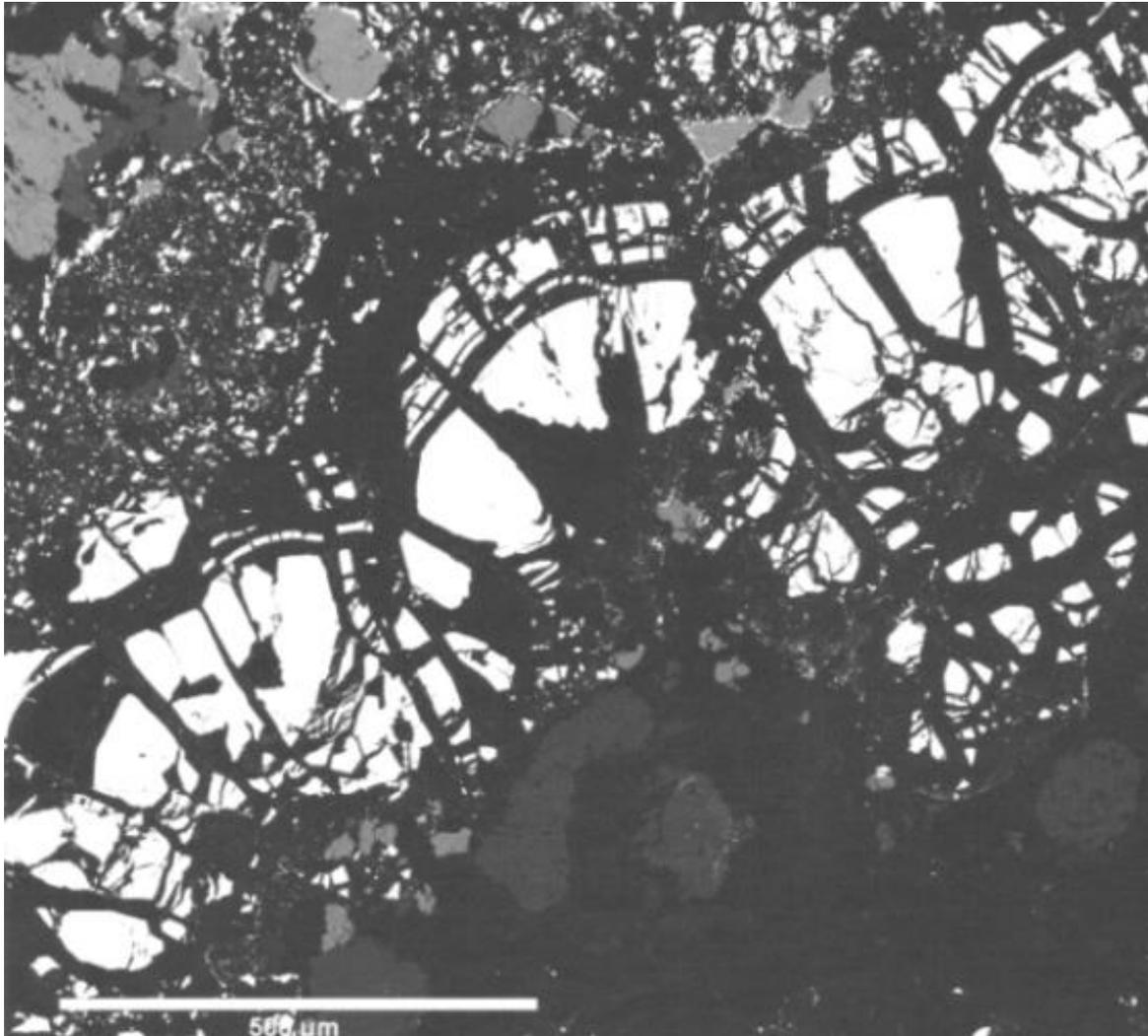


Fig. 4. Backscattered electron image of botryoidal uraninite (bright white) in black carbonaceous matter, and sulfides (small, grey) with coffinite (white, small veins ) around their grains.

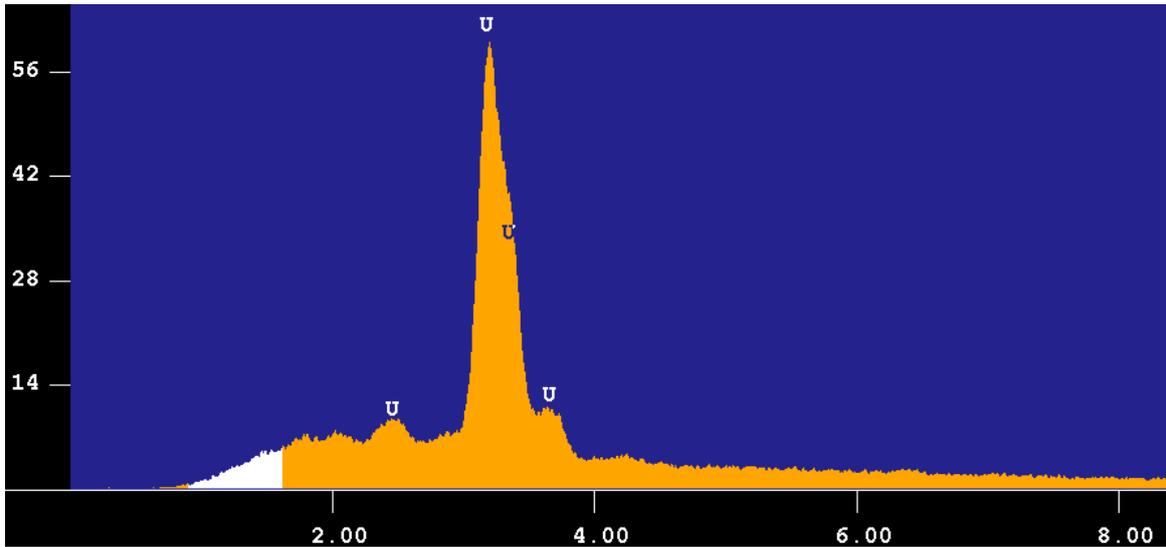


Fig. 5. Simplified electron diffractogram spectrum of the Crucea uraninite from the Fig. 4.

In the backscattered electron image of Fig. 4 the uraninite grains are enclosed in carbonaceous matter and all is hosted by dolomite rocks. On the cracks of uraninite grains and around the sulfide grains grows (intergrowth) the uranium silicate, which shows high U, low Si, and very low Ca, P, Fe, P, Si, and Al content, on its electron diffractogram spectrum (Fig. 5). The large sulfide grains appear in the left top corner of Fig. 4.

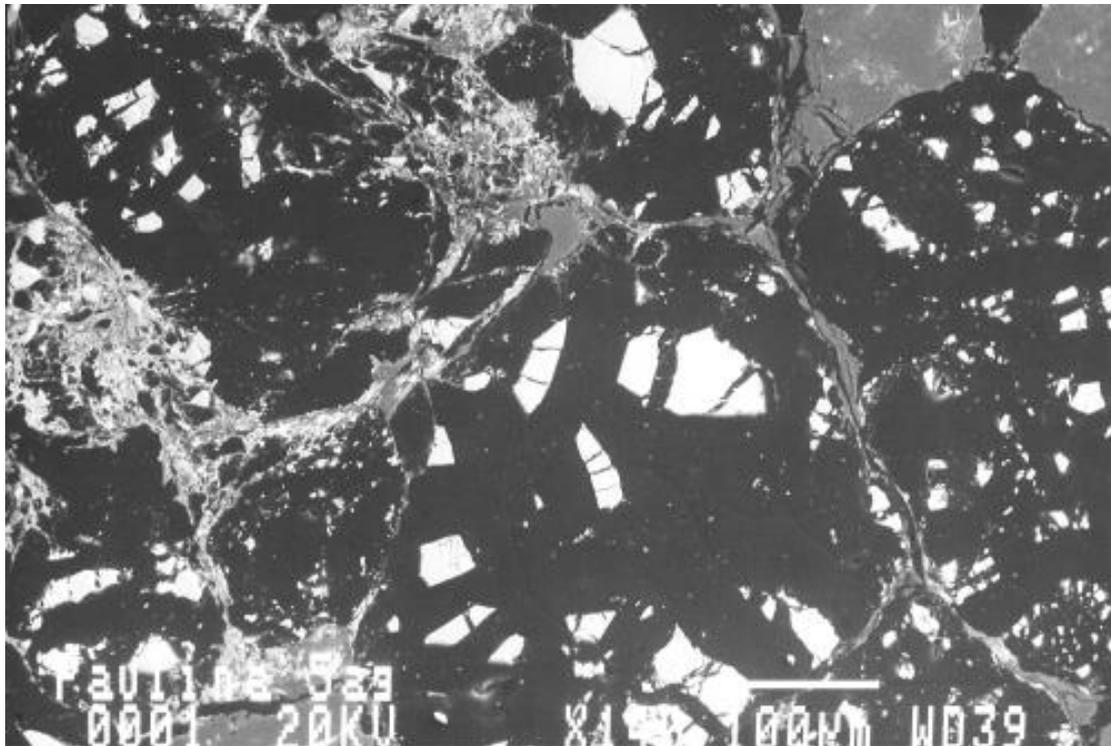


Fig. 6. Backscattered electron image of uraninite (white) in carbonaceous matter (black) and small sulfides (grey) intergrowth with coffinite (white grey) on veinlets, sample 5ag.

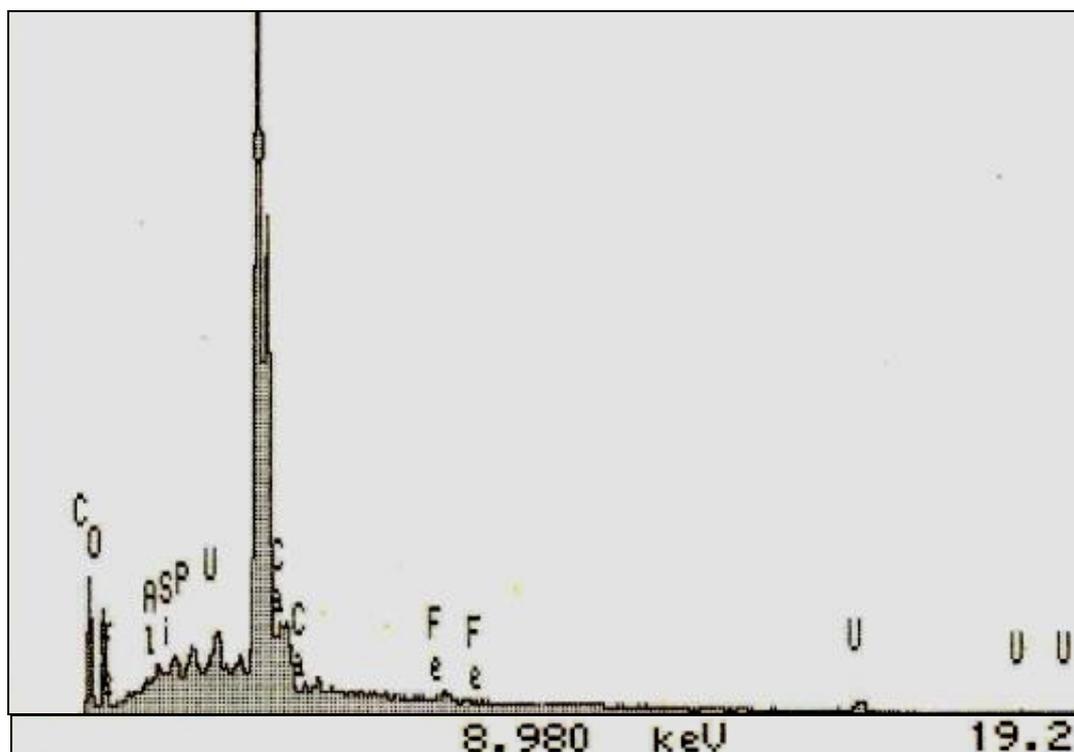


Fig. 7. Simplified electron diffractogram spectrum of uraninite of Fig. 6.

In Fig. 6 the backscattered electron image of uraninite can be seen, which appears as “relics” in carbonaceous matter. The carbonaceous matter contains, besides high C, also a very low sulphur. The S content of carbonaceous matter could originate from the various sulfides and sulfo-arsenides which always occur together with uraninite and U-silicates. The coffinite (white grey on Fig. 6) occurs tightly intergrowthed/associated with sulfides (grey) forming microveins around carbonaceous matter grains and inside uraninite grains. The simplified electron diffractogram spectrum of uraninite of Fig. 7 shows high U, and a very low Ca, P, Si, Al, Fe content.

### **B. The primary uranium silicates and secondary uranium silicates**

The uranium silicates occur as primary minerals and also as secondary one, which differ in Si and U content: the low Si and high U content for primary and high Si and low U for secondary ones. In the backscattered electron image of Fig. 8, the main large vein of low Si and high U coffinite (Ur, bright white) is substituted by high Si and low U silicates content (with different shades of grey). All these U-silicates, primary and secondary, form microveines and small nests in the quartz-mica rocks (Fig. 8).

The simplified electron diffractogram spectrum of primary coffinite can be seen in Fig. 9. It has a composition rich in U and low in Si, with very low Ti, Al, P and Pb content. The Pb content is most probable the decay product of uranium. The last product of the coffinite alteration (light grey on the Fig. 8.) could be uranophane, a hydrated uranium silicate, because it has high Si and low U content.

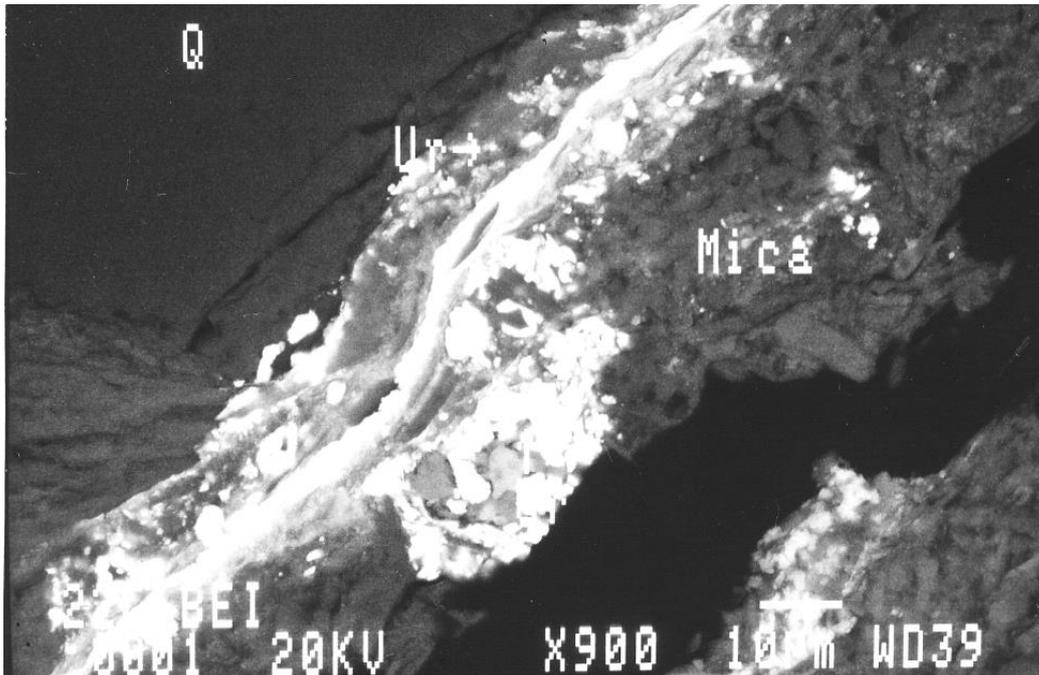


Fig. 8. Backscattered electron image of primary coffinite (Ur, large vein, bright white) altered in secondary U-silicates (white greyish), and uranophane (light grey), mica (Mica, grey), and quartz (black).

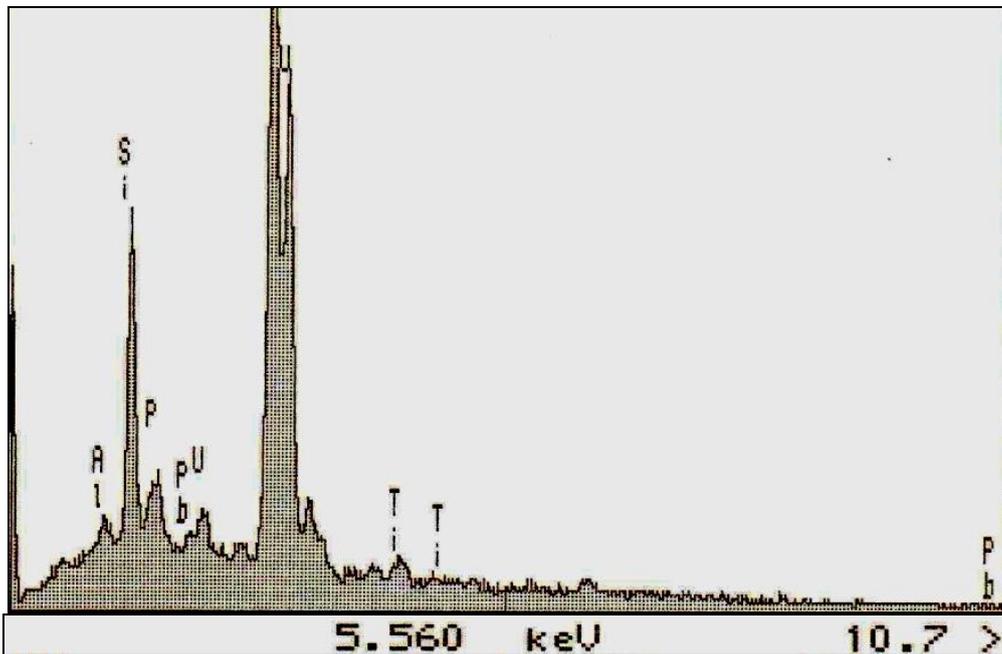


Fig. 9. Simplified electron diffractogram spectrum of coffinite.

**C. Associated sulfides and arsenides to uranium ore.** The uraninite and uranium silicates are tightly associated/intergrowthed with Ni, Co, Fe, As sulfides and arsenide. These associations were studied by scanning electron microscopy and their images can be seen in Figs.10, 12, 14, 15, and 18.

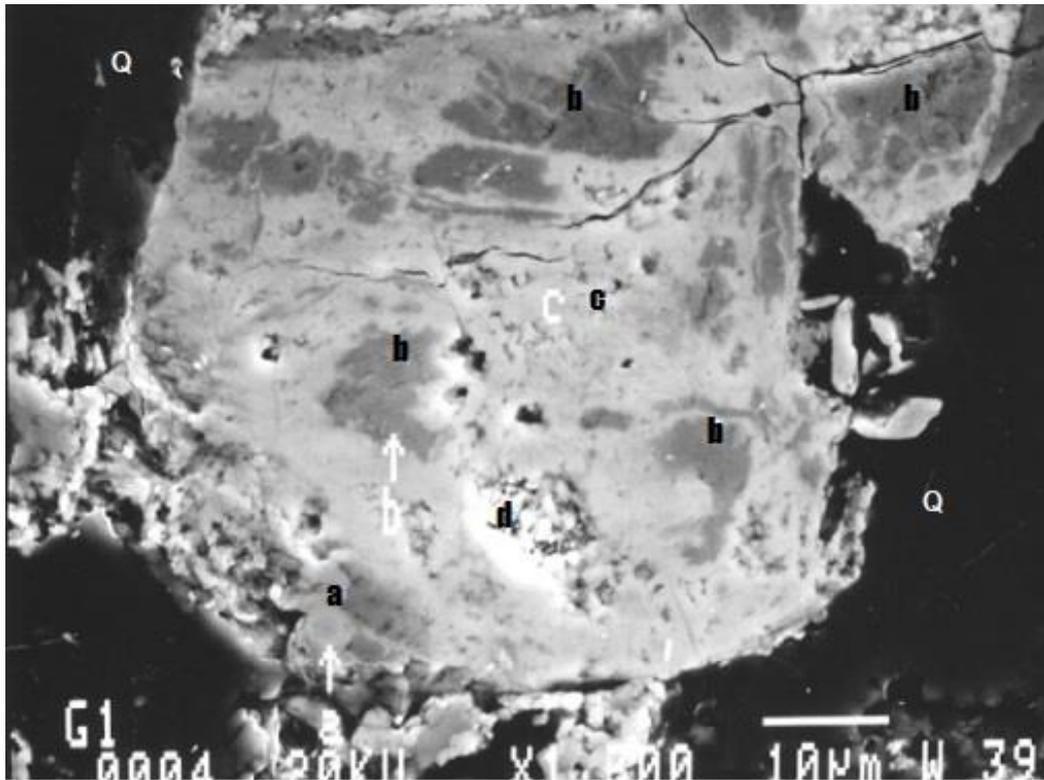


Fig. 10. Backscattered electron image of gersdorffite (a, grey white), pentlandite (b, grey, relics in coffinite), coffinite (c, white grey) and uraninite (d, bright white), in quartz (Q).

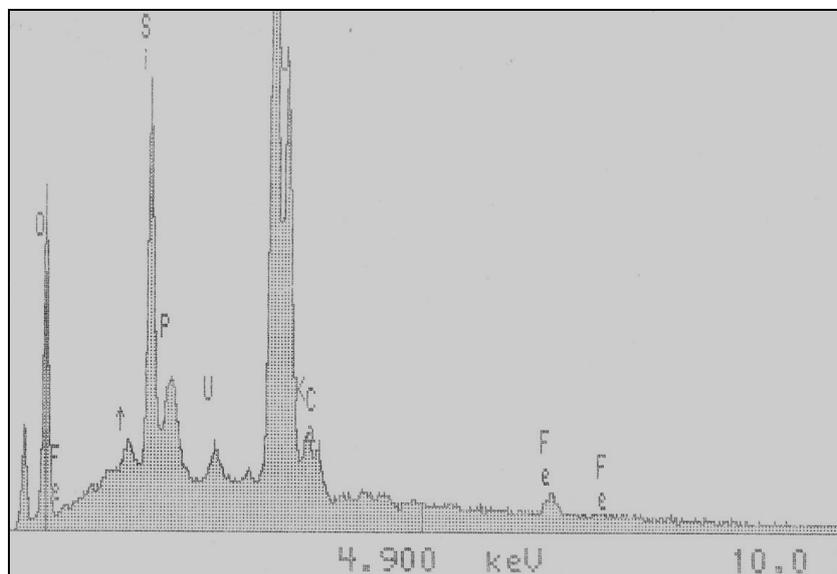


Fig. 11. Simplified electron diffractogram spectrum of uranium silicate (c) in Fig. 10.

In the backscattered electron image of Fig. 10, an uranium silicate/coffinite grain (c, white) has pentlandite inclusions//relics (grey) or could be intergrown together. The gersdorffite (a, light grey) grows around the coffinite grain, and the uraninite (d, bright white) is relics in this uranium silicate.

The electron diffractogram spectrum of U-silicate/coffinite (c) in Fig. 11 shows a high U composition and low Si, with low content of Ca, P, K, and Fe.

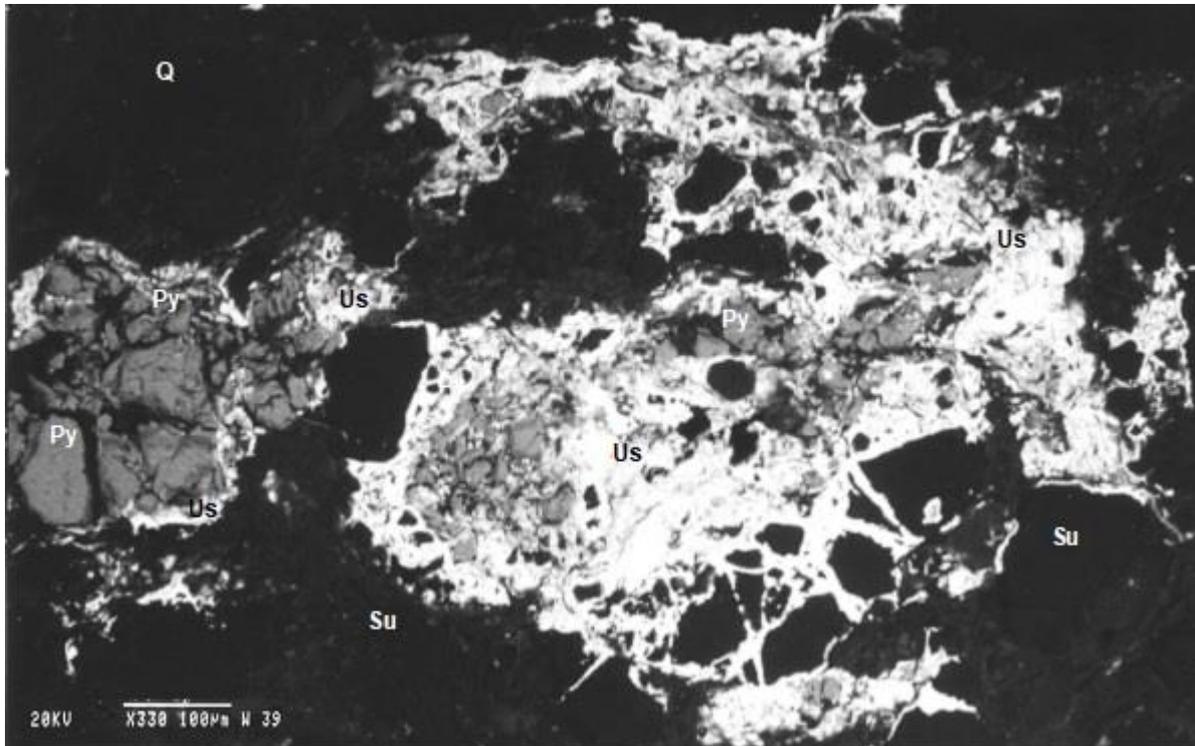


Fig. 12. Backscattered electron image of uranium silicate (Us, white) with pyrite inside it (Py, grey, centre), and large pyrite grain with uranium silicate (Us, white) around it, sudoite (Su, black), and quartz (Q, black).

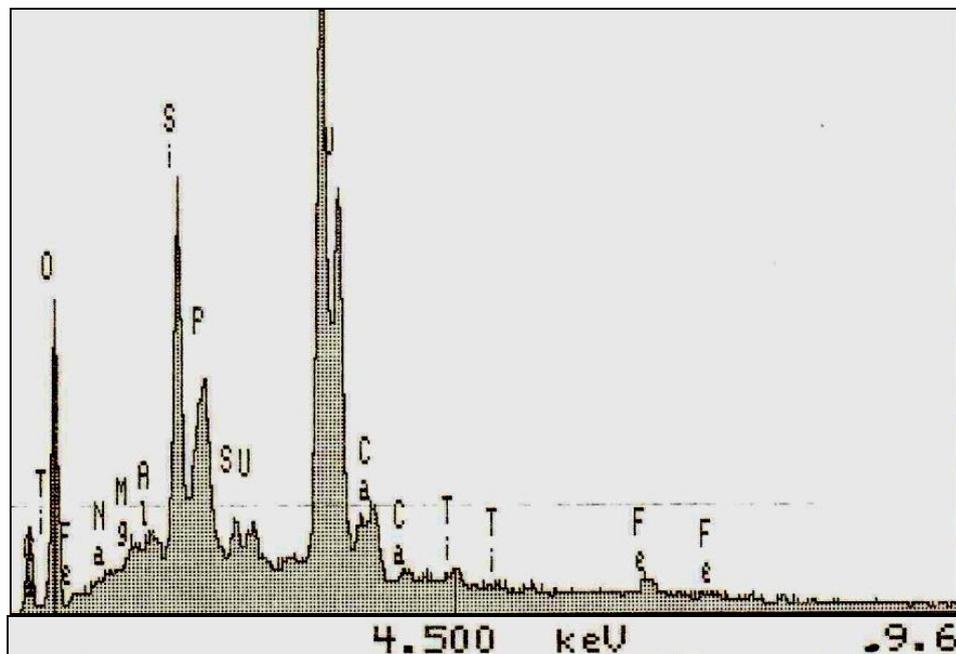


Fig. 13. Simplified electron diffractogram spectrum of uranium silicate from the picture above.

In the backscattered electron image of Fig. 12, the large uranium silicate grain grows on the pyrite, the latter remains as relics, and conversely, a large pyrite grain has U-silicate around it (left of Fig. 13). The gangue of U-Sulfide mineralizations are sudoite and quartz. The simplified electron diffractogram spectrum of uranium silicate in Fig. 12 can be seen in Fig. 13. It has high U and low Si, P, Ca, Al, Mg, Ti, Fe and Na content. The low S content comes probably for the associated sulfides.

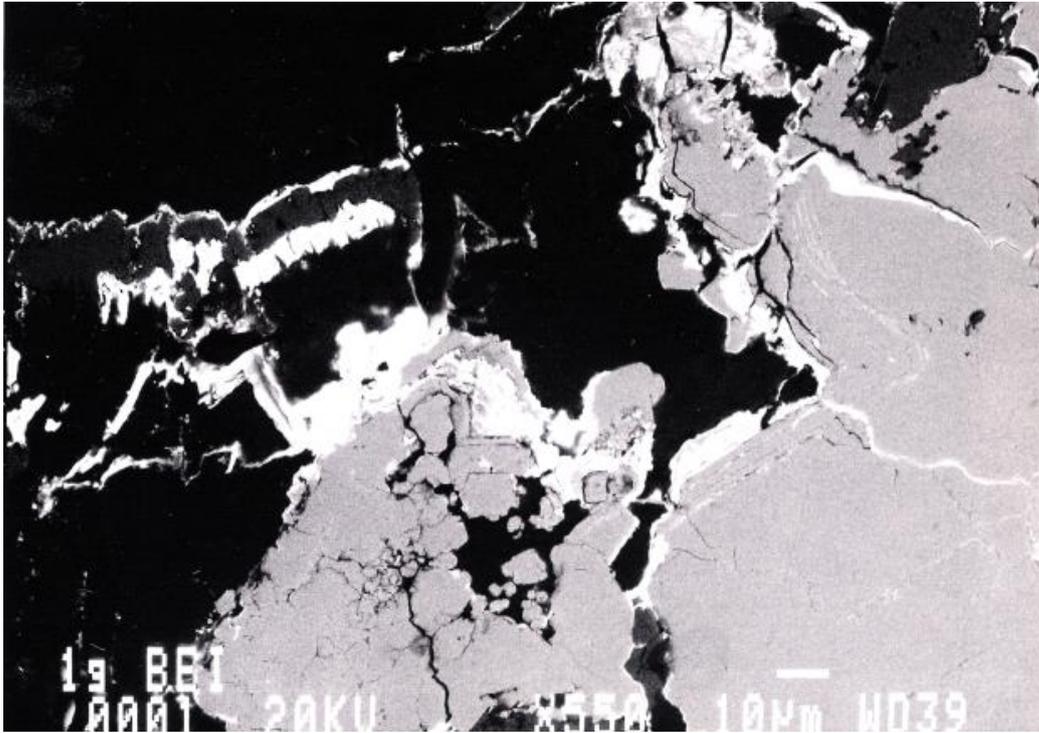


Fig. 14. Backscattered electron image of Ni-pyrrhotite (large light pink grain) with coffinite (white, veins around and inside it) and Fe, Mg rich carbonate (black), also with coffinite inside it.

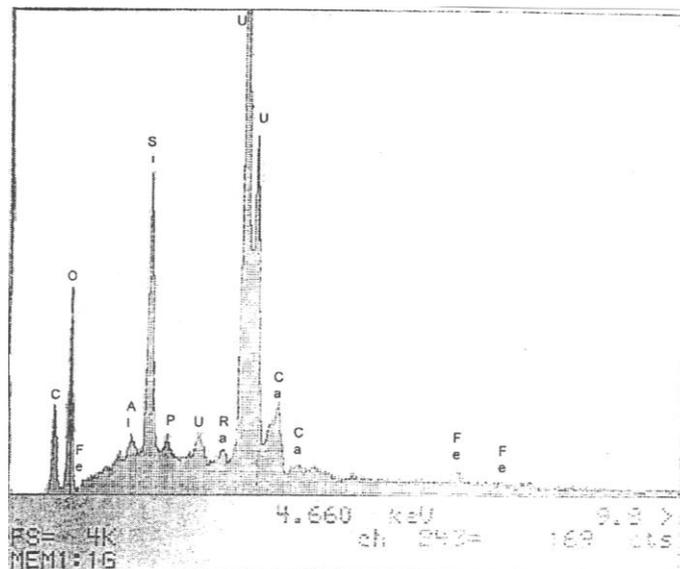


Fig. 15. Electron spectrum of U-silicate/coffinite in Fig. 14.

In the backscattered electron image of Fig. 14, the large Ni-pyrrhotite crystal is surrounded and penetrated by uranium silicate/coffinite microveins. The uranium silicate also occurs in the Fe-Mg-Ca carbonate gangue, as seen on this figure. The electron diffractogram spectrum of uranium silicate of Fig. 14 is displayed in Fig. 15. It shows a composition rich in U, and low in Si, and very low in Ca, Fe, P, and Al. It is worth noting the presence of Ra in the composition of this uranium silicate. The Ra content is most probably the main decay product of uranium.

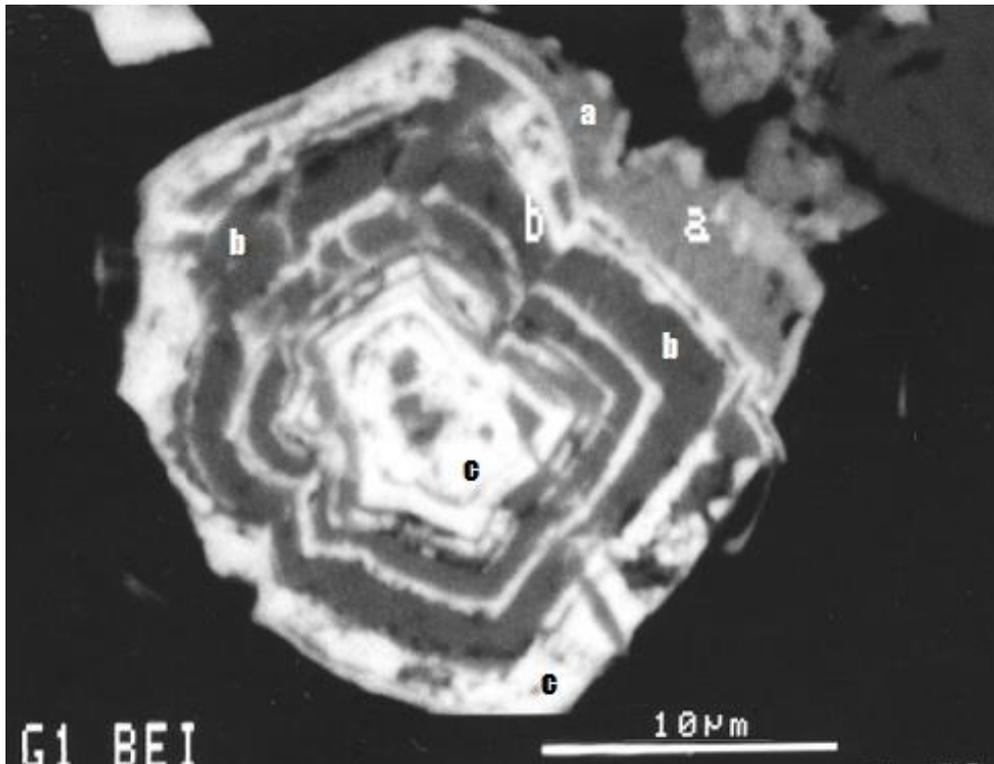


Fig. 16. Backscattered electron image of zoned grain: pentlandite (a, light grey, on the rim), Ni-pyrrhotite (b, dark grey, middle), and U silicate-sulphate (c, bright white, centre) and interspersed between a and b, and between b and c, sample G1.

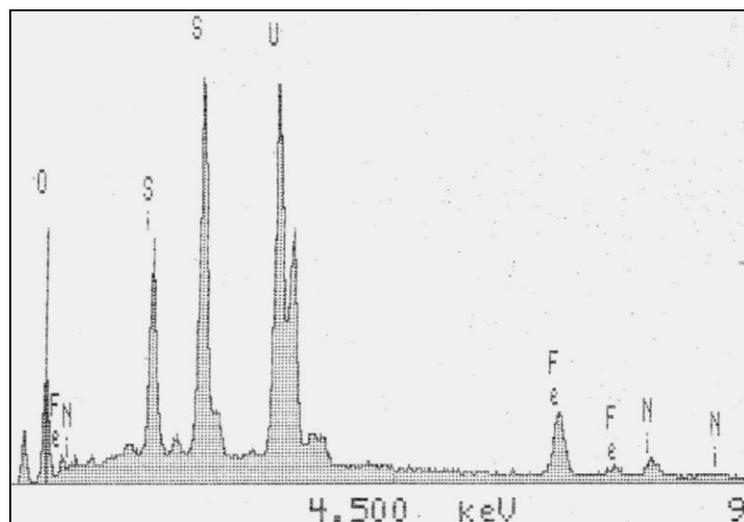


Fig. 17. Simplified electron diffractogram spectrum of the uranium sulphate-silicate (c, bright white) in Fig. 17, sample G1.

In the backscattered electron image of zoned grain of Fig. 16, the uranium silicate-sulphate constitutes the centre of the grain, followed/alternated by/with Ni-pyrrhotite, and pentlandite on the rims of the crystal. The uranium sulphate-silicate is also interspersed between the sulfide bands. The electron diffractogram spectrum of uranium sulphate-silicate displayed in Fig. 17 shows an U and S rich composition, low in Si, and with low Fe and Ni content.

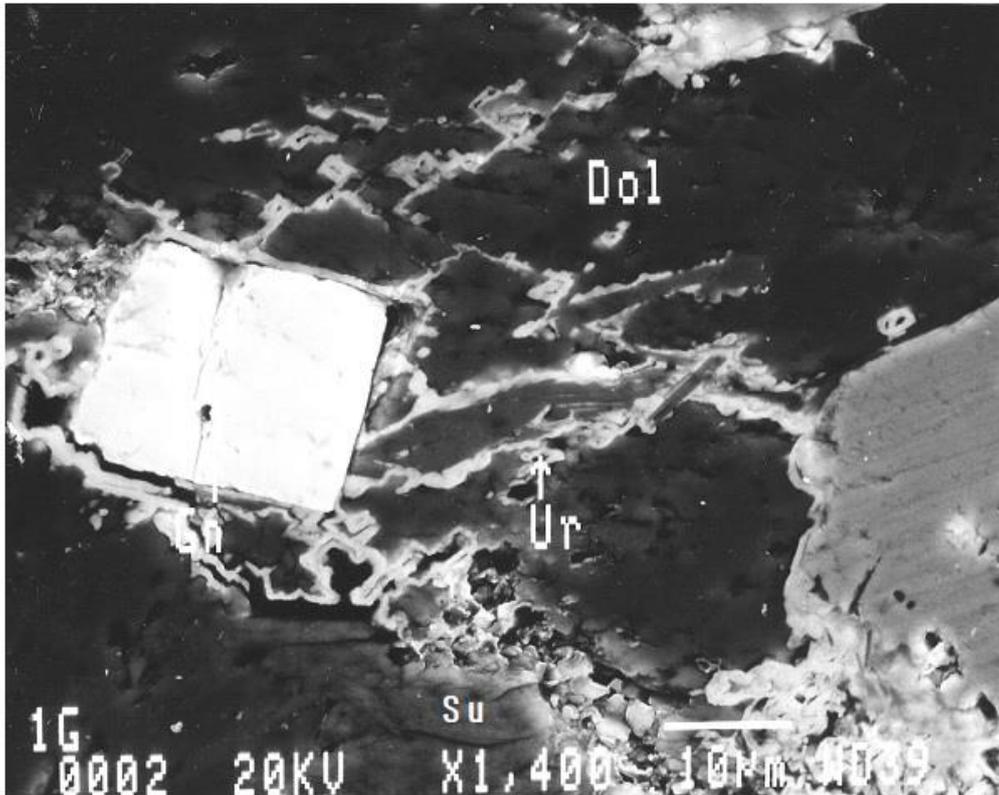


Fig. 18. Backscattered electron image of galena (bright white, square-shape), uranium silicate (Ur, veinlets, white), pyrite (right, large, light grey) with U-silicate around it, sudoite (Su), and dolomite (Dol, black).

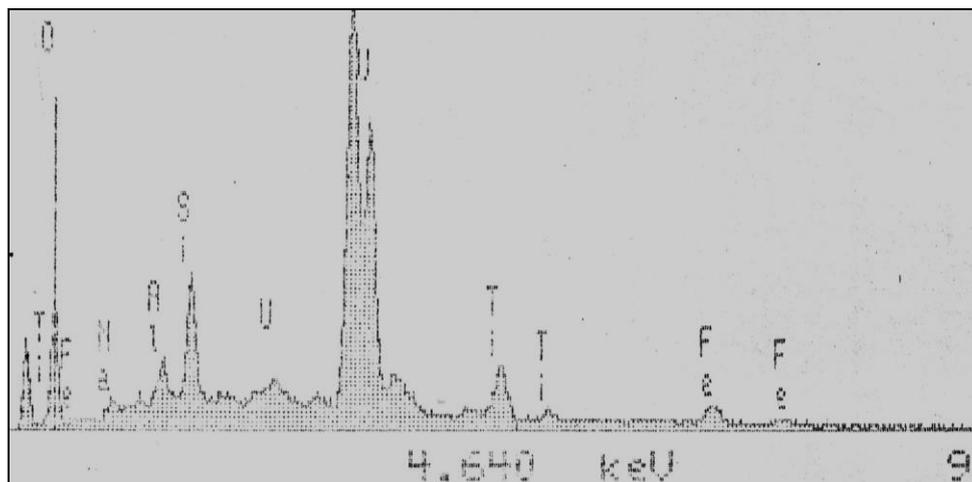


Fig. 19. Simplified electron diffractogram spectra of U silicate (Ur) in Fig. 19, sample 1G.

In the backscattered electron image of the Fig. 18, the galena crystal is surrounded by uranium silicate, which also forms veinlets in dolomite gangue and around the rims of large pyrite crystal. The electron diffractogram spectrum of the brightest zone of this uranium silicate is displayed in Fig. 19. It has a primary coffinite composition (high U and low Si content) with low Ti, Al, Fe, and Na content.

#### **D. The later hydrothermal uraninite crystals**

The new appearance of a new U mineralization, such as the euhedrale uraninite crystals/group of crystals, is most probably linked with a new locally hydrothermalism, which happened at  $T < 250^{\circ}\text{C}$  (Janeczek, Ewing, 1992). The uraninite crystals are due to the younger alteration and remobilization events, rather than the primary mineralization event. This new hydrothermal uraninite typically occurs as veins and in geodes, such as crystals/group of crystals as octahedral and cubic crystals, rarely dodecahedral, and a combination of these three types, especially cubes with octahedral corners. This new mineralization type is also always accompanied by sulfides/arsenides (Figs. 22 left and right). The gangue of hydrothermal uraninite crystals ore is represented by calcite, dolomite, siderite, ankerite crystals (Figs. 20 right, 21 right, 22 left and 22 right) and quartz crystals (Figs. 20 left and 21 left). The uraninite crystals have up to 0.5 cm in size and more (Figs. 20 and 21) (Hirtopan, 2019).



Fig. 20. Photo of geode/lens (20 cm long) with uraninite crystals enclosed in calcite/dolomite (white) and quartz (grey) (left); Photo of uraninite crystals of 0.5mm in size and/on calcite crystals as gangue (right),  $\times 10$ .

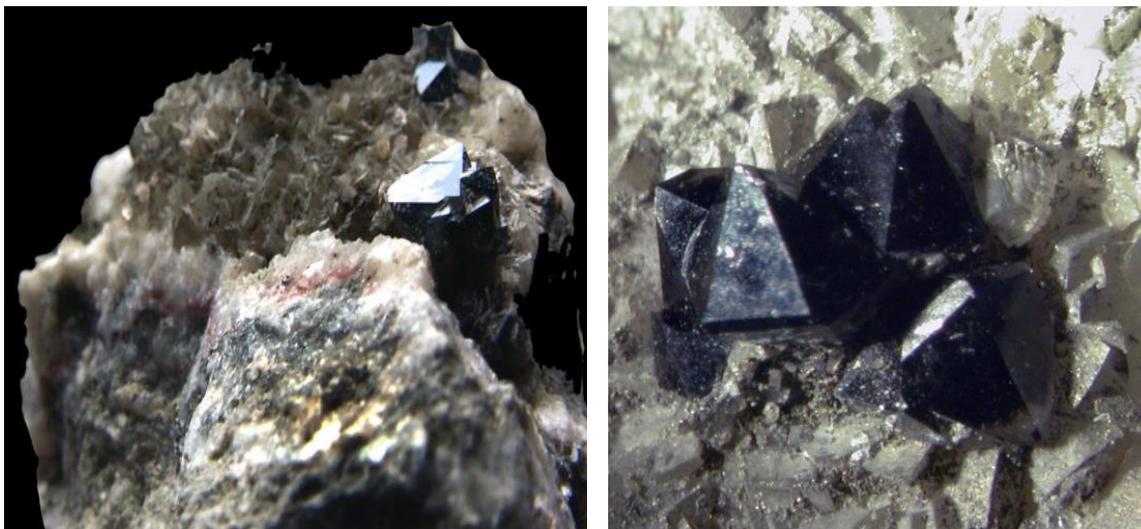


Fig. 21. Photo of uraninite crystals of 0.7mm in size grown on/with calcite crystals in quartz gangue (grey) (left); Photo of euhedral uraninite crystals grown on calcite crystals and with sulfide impregnation (right),  $\times 10$ .

The colour of uraninite crystals is black to steel grey with tints of deep blue. The structure of these crystals is highly symmetrical forming isometric crystals. It has a fluorite type cubic structure. Uraninite is isomorphous with cerianite and thorianite. The calcite, dolomite, siderite and quartz crystals accompany the uraninite crystals on the veins. They are hydrothermal minerals, constituting the gangue of hydrothermal uraninite crystal (Figs. 20, 21, and 22).

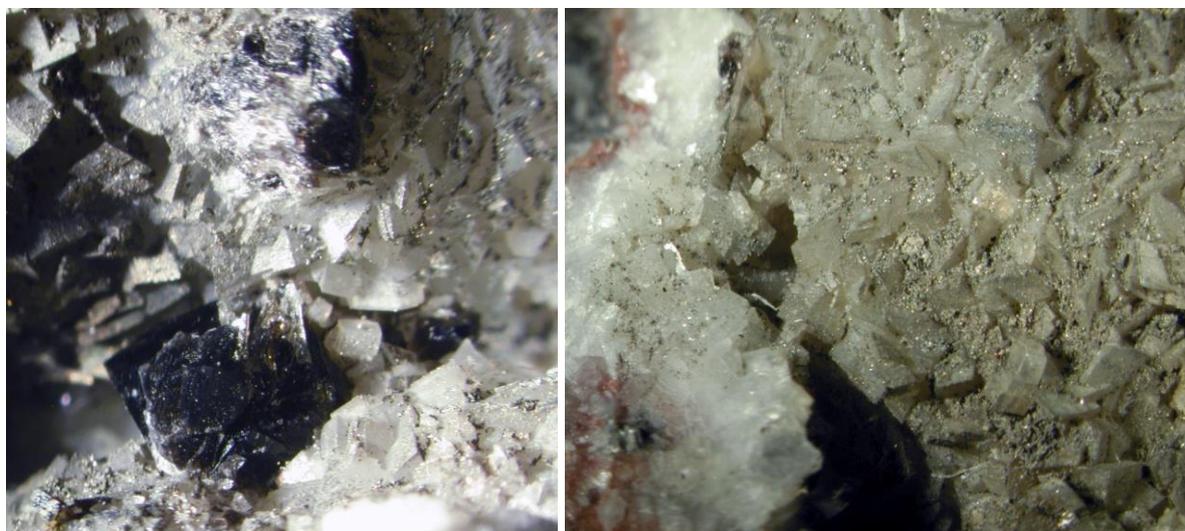


Fig. 22. Nests of uraninite crystals in calcite crystals, and microveins and nests of sulfide/arsenide around the calcite and uraninite crystals,  $\times 8$ . Uraninite/pitchblende (black, microvein) at the contact rhombohedral carbonate (grey)/ quartz (white), and sulfide (yellow, around) mineralization,  $\times 10$ .

The presence of Fe-Zn-Pb-Ni-Co-As sulfide/arsenide association in the Uranium Belt, which also occurs in the Mn Belt, Ba Belt, and Sulfide Belt, indicates that the UB mineralisation was hydrothermal submarine in origin, having genetic similarities with the other three belts. Nevertheless, it was tectonically transformed and remobilized from its original source, which was the TG4 level of



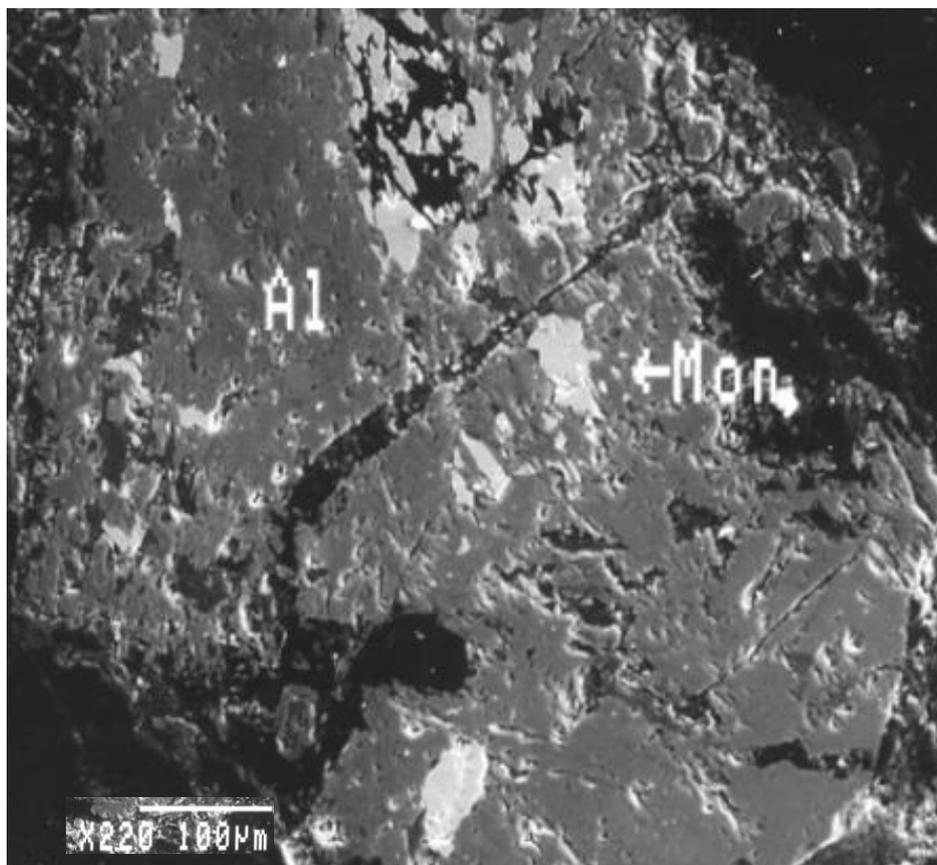


Fig. 24. Backscattered electron image of allanite-(Ce) (Al, grey, large grain) with inclusions of monazite-(Ce) (Mon, white-grey), and thorite (very small, bright white), sample 32G.

#### 4. GENETIC CONSIDERATIONS OF CRUCEA URANIUM MINERALIZATIONS

The chemical composition of Crucea carbonaceous matter (CM) shows only C with low S (which could come from associated sulfides). The uraninite enclosed in carbonaceous matter shows pure composition in Fig. 5, consisting only of uranium, and a composition with low Ca, Fe, P, Si and Al in Fig. 7. The electron microprobe analyses (Janeczek, Ewing, 1992) indicate that uraninite readily exchanges elements with the later fluids. In particular, radiogenic Pb is replaced by Ca, Si, and Fe via discrete alteration of uraninite (Janeczek, Ewing 1992). The electron diffractogram of Crucea uraninite shows that the most significant substitution of uraninite leads to its conversion to coffinite, with more than 10 wt% SiO<sub>2</sub> (Fig. 19). The other elements that change radiogen Pb into uraninite are: P, Ca, K, Fe, Ti, Al, Mg, and Na. The P and Ca appear to be the most common substituents within coffinite, and sometimes they have high content (Fig. 13), so probably a new mineral, named ningyoite, UCa(PO<sub>4</sub>)<sub>2</sub>·1-2H<sub>2</sub>O, occurs in Crucea U-deposit. The character of the substitutions depends on the amount and composition of the alteration fluids, particularly their capacity for oxidation and by the characteristics of the host rock through which the fluid circulates. In the backscattered electron image of Fig. 8 can be seen the transformation/substitution of primary uranium silicate from very low Si anhydrous coffinite, to low Si coffinite, and to high Si uranophane.

The geochemical evidence established for Mn mineralization (Hirtopanu, 2004) indicates its origin and evolution from an oceanic crust. The U mineralization evolved in the same subduction zone as the Mn ore. The Crucea U mineralization is a multistage type of genetic process. The fluid-geochemical Crucea uranium remobilization history has been recorded in at least 6 stages: (1) The precipitation of a urano-organic (?) and hydrothermal complexes on the Cambrian sea floor (TG4 level), the initial emplacement of U mineralization. (2) The metamorphism of these complexes determined the forming of CM with uraninite inside it through reduction of mobile  $U^{6+}$  to immobile  $U^{4+}$  due to the presence of sulfides which act as reductants. (3) The tectonically Variscan event, represented by the thrusting of Bretila Group (Rarău Nappe), over the level four (TG4) of Tulgheş Series (Putna Nappe), most probably caused the strongly remobilization of U mineralization, from its original source (TG4) to nearest and in/ under older Bretila Group. (4) The maturation of CM (now it looks like a graphite) by radioactivity caused the uranium enrichment, resulting in an increase in U minerals, especially U silicates, such as coffinite, uranophane, and nyngoite (?) which form veinlets in mineral gangue, in proximity to uraninite/pitchblende ore. (5) The new appearance of a new U mineralization, such as the euhedrale uraninite crystals/group of crystals, is most probably linked with a new locally hydrothermalism, which happened at  $T < 250^{\circ}C$  (Janeczek, Ewing, 1992). The uraninite crystals are due to the younger alteration and remobilization events, rather than the primary mineralization event. This hydrothermal uraninite typically occurs as veins and in geodes. In the hydrothermal systems, the transport of hexavalent uranium ( $U^{6+}$ ) occurs as soluble uranyl ( $U^{6+}O_2$ )<sup>2+</sup> complexes in oxidizing hydrothermal solutions along faults. The uraninite precipitation is often controlled by fluid interaction with country rocks or mixing with reducing fluids, causing physicochemical changes to a hydrothermal fluid, especially a decrease in the oxidation state of a fluid (Janeczek, Ewing, 1992). The hydrothermal uranium ores are commonly structurally controlled and related to fracture and fault zones. (6) Under the oxidizing conditions, tetravalent uranium of uraninite and uranium silicates changes to hexavalent uranium and forms secondary oxide, vanadate, arsenate, silicate, sulphate, and carbonate compounds, most of them bright yellow or green. Thus, the uraninite and uranium silicates tend to form under reducing conditions, whereas various uranyl minerals tend to form under oxidizing conditions.

## 5. CONCLUSIONS

The Uranium Belt evolved in the Cambrian sea floor, following the Mn, Ba, and Sulfide Belts, in a subduction zone, in a narrow active paleotrench area, reflected in their linear development as belts. In the upper Cambrian (TG4) the sea floor was moved to the east, being subducted towards east, under/near the oldest Bretila Group. The hydrothermal submarine activity changed its composition and the uranium and sulfide mineralizations were deposited at some distance from the Sulfide Belt and with the same orientation. The four mineralized belts indicate that a hydrothermal submarine system have been active/reactivated from TG1 to TG4. The submarine hydrothermal activity was fluctuant, a phenomenon also occurring in the current hydrothermal submarine deposits (Vaughan, Lennie, 1991). The U mineralization is a multistage type of genetic process which starts with the precipitation of some hydrothermal complexes on the Cambrian sea floor, its initial emplacement, followed by metamorphism, and finished with strongly remobilization from its original source (TG4), caused by the Alpine thrusting of old Bretila Group, over the younger level four (TG4) of Tulgheş Series. The later locally new hydrothermalism determined the occurrence of a new euhedrale uraninite crystals/group of crystals.

Therefore, the Uranium Belt mineralization was hydrothermal submarine in origin, having genetic similarities with the other three belts, Mn, Ba, and Sulfide. Nevertheless, it was tectonically strongly transformed and remobilized from its original source, which was the TG4.

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